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VALORIZATION OF PHOSPHATE WASTES FROM THE DJEBEL ONK MINE FOR BETTER ENVIRONMENTAL MANAGEMENT

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ABSTRACT

Algerian phosphates are the most exploited mineral resource and are considered an important source of foreign currency and a vital element in the mining sector. However, phosphate waste must be valorized for the product to be marketable. Phosphate waste, treated through washing and calcination, meets industrial requirements and international standards, with a P_2O_5 content of 31 %.
Various tests of calcination and washing of phosphate waste are carried out to thermally dissociate the carbonates of the exogenous and endogenous gangue from the ore within a temperature range typically between 700 and 1000 °C. To reduce the proportions of CaO and MgO compared to P_2O_5, the second important step involves hydrating the oxides of Ca and Mg to subsequently remove them.
According to this study, it can be concluded that the calcination and washing method can be applied to phosphate waste, as it has increased P_2O_5 content. This technique is simple and cost-effective and does not require heavy investments in industrial equipment.

Keywords: Calcination; Environment; Tebessa; Temperature; Washing; Waste treatment.

1 INTRODUCTION

We live in a world where the demand for raw materials is increasing every year due to population growth. Among these raw materials, phosphate plays a significant role in the international market [1]. Phosphate has extensive use, representing 80 to 90 % of global production, particularly in the manufacturing of fertilizers and phosphoric acid. It is also utilized in other sectors such as the paint industry, ceramics, cosmetics, pharmaceuticals, food industry, and other sectors. Phosphate rocks are considered a potential source of rare earth elements [2-7].

The Djebel Onk phosphate deposit is located approximately 100 km south of the city of Tebessa, 20 km from the Algerian-Tunisian border, and near the road that connects Tebessa to El Oued. This area is bordered to the north by the Souk Ahras province, to the south by the El Oued province, and to the west by the Khenchela and Oum El Bouaghi provinces.

The Djebel Onk mine employs an open-pit mining method characterized by mountainous terrain. It extracts phosphate ore with an average grade of 29 %. However, it generates thousands of tons of mining waste in the form of sterile rocks annually [8,9,10]. These waste materials are deposited near the mining village located downstream from the mine [11]. Unfortunately, these mining tailings can have direct impacts on the natural environment and

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the health of the surrounding population [12]. Pollutants can be leached into groundwater during episodes of heavy rainfall [13,16]. This situation calls for urgent solutions [17,15]. To address this environmental issue, an integrated management approach through the valorization of mining waste is required. This approach aims to reduce the volume of waste stockpiles and minimize their environmental impacts.

Several technological solutions for the valorization of phosphate waste have been proposed in the literature. These include using the waste as construction material, filling open voids, substrate for vegetation on mining sites, raw material for cement production [18-19], concrete manufacturing, ceramics production [13], brick manufacturing [20-22], alternative materials for fired bricks [23], geopolymerization applications [24], concrete industry [25], road construction [26-27], and lightweight aggregates [28][14]. However, these solutions have proven to be unsuitable and not cost-effective in the current context [14][29]. Other potential applications of phosphate waste include its use in controlling acid mine drainage (AMD) [30] and the recovery of rare earth elements from phosphate rocks [6-7]. The valorization and management of mining waste present significant challenges for the Algerian mining industry in terms of ecology, economy, and social aspects [31].

To achieve this, characterization studies were conducted on representative samples of the mining waste from the Djebel Onk phosphate mine. These studies involved particle size analysis, chemical analysis using X-ray fluorescence, microscopic observation using a scanning electron microscope (SEM), heavy

metals analysis, X-ray diffraction (XRD) analysis, and infrared (IR) analysis. The objective of these studies was to recognize and identify the mineralogical composition, chemical composition, and physicochemical properties of this type of waste.

Phosphate ores, characterized by important carbonate content, negatively affect the quality of the commercial product. This necessitates a treatment process to remove these carbonates using a simple and effective method, such as calcination. Over 10% of the global market for marketable phosphate is valorized through calcination. Typically, thermal treatment of phosphate ores is performed to thermally dissociate $CaCO_3$ and $MgCO_3$ into CaO, MgO, and gaseous CO_2, separating them from the ore's exogenous and endogenous gangue within a temperature range usually between 700 and 1000 °C. To reduce the proportions of CaO and MgO relative to P_2O_5, the second important step involves hydrating the Ca and Mg oxides for subsequent elimination [32-34]. High-temperature thermal treatment has an influence on the quality of the calcined products. Numerous studies investigating the influence of calcination temperature on porosity, reactivity, and specific surface area have shown a sharp decrease in these characteristics within a narrow temperature range.

In our case, calcination and washing tests are carried out with the aim of thermally dissociating the carbonates from the exogenous and endogenous gangue of the ore. This process is conducted to ensure that the phosphate waste is suitable for use in the fertilizer industry and for the production of phosphoric acid.

2 METHODS AND MATERIALS

The studied sample was collected from a large area within the study zone. The quantity of the sample collected weighed 70 kg with a maximum diameter of approximately 100-120 mm. The collected sample was transported to the sample preparation laboratory at the Djebel Onk mining complex. It was dried and divided (into two rifles) until obtaining a quantity of 1.5 to 2 kg. This quantity underwent crushing, quartering, and successive homogenization steps to obtain a representative sample. An initial portion of this representative sample was characterized using X-ray diffraction (XRD) and scanning electron microscopy (SEM), infrared spectroscopy (IR), and a quantity of 1000g of this representative sample was used for particle size analysis and granulo-chemical analysis.

2.1 Particle size analysis (The granulometric)

The particle size analysis was performed on a 1000 g sample of phosphate waste to separate the sample into different particle size fractions. Standard sieves with square meshes were used, including +8mm, +2mm, +0.50mm, +0.20mm, +0.10mm, +0.040mm, and -0.040mm. The sample was sieved for 10 to 15 minutes to minimize attrition effects on a sieve column using a CISA shaking machine with 200 mm x 50 mm diameter sieves.

The quantities of particles retained on each sieve were weighed using a balance with a precision of 0.01 g. Figure 1 illustrate the weight percentages of the retained and cumulative fractions for the studied phosphate waste.

The results indicate that the majority of the total mass of the studied samples (41.17%) is represented by the +8 mm particle size fraction. This fraction represents the optimal liberation mesh size for separating the phosphate elements. The largest portion of the total sample mass falls within the -8 + 0.2 mm range, amounting to approximately 455.4 g with a weight yield of 45.54%. On the other hand, the yield of the fine particle size fraction (< 0.04 µm) accounts for 2.53% by weight of the overall sample.

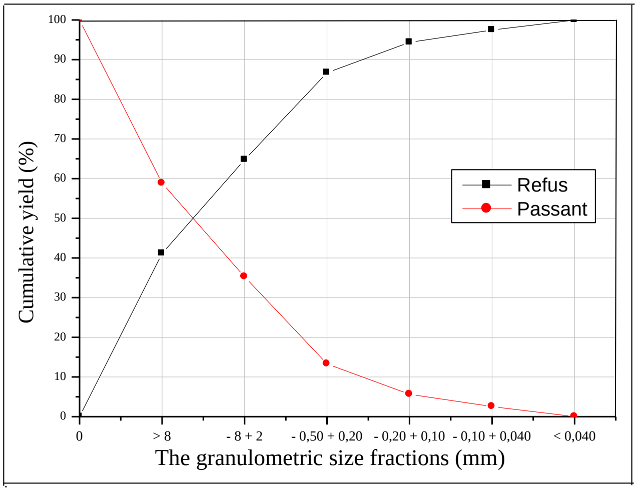

***Figure 1**. Particle size analysis by sieving of phosphate wast*

2.2 Chemical analyses

Table 1 illustrates the results of the distribution of chemical contents of major elements according to the granulometric fractions used in the sample of phosphate waste.

***Table 1.** Chemical analyses by granulometric classes of the phosphate waste sample*

The granulometric size fractions (mm)	**% massique**		
	P_2O_5	**MgO**	**CO_2**
Initial	20.54	5.24	15.72
> 8	17.64	6.02	19.06
- 8 + 2	21.70	5.26	14.38
- 2+ 0,50	24.02	3.60	13.04
- 0,50 + 0,20	26.45	2.54	10.37
- 0,20 + 0,10	22.83	4.10	14.71
- 0,10 + 0,040	14.60	7.13	23.74
< 0,040	17.24	6.23	20.06

The P_2O_5 content increases to a maximum in the granulometric fraction of dimension - 0.50 + 0.20 mm and drops significantly from - 0.1 mm. The opposite is the case for MgO and CO_2. These results show that the chemical composition of major elements varies significantly depending on the granulometric classes, especially the contents of P_2O_5, MgO, and CO_2.

Effectively, the P_2O_5 contents increase and reach their maximum of 26.45% in the granulometric fraction - 0.50 + 0.20. The high contents of P_2O_5 correspond to low contents of MgO (2.54%) and CO_2 (10.37%). The evolution of the contents of MgO and CO_2 reflects the evolution of dolomite and carbonates in the different granulometric fractions. Therefore, it can be said that the phosphate content increases with the decrease of dolomite and carbonates content.

The chemical analyses of phosphate waste samples were carried out at the FERPHOS laboratory using the following methods: phosphomolybdate spectrophotometry, atomic absorption spectrometry (A.A.S), and calcimetry.

Comparing the content of phosphates (P_2O_5) and the dominant minerals in the gangue (MgO and CaO) of the sample (Table 1) confirms the depletion of phosphates in the waste and their richness in carbonates. The very high CaO/P_2O_5 ratio of 2.13 (higher than 1.57, which indicates the presence of free carbonates) reflects the presence of carbonates mainly linked to dolomite and calcite [35], rather than substitution of PO_4^{3-} by CO_3^{2-} in apatite.

Based on these chemical analyses, it can be concluded that the phosphate waste contains a high content of CaO, up to 44.86%, indicating that it mainly consists of a carbonate gangue. The P_2O_5 content reaches 26.45%, confirming that this material is rich in P_2O_5 and economically viable.

2.3 Heavy metals trace elements

The phosphate waste sample was analyzed by a Perkin Elmer AAS 3110 atomic absorption spectrometer, using appropriate hollow cathode lamps for each element after extraction with nitric acid, except for mercury, where a hydride treatment was necessary (see protocols). Calibration curves were plotted and the results are shown in the table above.

Table 2. *The trace element concentrations of the initial sample of phosphate waste*

Trace elements	**Ni**	**Pb**	**Cu**	**Cs**	**Cd**	**Zn**	**Sr**	**Cr**	**V**	**U**	**Y**	**Ce**	**La**	**Nd**	**Sb**	**Er**
Content (ppm)	9,7	132	155	65	8.4	211	270	22	50	33	43	77	40	90	6,7	50

One can notice that phosphate wastes are relatively rich in metals such as Cu, Zn, Pb, which is due to the presence of minerals such as sphalerite, galena, etc. However, mercury is completely absent. Serventite, senarmontite, and stibnite are relatively low traces represented in antimony. These wastes also contain high concentrations of elements such as cerium, yttrium, neodymium, erbium, lanthanum, and cesium, and average concentrations of vanadium and uranium, and low concentrations of nickel, chromium, and cadmium.

2.4 Mineralogical analysis by X-ray diffraction (XRD)

According to Figure 2, it can be observed that the mineralogical composition of the phosphate wastes includes the following minerals: quartz, fluorapatite carbonate, albite, montmorillonite, orthoclase, dolomite, and calcite. However, it is noticeable that the peaks of fluorapatite carbonate and dolomite, which have high intensity, are well expressed, making their identification easy.

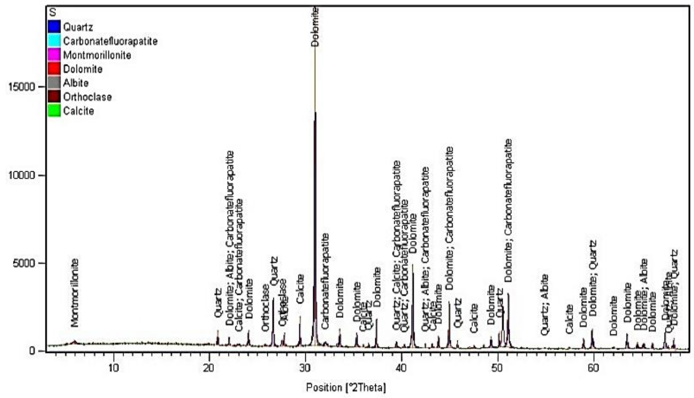

Figure 2. *XRD analysis of phosphate wastes*

2.5 Microscopic observations

The results of these observations are illustrated in (figures 3). They have allowed for the identification of the microscopic composition of elements such as P, Ca, Mg, Si, Fe, and O. The significant presence of oxygen is due to its contribution to the composition of P_2O_5, CaO, MgO, SiO_2, and Fe_2O_3.

The EDX diffractograms of the surfaces scanned by SEM (Figure 4) reveal the presence of P and O, which are characteristic of fluorapatite and carbonate fluorapatite. The high presence of Ca confirms the presence of carbonates (calcite, dolomite) among the essential components of this ore. The peaks of Mg indicate the presence of dolomite, while the peaks of Si indicate the presence of quartz.

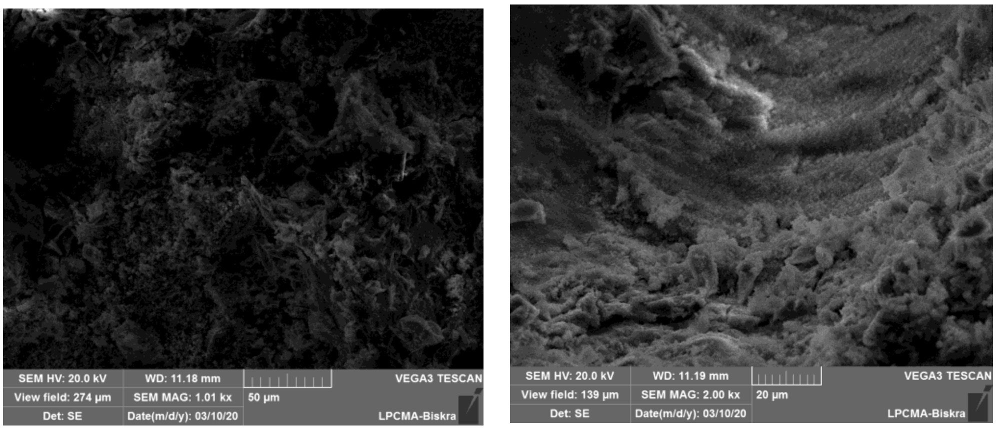

Figure 3. *Observation of phosphate wastes by SEM*

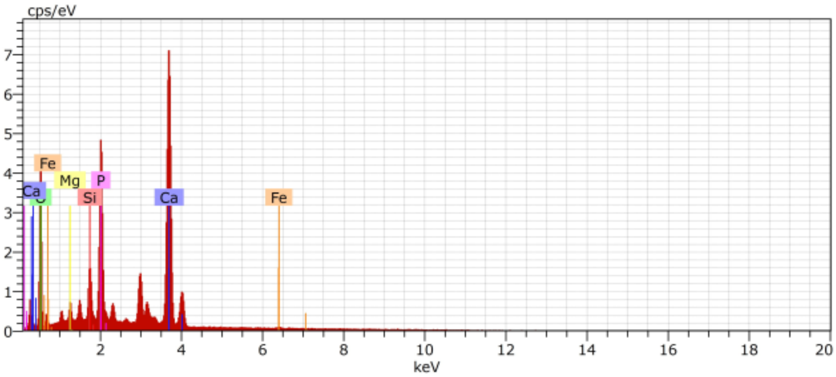

Figure 4. *EDX diffractogram analysis of phosphate waste*

3 STUDY OF THE VARIATION OF P_2O_5, CO_2, AND MGO CONTENTS AS A FUNCTION OF CALCINATION TEMPERATURE VARIATION (300, 600, 800, AND 1000°C)

Calcination is a thermal process aimed at separating carbonates from the external and internal components of the ore. This process typically occurs at temperatures between 700 and 1000°C.The elimination of organic matter takes place in several thermal stages:

- 200 to 450°C: vaporization of volatile materials
- 650 to 750°C: elimination of carbonates
- 750 to 800°C: cracking and combustion

The efficiency of separating carbonates and phosphate elements is evaluated by comparing the chemical composition of enriched products to that of raw ores and the calcination feed. Tests have been conducted to study calcination as a complementary enrichment method, with the goal of increasing the P_2O_5 concentration up to 32% in the dry process.

A sample of 100 grams of feedstock was placed in a preheated furnace and maintained at the given temperature for 15 minutes. The sample placed in the furnace has a thin thickness, allowing for constant heating of the entire sample. The sample was then cooled and ground for chemical analysis.

The following tables 3,4,5 and 6 represent the evolution of P_2O_5, MgO, and CO_2 contents as a function of granulometric fractions (-2+0.50) (-0.50+0.20) (-0.20+0.10) calcined for 15 minutes at 300, 500, 800, and 1000°C.

Table 3. *Variation of P_2O_5, MgO, and CO_2contents as a function of granulometric fractions of calcined phosphate waste at 300°C*

Calcination for 15 minutes at 300 °C.			
Content (%)	**The granulometric size fractions (mm)**		
	- 2+ 0,50	**- 0,50 + 0,20**	**- 0,20 + 0,10**
P_2O_5	25,90	27,10	23,45
CO_2	12,01	10,10	13,75
MgO	3,90	2,59	4,50

Table 4. *Variation of P_2O_5, MgO, and CO_2 contents as a function of granulometric fractions of calcined phosphate waste at 500°*

Calcination for 15 minutes at 500 °C			
Content (%)	**The granulometric size fractions (mm)**		
	- 2+ 0,50	**- 0,50 + 0,20**	**- 0,20 + 0,10**
P_2O_5	26,00	28,32	24,06
CO_2	11,89	10,00	13,15
MgO	3,70	2,46	4,33

Table 5. *Variation of P_2O_5, MgO, and CO_2 contents as a function of granulometric fractions of calcined phosphate waste at 800°C*

Calcination for 15 minutes at 800 °C			
Content (%)	**The granulometric size fractions (mm)**		
	- 2+ 0,50	**- 0,50 + 0,20**	**- 0,20 + 0,10**
P_2O_5	28,04	30,22	25,87
CO_2	2,20	1,05	2,70
MgO	2,20	1,21	2,30

Table 6. *Variation of P_2O_5, MgO, and CO_2 contents as a function of granulometric fractions of calcined phosphate waste at 1000°*

Calcination for 15 minutes at 800 °C			
Content (%)	**The granulometric size fractions (mm)**		
	- 2+ 0,50	**- 0,50 + 0,20**	**- 0,20 + 0,10**
P_2O_5	28,54	30,70	26,97
CO_2	1,40	1,00	1,70
MgO	0,75	0,40	0,93

According to the results of the chemical analysis indicated in tables 3,4,5 and 6, it is observed that the P_2O_5content increases with the increase in calcination temperature, while the percentages of CO_2 and MgO decrease. It is also observed that the P_2O_5 content increases after the calcination temperature of 800°C, while the percentages of CO_2 and MgO decrease. This is probably due to the effect of the thermal decomposition of dolomitic or calcic carbonates into CaO and MgO, after the release of CO_2, carried out in a temperature range between 700 and 1000°C.

These results show that the variation in temperature significantly influences the P_2O_5, MgO, and CO_2 contents of the calcined products. Indeed, an increase in temperature has a positive effect on phosphate yields (% P_2O_5), as P_2O_5 contents increase with temperature. The carbonate contents, expressed by the percentages of MgO and CO_2, decrease inversely with temperature.

In most cases, P_2O_5 contents increase with temperature. For a calcination time of 15 minutes in the granulometric fraction range of -2+0.50 mm, these contents reach 25.90 % at 300°C, 26 % at 500°C, 28.04% at 800°C, and 28.54% at 1000°C. In the granulometric fraction range of -0.50+0.20 mm, these contents reach 27.10 % at 300°C, 28.32 % at 500°C, 30.22% at 800°C, and 30.70 % at 1000°C. In the granulometric fraction range of -0.20+0.10 mm, these contents reach 23.45 % at 300°C, 24.06 % at 500°C, 25.87 % at 800°C, and 26.97 % at 1000°C. The increase in yields at high temperature suggests that the combination of lime (released after the departure of CO_2) with siliceous compounds (secondary reactions) is not highlighted under these conditions.

4 INFLUENCE OF WASHING

The calcination process itself serves to decompose carbonates from both the exogangue and endogangue, eliminate constitutional water, and destroy organic matter. Carbonates break down into alkaline earth oxides (CaO and MgO) after the release of CO_2. The sample obtained after calcination is washed, then deslimed, in order to reduce as much as possible the CaO and MgO content (obtained after carbonate decomposition) in the form of calcium and magnesium hydroxides. The separation performance of carbonates and phosphate elements is expressed by the chemical composition of the enriched products, compared to that of raw ores and the calcination feed.

The study by Tahri et al. on the different layers of phosphate from Bled el Hadba (summit, main, and basal) showed that wet sieving is more effective than dry sieving. The waste sample obtained after mechanical treatment is subjected to a desliming operation (40 µm) by washing to remove the fine particles of the exogenous gangue, which are rich in siliceous and dolomitic materials. The sample thus obtained is intended for calcination tests at a temperature of 1000°C for 15 minutes.

Table 7. *Variation of P_2O_5, MgO, and CO_2 contents as a function of granulometric fractions of phosphate waste before and after washing*

Content (%)	**The granulometric size fractions (mm)**		
	- 2+ 0,50	**- 0,50 + 0,20**	**- 0,20 + 0,10**
Before washing			
P_2O_5	24,02	26,45	22,83

CO_2	13,04	10,37	14,71
MgO	3,60	2,54	4,10
After washing			
P_2O_5	24,95	27,25	23,29
CO_2	12,75	10,10	14,52
MgO	3,10	2,40	3,79

For the granulometric fraction range -2+0.50 mm, P_2O_5 contents vary from 24.02 to 24.95%, MgO contents vary from 13.04 to 12.75%, and CO_2 contents vary from 3.60 to 3.10%. For the granulometric fraction range -0.50+0.20 mm, P_2O_5 contents vary from 26.45 to 27.25%, MgO contents vary from 2.54 to 2.40%, and CO_2 contents vary from 10.37 to 10.10%. For the granulometric fraction range -0.20+0.10 mm, P_2O_5 contents vary from 22.83 to 23.29%, MgO contents vary from 4.10 to 3.79%, and CO_2 contents vary from 14.71 to 14.52%. These results show that wet sieving is more effective than dry sieving.

The results of chemical analyses obtained from washed and calcined (1000°C for 15 min) phosphate waste samples at different granulometric fractions (-2+0.50) (-0.50+0.20) (-0.20+0.10) are mentioned in table 8.

Table 8. *Variation of P_2O_5, MgO, and CO_2 contents as a function of granulometric fractions of washed and calcined phosphate waste at 1000°C*

Calcination for 15 minutes at 1000 °C			
Content (%)	**The granulometric size fractions (mm)**		
	- 2+ 0,50	**- 0,50 + 0,20**	**- 0,20 + 0,10**
After calcination			
P_2O_5	28,54	30,70	26,97
CO_2	1,40	1,00	1,70
MgO	0,75	0,40	0,93
After washing and calcination			
P_2O_5	29,01	31,20	27,92
CO_2	1,05	1,00	1,10
MgO	0,70	0,35	0,70

From these results, it can be observed that P_2O_5 contents increase after washing and calcination. Except for a difference recorded between calcination and calcination after washing, for the granulometric fraction range -2+0.50 mm, P_2O_5 contents vary from 28.54 to 29.01%, MgO contents vary from 0.75 to 0.70%, and CO_2 contents vary from 1.40 to 1.05%. For the granulometric fraction range -0.50+0.20 mm, P_2O_5 contents vary from 30.70 to 31.20%, MgO contents vary from 0.40 to 0.35%, and CO_2 remains stable at 1%. For the granulometric fraction range -0.20+0.10 mm, P_2O_5 contents vary from 26.97 to 27.92%, MgO contents vary from 0.93 to 0.70%, and CO_2 contents vary from 1.70 to 1.10%.

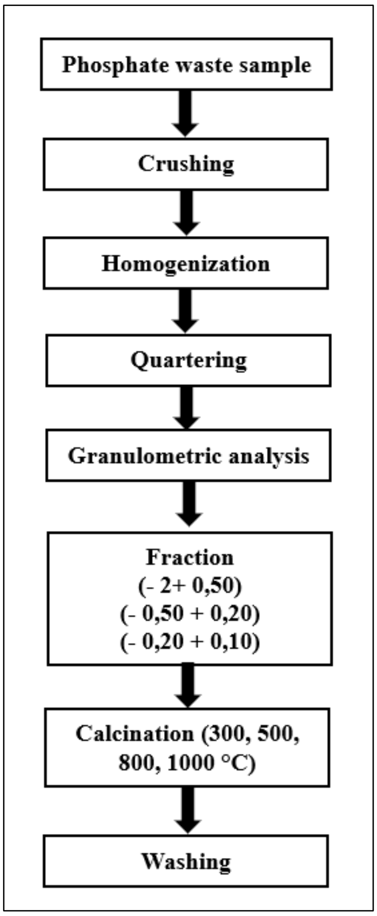

Figure 5. *Proposed schematic for enrichment by calcination of phosphate waste from Tebessa*

5 CONCLUSION

Choosing a method for phosphate valorization is essentially linked to the type of phosphate ore and associated non-phosphate minerals (gangue). There are two types of calcination processes: the first process is used for the valorization of organic ores, while the second type of calcination is used for phosphate ores with carbonate gangue. In this case, the calcination temperature varies between 850 and 1000°C.

In our study, the washing and calcination operation at 1000°C increased the P_2O_5 content in the granulometric fraction range -2+0.50 mm from 24.02 to 29.01%, in the fraction range -0.50+0.20 mm from 26.45 to 31.20%, and in the fraction range -0.20+0.10 mm from 22.83 to 27.92%. Therefore, this technique is effective in producing a product that meets the required cut-off grade for phosphate exploitation. This allows for the valorization of phosphate waste and their reuse, thus preserving natural resources.

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