

Effect of temperature and residence time of calcination phosphate on the chemical reactivity: Application to the case of Bouchane phosphate (Morocco)

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ABSTRACT: The calcination of phosphate consumes the fossil energy and generates greenhouse gas emissions. This later owed not only on the consumption of these energies, but also in the decomposition of carbonates and in the combustion of the organic matter. The energy consumption and the emission of gases require an optimization of the calcination depending on the residence time and temperature of calcination. These walking parameters influence the chemical reactivity and the solubility of finished product. To assist in that, we have studied the evolution of the main components of the control in the calcination (C_{org} , CO_2 , P_2O_5 , CaO), the specific surface area and density of the ore according to the time and temperature. This treatment was performed in the laboratory in a fixed bed. The different analytical techniques that were applied are: sieve analysis, quantitative study by ICP, the mineralogical characterization by X-ray and differential thermal analysis coupled with thermogravimetric analysis. The obtained results show that mechanisms relative to the heat treatment of the phosphate are multiple and are strongly influenced by the nature of the matrix and the parameters of the treatment. The obtained product answers well the trade profiles and the requirements for use under the conditions of a temperature approximately of $800^\circ C$ and a period of 30 minutes. In these conditions, we note a decrease of 89.29% organic carbon and carbon dioxide of 72.72% with the increase in weight of Bone Phosphate Lime to 12.63%. However, the chemical reactivity and the solubility are affected.

KEYWORDS: Physical properties, Phosphate, Impurities, Optimization, Calcination, Energy.

1 INTRODUCTION

1.1 THE EFFECT OF CARBONATE SUBSTITUTION ON THE PHYSICO-CHEMICAL PROPERTIES OF PHOSPHATES

The sedimentary phosphates are granular materials and are more commercialized than 90%, they present themselves with physico-chemical properties and crystallographic varied due to geological conditions and alterations after-deposit. They are mainly composed of the group of apatite in liaison n with other accessory minerals and impurities [1] - [5]. These sediments are represented mainly by the poles fluorapatite-hydroxylated $[Ca_{10}(PO_4)_6(OH, F)_2]$ and / or carbonated fluorapatite (francolites) $[Ca_{10}(PO_4)_{6-x}(CO_3, F)_x(OH, F)_2]$ where x is generally about "1" [1]. They admit a large number of substitutions (impurities) at contents sometimes high that can modify strongly their physic-chemical properties. They allow the incorporation of a large number of elements in the crystal structure. The replacement of certain groupings by others in the apatitic network is accompanied generally with a variation of the crystallographic parameters according to the volume of the substituted groupings [1], [5], [6]. At the atomic scale, either by creating gaps and / or for reasons of steric hindrance, ionic substitutions changing the parameters of the mesh the apatite structure. A larger scale, the substitutions generate, in general, the variations in crystallinity, of thermal stability and solubility [4]. Particularly, the Francolites having one significant substitution of carbonates are very reactive. They are metastable with respect to fluorapatite and can be systematically altered by the combined effects of leaching, the metamorphism and the time. The francolites is different from fluorapatites by their chemical compositions [3]. Being porous, they offer a larger surface area and therefore a high solubility and high

chemical reactivity [2], [3]. We note that, the CO₂ content in francolites with excess fluoride varies by geological ages. Indeed, old layers the francolites usually contain a limited amount of carbonate substitution while younger layers may have compositions that include the model francolite.

The chemical reactivity is a principal parameter during the attack phosphate or in its direct use. In neutral ammonium citrate, the solubility of francolites having a maximum of substitution CO₃²⁻ (For CaO/P₂O₅ = 1.67 the solubility is about 7 % the P₂O₅). This value declines with decrease of the carbonate substitution up to approximately 1 à 2 % du P₂O₅. For the francolites having very low carbonate substitution (CaO/P₂O₅ = 1.33), this property is the same as in magmatic apatite. We note that, the Moroccan phosphates have a value that varies between 4.5 à 7 %. It appears that, the chemical reactivity of francolites increases with decreasing crystallographic parameter "a" and the growth degree of substitution carbonate. It is reported here that, carbonates bound only with apatite which determine the solubility of francolites. Contrariwise, the free carbonates affect the dissolution of phosphate rock because they are more soluble than the latter. The presence of carbonates in significant quantities may cancel the solubility of phosphate [6]. Thereby, other impurities also affect the reactivity [3]. Consequently, the rate of impurities determine the issues and laws of development of rock phosphates.

1.2 THE IMPURITIES OF PHOSPHATES AND THESE EFFECTS

The deposits of high-quality of natural phosphates are depleted day by day in the world. While the present sources are derived from sources grade containing various impurities. These impurities are sometimes well separated (exogangue) or intimately mixed with ore (endogangue), the levels of these impurities vary widely amongst the sources of phosphate rock in the same deposit and according to conditions of sedimentation [7]. They include, in various combinations and concentrations, the organic matter, the quartz, clay minerals, carbonates, radioactive elements and metal oxides.... Indeed, the organic material is a constituent characteristic of sedimentary phosphates, it presents in association with minerals (clay or carbonate) [8]. The carbonates are mainly represented by calcite, the dolomite, the iron and ankerite, therefore they introduce calcium (Ca), Iron (Fe) and Strontium (Sr) as main impurities in the crystal structure [8]. Moreover, the quartz can occur as detrital grains or as microcrystalline varieties. The other silicates may include feldspars and micas (biotite and muscovite). The content of silica will depend mainly on the proportion of quartz and detrital minerals or neofomed clays (muscovite, illite, kaolinite, montmorillonite ...) during the diagenesis. The quartz may represent a significant proportion of the phosphate matrix. Among other, zeolites, including clinoptilolite and heulandite are occasionally found [2], [3], [8], [9].

The natural phosphates also contain dangerous elements including heavy metals, such as cadmium (Cd), chromium (Cr), mercury (Hg) and lead (Pb). And the radioactive elements such as uranium (U), which comes in different forms oxides, more or less in radioactive equilibrium with its descendants, the uranium values so highly dependent on the intensity of reducing conditions. It is noted that, the organic matter may be responsible for high contents of uranium, arsenic (As) and barium (Ba), and much less lead (Pb), cadmium (Cd) and zinc (Zn) [10].

All impurities, as well as major trace, manifest adverse effects during the various stages of processing of phosphates in its derivatives as well as on the direct use [11]; [12]. In the industrial sector, the organic matter poses serious problems. It is very strong, on the slow kinetics of the crystallization of dihydrate crystals. It also affects the shape of the hemihydrate crystals that have a direct role on the filterability and permeability of phosphoric acid during its separation from the phosphogypsum [11] - [13]. Indeed, the organic matter results in the formation of foams disadvantage cooling the reaction of the attack phosphate with sulfuric acid (exothermic reaction). Thus, the temperature and viscosity of the slurry increases, which leads to the formation of hemi-hydrate phosphogypsum.

In addition, the presence of organic compounds constitutes a disturbing element [11] - [14]:

- They reduce sulfates to sulfides and subsequently results in severe corrosion of reactors [15], [16].
- They also contaminate the finished product giving black color with phosphoric acid varies from bright green to dark green [15].
- They significantly impede the recovery of heavy metals, during extraction interacting with organic solvents to form stable emulsions and / or the drosses in organo-aqueous interface.
- They have a negative effect on the storage business phosphoric acid [11].

The clays occupy an important place among the minerals associated with phosphates. Their impact on the treatment and recovery of phosphate ores are also present, they affect the filterability and product quality acid [15]. Thus, they generate dirt along the transformation process.

In addition, the components MgO, Al₂O₃, Fe₂O₃ and F affect the chemical quality of the product phosphoric acid and

change its physical characteristics, in particular its viscosity and density. They are also generating trouble when the concentration of the acid (sludge formation), its storage and its shipping (post-precipitation). Thus, fluorine is considered a depressant the reactivity. While calcium and free carbonates reduce the solubility of phosphate [12].

For heavy metals, such as cadmium (Cd), which is probably the most sought after because of its potentially high toxicity to human health. It can be contained in foods that come from phosphate fertilizer containing a quantity of cadmium than the norm. In addition, there are chromium (Cr), mercury (Hg) and lead (Pb). These metals can change shape and thereby become more or less mobile [17], [18]. They have no positive biological activity. Moreover, their life is infinite. Two factors increasing the severity of metal pollutants. On one hand, they are not biodegradable, and secondly, they accumulate in the environment and in particular in sediments by partnering with organic and inorganic materials by the interplay of adsorption phenomena, the complexation and the chemical combinations [19], [20]. Thus we find in phosphates radioactive elements, which are considered as toxic to humans and animals [10], [11].

Therefore, impurities have no economic interest and are, on the contrary, a lower value for the commercial product. The enrichment of phosphate therefore appears as a significant step, to essentially get rid of at least a large part of these drawbacks.

1.3 THE CALCINATION OF PHOSPHATES

The sediment phosphates may suffer, depending on the impurities, to mechanical and / or thermal operations enrichment, such as: crushing, screening, washing, screening, drying, calcination, magnetic separation, flotation and dry beneficiation. These operations have been studied by many authors that are cited by A. Bendada [11]. The contents of impurities and BPL (BPL: Bone Phosphate Lime) are correlated with each other. That is why depending on the content of BPL four categories are distinguished of phosphates: extra low content (ELC), low content (LC), average content (AC) and high content (HC). The phosphates HC and AC have the levels of BPL = 68% and are considered marketable products, in the case of conventional methods such as washing and drying are used to eliminate, respectively, the moisture and the fine clay fractions. Other separation methods can also use, for example the crushing and screening, to remove the large hard siliceous materials. By against, for phosphates LC and ELC previous few mechanical operations followed by calcination are often used. The aim of the latter is the stabilization of heavy metals, dehydration of humidity adsorption and structural water, the roasting of organic matter, decomposition of carbonates and other volatile compounds in gaseous form or in the form of fine. The calcination is also on the physical properties (composition, grain size, density, porosity, specific surface area, hardness, heat capacity, thermal conductivity ...) [16], [21], [22]. This is often associated with extinction to remove the magnesium, it is used in areas with a low energy cost and limited water resources [2]. The behavior of the ore to the conditions of calcination a direct impact on the course of treatment processes, it conditions the operation of the process and stability. We note that studies of the thermal stability of carbonated apatite converge to the same decomposition scheme of the product with temperature: (i) dehydrating material (humidity and all or part of the water content), (ii) burns of the organic material and (iii) decomposition of the carbonates species [23]. The residence time, the temperature and the physico-chemical properties of the phosphates are the main parameters of the calcination [2], [3]. They have a direct impact on the course of industrial processes and consequently, on overall yield. In addition, the method of calcination is an interesting factor to take into account. In this context, a comparative study of the calcination of phosphate in rotary furnace for 30 minutes, and in flash furnace (Flash) for 4 seconds, was carried out by Blazy. It follows that dynamic flash furnace calcination at 1000 °C gives more interesting than the rotary furnace calcination at 950 °C results, both in terms of the quality of the phosphate washed calcined than at the manufacture of the phosphoric acid [14]. Therefore, the rapidity of temperature rise inside the particles generates water vapor and volatile gas can escape by diffusion. Although most of the chemical and physical transformations affect the thermokinetic phenomena, the residence time in the furnace leads to transformations that cannot be partially closed; changes are kinetically blocked and roasted ore incompletely if the exposure time is very short. In addition, a long service causes of energy waste with the presence of bonding and aggregate formation.

In addition, those aspects of chemical reactions that occur during calcination, have been the studied extensively both theoretically and experimentally [2], [3]. View of the complexity of phosphates, the calcination involves several chemical reactions whose kinetics depends on the operating parameters. We note here that the distribution of heavy metals in the calcined phosphate and volatile gases depends on their vapor pressures. The calcination leads, in general, the emission of organic pollutants. The concentration and the extent of this depend on the initial amount of the behavior and origin of these pollutants in the middle. The most common compounds found are: SO_x , NO_x , N_2O , CO , CO_2 and F. the most metals are concentrated in the more solid than in gases. The vaporization is very low below 700 °C and beyond, even though it is significant, due to their very low concentrations in gases [24] - [26]. So, unlike the organic part, heavy metal phosphates are

only partially destroyed during calcination. The greater part remains in the solid residue and more volatile, in very small quantities, evaporates depending on their property and their speciation [26].

1.4 THE STATES OF MATTER (GROSS, DRY, CALCINED)

The proportion of a certain chemical element material varies depending on the heat treatment. These changes are specific to each material. They are caused from moisture after drying and from the loss to fire the product after calcination.

The mass percentage (P_i) a chemical composition on a dry matter basis wherein the moisture content is zero, taking into account the absence of the volatile during drying, will be obtained with the following formula:

$$P_d = P_c \times \frac{100}{100 - RH} \quad (1)$$

With

P_d : Mass percentage of component "i" in dry matter;

P_c : Mass percentage of component "i" the crude;

RH : Rate of humidity (%).

With losses to fire, is distinguishes between the degradable material with the other non-degradable. In both cases, it will be possible to calculate a simple rule of three, from the characteristics of the dry matter, the percentage by mass of the chemical compositions in the calcined product. This weight ratio is obtained with the following formula:

$$P_{CUD} = \frac{P_d}{100 - fl} \times 100 \quad (2a)$$

$$P_{CD} = P_d \times \frac{fl}{100} \quad (2b)$$

With

P_{CUD} : Mass percentage of component "i" undegradable in the calcined material;

P_{CD} : Mass percentage of component "i" degradable in the calcined material;

fl : Fire losses by %.

From the formulas (1) and (2) one can linking the mass percentage of a component "i" calcined with the crude by the following formulas:

$$P_{CUD} = P_d \times \frac{10^4}{(100 - fl)(100 - RH)} \quad (3a)$$

$$P_{CD} = P_d \times \frac{fl}{100 - RH} \quad (3b)$$

The rate of advancement (X) the chemical constituents of a calcined product is obtained with the following formulas :

$$X_{CUD}(\%) = \frac{P_{CUD} - P_c}{P_c} \times 100 \quad (4a)$$

$$X_{CD}(\%) = \frac{P_{CD} - P_c}{P_c} \times 100 \quad (4b)$$

With

X_{CD} : Rate of advancement of a constituent "i" degradable in the calcined material;

X_{CUD} : Rate of advancement of a constituent "i" undegradable in the calcined material.

Using the formulas (3) and (4), the rate of advancement of chemical constituents rate can be expressed by the following formulas:

$$X_{CUD}(\%) = \left[\frac{10^4}{(100-fI)(100-RH)} - 1 \right] \times 100 \quad (5a)$$

$$X_{CD}(\%) = \left(\frac{fI}{100-RH} - 1 \right) \times 100 \quad (5b)$$

In the case of calcination the phosphate, the quantity of volatile chemicals elements decreases, they do not disappear completely, with the additional presence of an amount of adsorption water in the calcined phosphate due to the hygroscopic equilibrium. For against, the amount of minerals remains almost constant even if the relative amount expressed as a percentage mass increases dramatically. For this, it must be taken into account the rate dehydration, the adsorbed moisture and the rate conversion of volatiles.

2 CHARACTERIZATION OF THE BOUCHANE PHOSPHATE

2.1 THE PRINCIPAL PHOSPHATE DEPOSITS IN MOROCCO AND GEOLOGICAL DATA

The deposits of phosphates in Morocco are located in a number of basins in four different geographical areas. It differs from North to South [30] (Figure 1). The Moroccan phosphate sedimentary series contain relatively large amounts of associated minerals [1]. These general properties have been described in several previous studies [2], [8], [27] - [29].

The phosphate test before valuation is an important study of the feasibility of a project. It is therefore necessary, as a first step, to characterize and determine the physicochemical properties of phosphate in the study area.

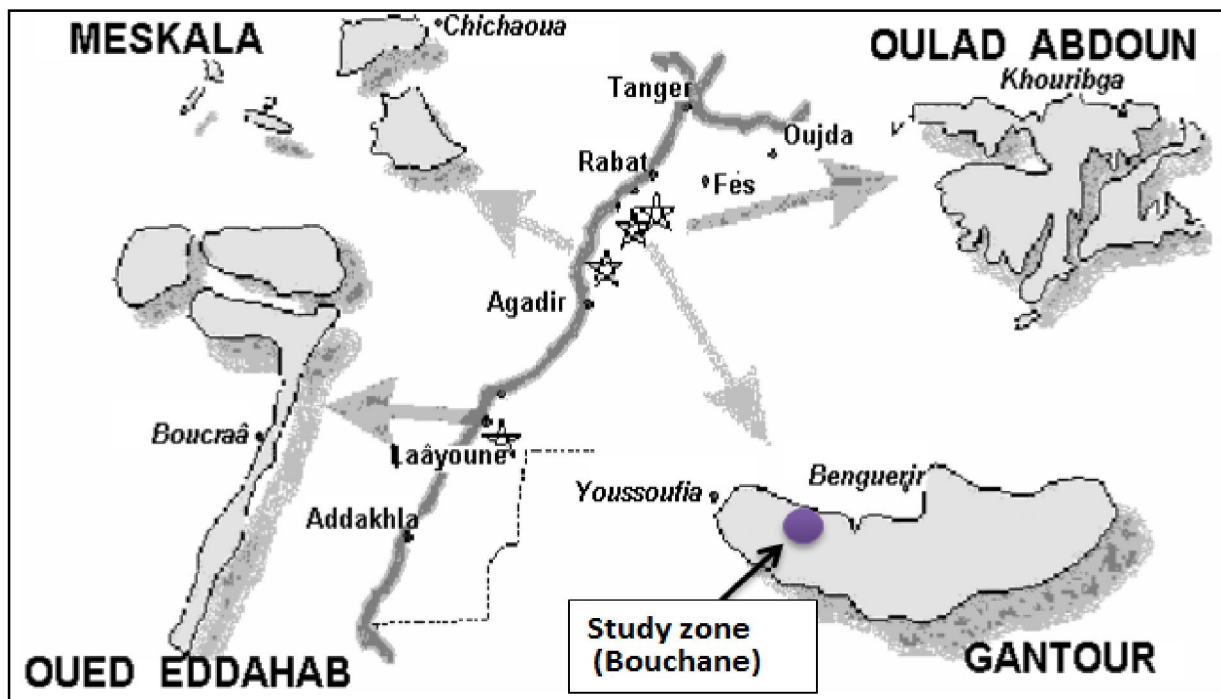


Fig. 1. Card the basins phosphates in Morocco [31].

The phosphate studied comes from the region of Bouchane, field, located 40 km to the east of the city of Youssofia which is the western part of the deposit basin Gantour (Figure 1). This deposit has large reserves of phosphates. It is the subject of special attention because of the particle size and chemical properties interesting, as the presence of in small quantities, of the organic material and carbonates and abundance of grain phosphate particle size distribution lower and upper. In addition, the operating cost is reduced by the fact that it is carried out in open. The ore of this deposit is currently undergoing a washing enrichment, for eliminating clays, and then it will be transferred to units of heat treatment (drying or calcination).

2.2 PREPARATION OF THE SAMPLES

A series of samples of the phosphate deposit was taken. The total mass is concentrated in the range of 125 to 800 μ m. In the laboratory, samples were mechanical treatment and brought into contact with the open air in plastic bags before being subjected to analysis (qualitative and quantitative), measurements and thermal treatments. One of the difficulties of phosphates is their heterogeneity, so sampling is an essential step. To have a good statistical representation, a pretreatment of homogenization was carried out according to standard NF X31-101.

2.3 PHYSICAL-CHEMICAL CHARACTERIZATION THE RAW PHOSPHATE OF STUDIED AREA

2.3.1 THE QUANTITATIVE CHEMICAL ANALYSIS

The Bouchane phosphate consists mainly of carbonate fluorapatite, it also contains several other minor elements such as: Si, K, Al, S, Mg, Cd, Cr and Fe [32]. The chemical composition of the sample of phosphate rock, determined by volumetry, is shown in the table below (Table 1).

Table 1. Average chemical composition of the crude phosphate

Elements	weight Percent (%)
P ₂ O ₅	30.39 \pm 0.15
CaO	48.20 \pm 0.25
CO ₂	6.60 \pm 0.08
C _{org}	1.40 \pm 0.03
H ₂ O	5.60 \pm 0.01
Other	7.81 \pm 0.52

With C_{org} : Carbon organic

The analysis by ICP-AES, of a few controllable elements along the recovery process and its phosphate derivative shows that our sample is similar to a rather poor carbonated magnesium phosphate, in silica and metal oxides while the pyrite is not present (Table 2).

Table 2. Chemical compositions of raw phosphate Bouchane determined by ICP – AES

Chemical compositions	Raw phosphate (%)
P ₂ O ₅	31.10
CaO	49.10
F ⁻	3.50
CO ₂	6.50
SiO ₂	1.38
H ₂ O	5.15
Al ₂ O ₃	0.42
K ₂ O	0.07
MgO	0.65
Na ₂ O	0.60
SO ₃	1.52
Cd	16.21 ppm

Several authors have linked the content of metallic pollutants with organic matter. They advocate the affinity between heavy metals and organic carbon [9], [24], [25], [33]. The result of analysis by ICP - AES shows that the Bouchane crude phosphate contains little of these metals. Therefore we are not interested to study the thermal behavior and stability of these metals in this paper.

2.3.2 DIMENSIONAL RANKING

The particle size distribution of our phosphate was performed by manual sieving dry with a series of screens Canvas Nylon mesh with round holes in geometric progression. The results obtained in Figure 2 showed that the majority is concentrated in the range of 125 to 800 μm (close to 87%) [32]. we note that the most phosphorus-rich grain size distribution between 160 and 350 μm [34].

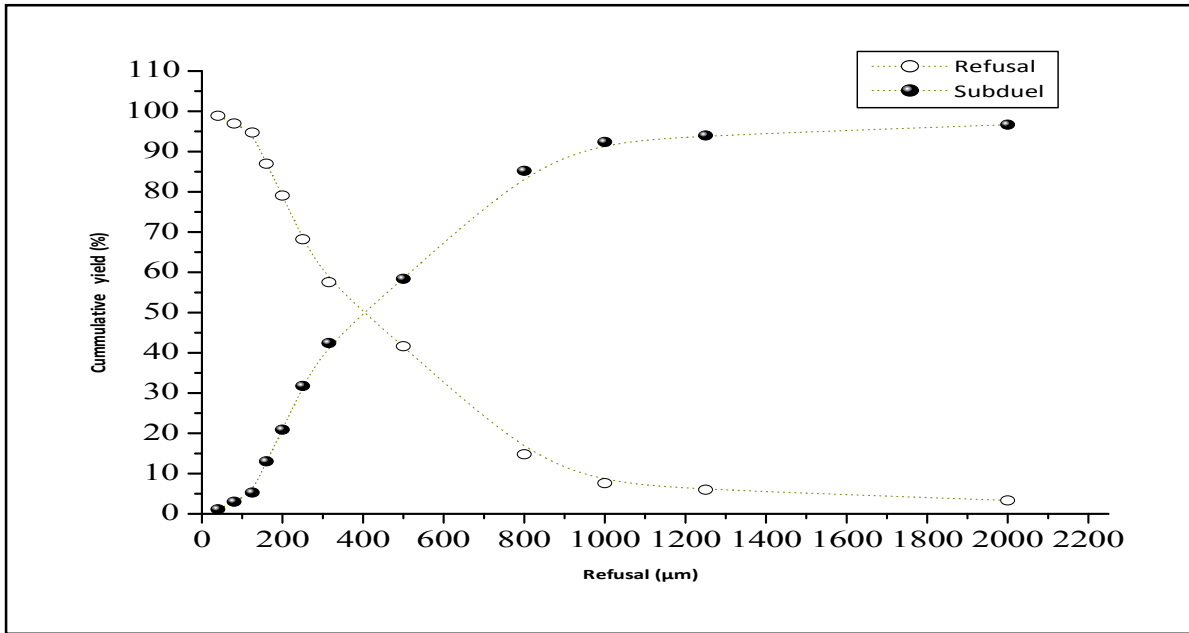


Fig. 2. Ranking dimensional sieving before classification phosphate

In the laboratory, samples of phosphate were subjected to mechanical treatment (grinding, homogenization and quartering) using a hammer mill. We performed successive operations on the refusal mesh than 500 μm and screening of fine fraction less than 40 μm . Thus, one gets the size between 40 μm and 500 μm high in phosphorus [35], [36]. This granulometric distribution is consistent with that used on an industrial scale, especially in transformation methods of phosphates in these derivatives, for a better reactivity. The classification results are shown in figure 3 [32].

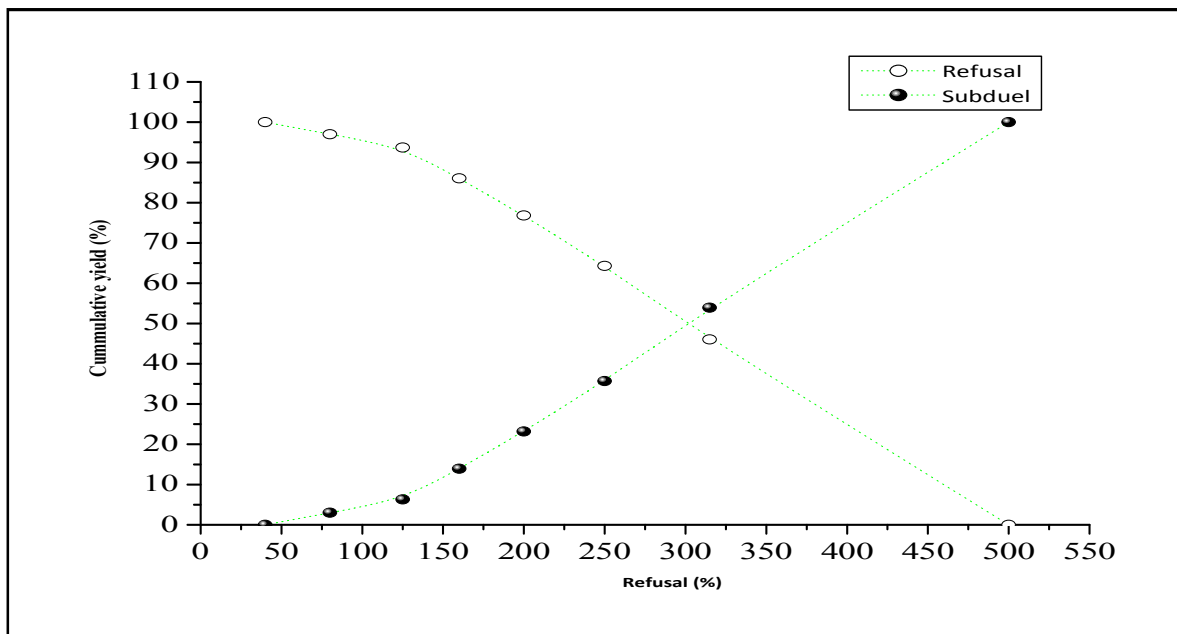


Fig. 3. Ranking dimensional sieving after classification phosphate

2.3.3 THE MINERALOGICAL ANALYSIS OF THE BOUCHANE PHOSPHATE

- **Thermal analysis:**

The thermal measurements DTA-TGA were performed in air with a heating rate of 10 °C / minute, from room temperature to 1000 °C on the wafer classified.

The thermal behavior was studied in order to predict the temperature and calcination conditions necessary to obtain a better phosphate. Three successive losses masses have been identified in connection with three temperature ranges respectively assigned, to humidity, water content, organic matter and to decomposition of carbonates [32] and this for a sample of particle size and chemical properties mentioned above (Tables 1 et 2 et Figure 3). The DTA-TGA curve of the studied crude phosphate is shown in figure 4.

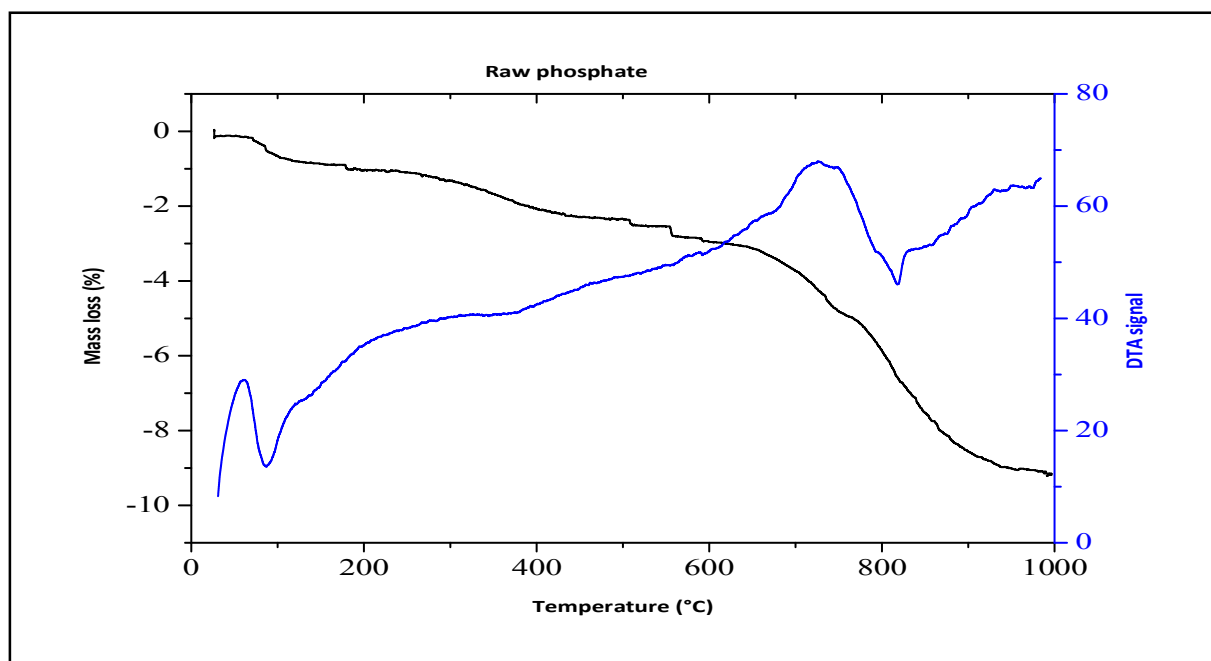


Fig. 4. DTA-TGA curve of a sample of Bouchane crude phosphate

The thermal analysis DTA - TGA shows three main mass losses:

- ✓ The dehydration represented by endothermic peak of low amplitude initially attributed to adsorption water (moisture) and observed at room temperature up to 100 °C (peak at about 80 °C). This step does not change the crystal structure of apatite. It corresponds to physisorbed water from which depends on the value of the gross surface area of the phosphate, the partial pressure of water vapor and handling conditions. The rate of humidity level of the sample used is of the order of 1%.
- ✓ The second low mass loss (2 at 3%) starts around 200 °C and which lasts up to 550 °C. The result, certainly and simultaneously, from the superposition of an endothermic reaction (from structural water) and an exothermic reaction (combustion of organic matter). We note here that the decomposition temperature depends on the raw phosphate, the experimental conditions and the partial pressure of the volatile.
- ✓ The third mass loss starts from 550 °C. It is due to continuity in the field of low exothermicity, visible and might originate from the combustion of the residual organic material and an area of strong endothermic reflecting the decomposition of carbonates (calcite (CaCO_3) and dolomite ($\text{CaMg}(\text{CO}_3)_2$)) with release of CO_2 . Thus, there is a sharp increase in the rate of mass loss between 700 and 900 °C which is due to the increase in the thermal decomposition kinetics of calcite. In addition, there is a uniform exothermicity is due to recrystallization phenomena and sintering [37]. Let us note that 1000 °C, the total mass loss is about 9.2%. This value differs between Moroccan minerals according to the level of impurities [23].

- **Characterization by X-ray diffraction (XRD):**

The X-ray diffraction was performed using a diffractometer XPRT MPD Panalytical - Philips in copper anticathode ($\lambda_{\text{CuK}\alpha} = 15.405 \text{ nm}$) at ambient temperature (Figure 5).

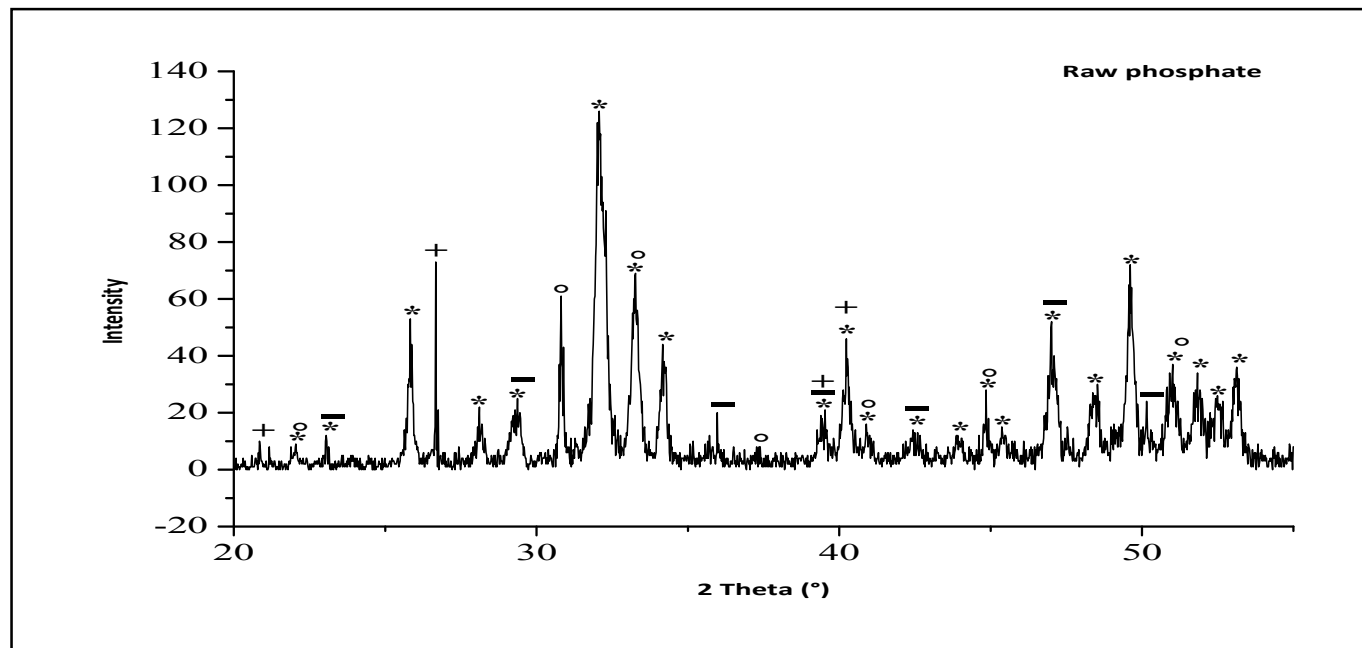


Fig. 5. RX diffractogram of a sample of the crude phosphate (*: Fluorapatite, +: Quartz, x: Calcite, °: Dolomite)

The diffractogram reveals the presence of the following phases: fluorapatite $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$ (2θ : 32.2° ; 49.8° ; 25.8° ; 34.33° ; 53° ; 51.8° ; 48.4° ; 49.6° ; 28.2° ; 52.2°), quartz SiO_2 (2θ : 26.587° ; 50.1° ; 20.885°) and carbonates which are in the form of dolomite $\text{CaMg}(\text{CO}_3)_2$ (2θ : 30.9° ; 37.1°) and calcite CaCO_3 (2θ : 36.041°) (Figure 5). It appears that the recorded dolomite, calcite and quartz phases due to their nature exogangue, while the interference of these phases with fluorapatite are due to their natural endogangue. They constitute the francolite. These overlaps can be removed, to a certain percentage, during heat processing by calcination [32]. We also note a good peak resolution X-ray diffraction, which reflects indicates a certain level of crystallinity of the phosphate. Thus, the similar diffractograms RX has been identified for other Moroccan phosphate especially those deposits Khouribga [38] and Youssoufia [39], [40].

3 BEHAVIOR OF THE MAIN CONSTITUENTS OF CONTROL

The behavior of the main components of control (C_{org} , CO_2 , P_2O_5 et CaO) during calcination was carried out by following the evolution of their weight percentages as a function of time and a function of the temperature. With the aim of determine the optimum conditions for the calcination without affecting the enrichment [32], [41].

3.1 EXPERIMENTAL PROCEDURES

The tests were carried out on samples of classified phosphate of particle size of between 40 and 500 μm . each one of these samples, the mass of about 200 grams, was placed in a vertical cylindrical enclosure in stainless steel, then in an adjustable electric furnace. The experimental procedure is as follows:

- **Protocol "1"**: Study of the calcination temperature by introducing into the furnace at 600 $^\circ\text{C}$, samples. Sampling, at different temperatures ($T_1 = 650^\circ\text{C}$; $T_2 = 700^\circ\text{C}$; $T_3 = 750^\circ\text{C}$; $T_4 = 800^\circ\text{C}$; $T_5 = 850^\circ\text{C}$ and $T_6 = 900^\circ\text{C}$), of a sample to submit to chemical analysis.

- **Protocol "2"**: The tests were performed on the same source of phosphate. We studied the residence time of calcination by proceeding in two ways:

a- First procedure (calcination in crucibles): Introduction of eight samples in crucibles in the furnace at a fixed temperature. Sampling, every five minutes, a sample for analysis of the main components of control (C_{org} , CO_2 , P_2O_5 et CaO). The temperature range is 600 to 900 °C for 40 minutes.

b- Second procedure (calcination in the fixed bed): Before introducing the fixed bed, including the sample, in the electric furnace adjustable by temperature, the latter are fixed each time to a fixed value ($T_1 = 600$ °C; $T_2 = 650$ °C; $T_3 = 700$ °C; $T_4 = 750$ °C; $T_5 = 800$ °C; $T_6 = 850$ °C and $T_7 = 900$ °C). Sampling, a function of time, of a sample for analyzing constituents of the principal control (C_{org} , CO_2 , P_2O_5 and CaO). The interval time is explored from 0 to 40 minutes.

Before all analyzes, The calcined product was cooled under the conditions of room temperature and atmospheric pressure, and submitted to extinction, by injecting air, and sieving to remove the volatile material and the adsorbed fraction with particle size bottom at 40 mm, low phosphorus [34], [36].

3.2 RESULTS AND INTERPRETATIONS

- **Study of the calcination temperature:**

The experimental protocol "1", described above, allowed us to study the variation of the composition of C_{org} , CO_2 , P_2O_5 and CaO depending on the temperature. The results of chemical analyzes are shown in figures 6a, b, c and d.

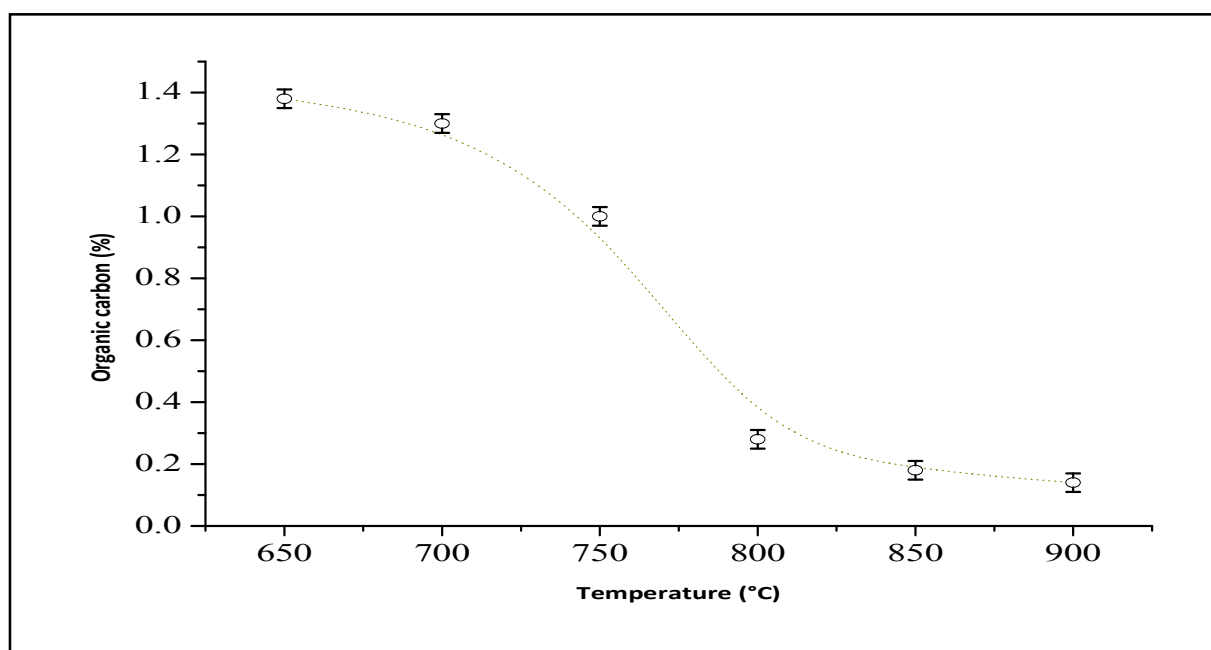


Fig. 6a. Variation of the C_{org} as a function of temperature

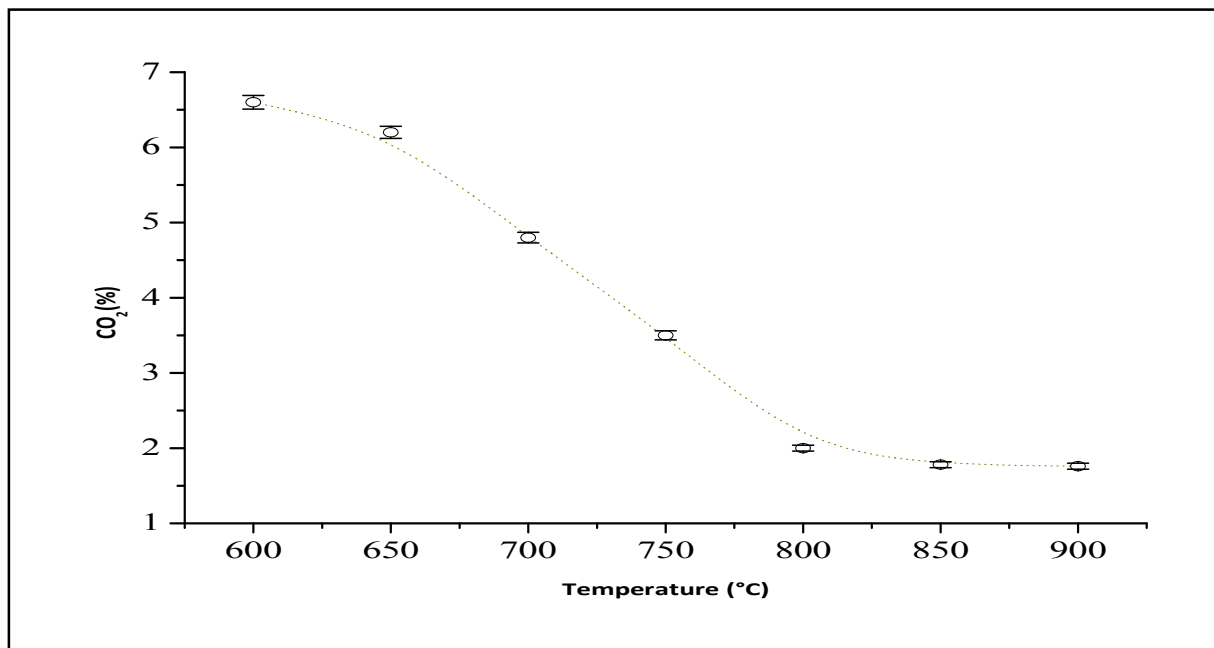


Fig. 6b. Variation of the CO₂ as a function of temperature

As shown in Figure 6a, the organic carbon content varies slightly from its initial concentration (1.4%) at temperatures between 600 and 700°C. From 700°C, the roasting of organic matter increases and appears to be complete to 800°C. Beyond 800 °C the mass percentage of C_{org} remains, significantly, substantially constant and with a value minimum about 0.15%.

In addition, the carbon dioxide begins to clear starting from 600 °C to reach a minimum value of the order of 2% at 800 °C (Figure 6b). This value remains relatively the same beyond this temperature.

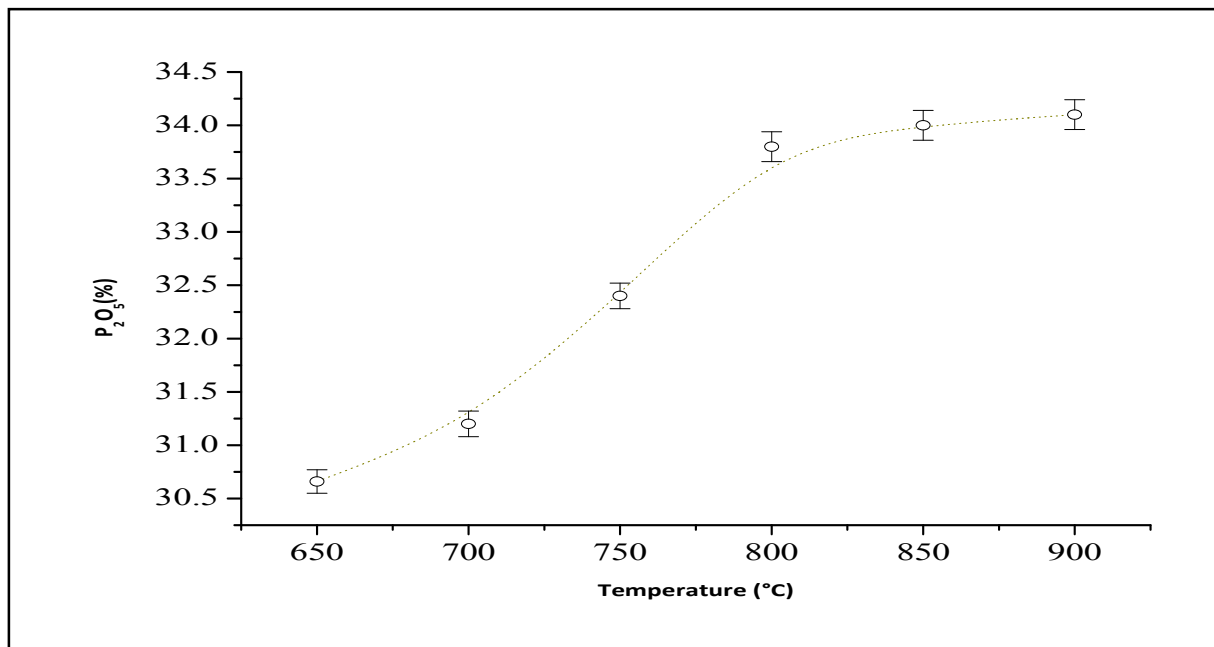


Fig. 6c. Variation of the P₂O₅ as a function of temperature

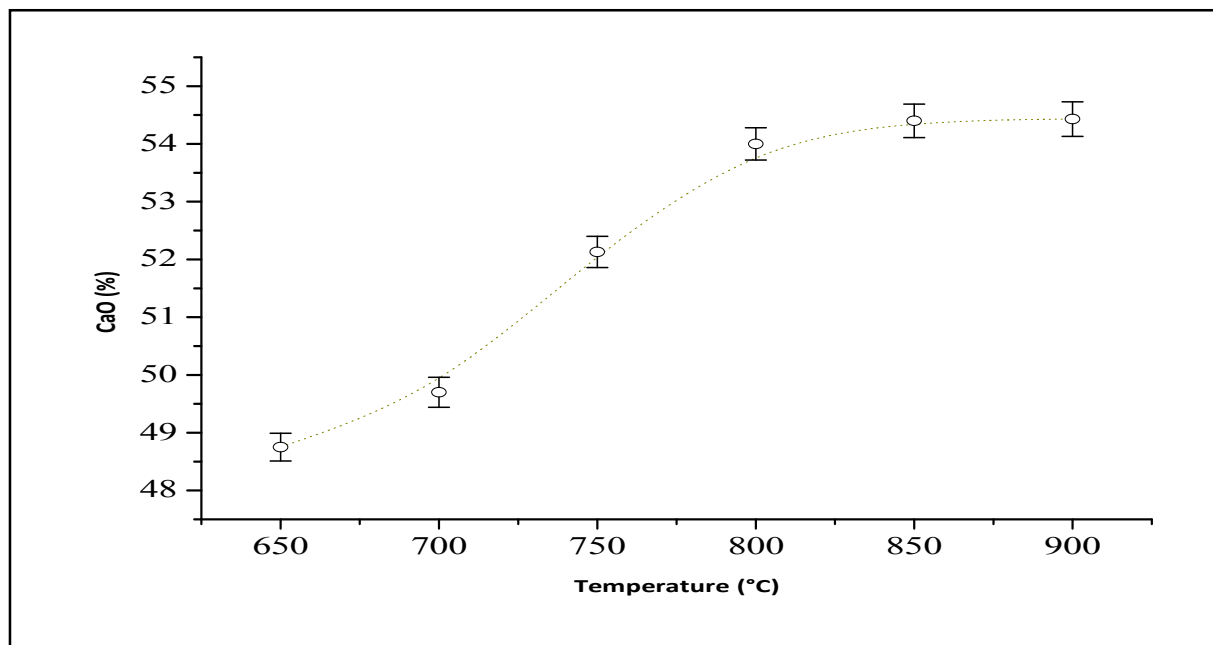


Fig. 6d. Variation of the CaO as a function of temperature

Consequently, the respective weight percentages P_2O_5 and CaO vary in the same way with temperature (Figures 6c and 6d). They believe between 600 and 800 °C. Beyond 800 °C, these values are almost invariant.

It is therefore concluded that from 800 °C, the values of the main components of control become almost invariable.

- **Study of residence time:**

The study of the residence time is of paramount importance in any energy optimization for the calcination. On an industrial scale, the residence time depends on the reaction medium, equipment characteristics and operating parameters of the process.

In our case of thermal treatment of calcination, we tried in protocol 2 to study the variation of the principal constituents of control (C_{org} , CO_2 , P_2O_5 and CaO) as a function of time at different temperatures between 600 and 900 °C [32], [41]. The figures 7a, b, c and d include the results of tests.

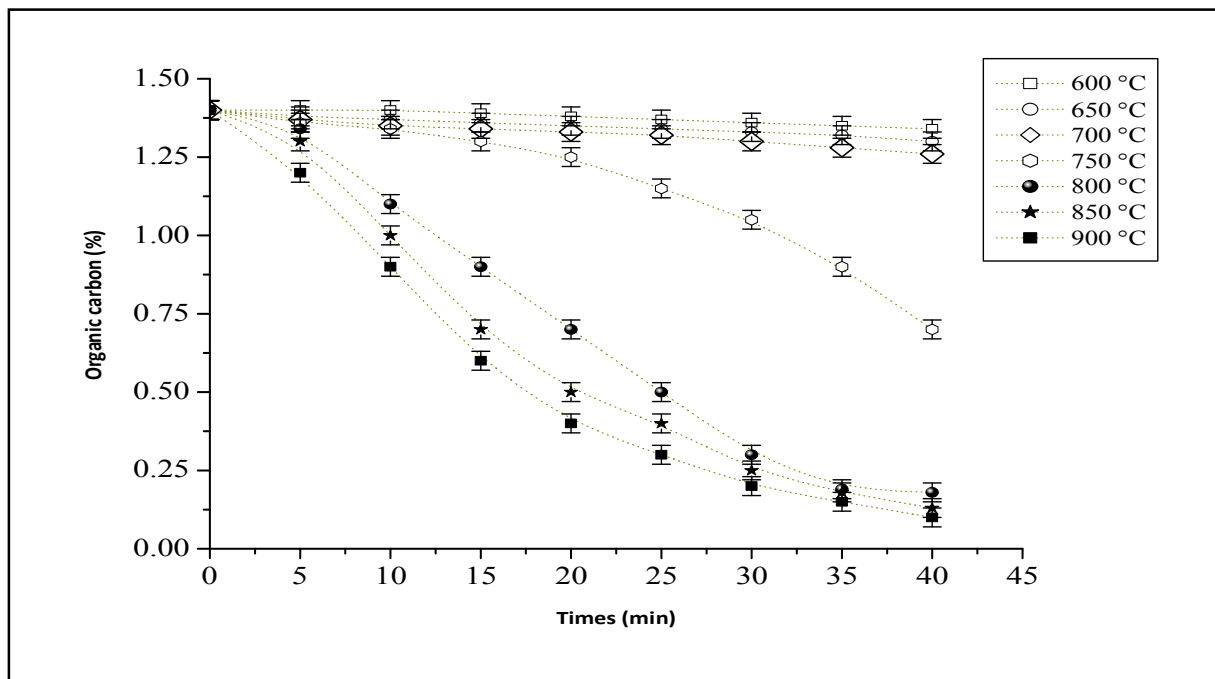


Fig. 7a. Variation of the C_{org} as a function of time at different temperatures

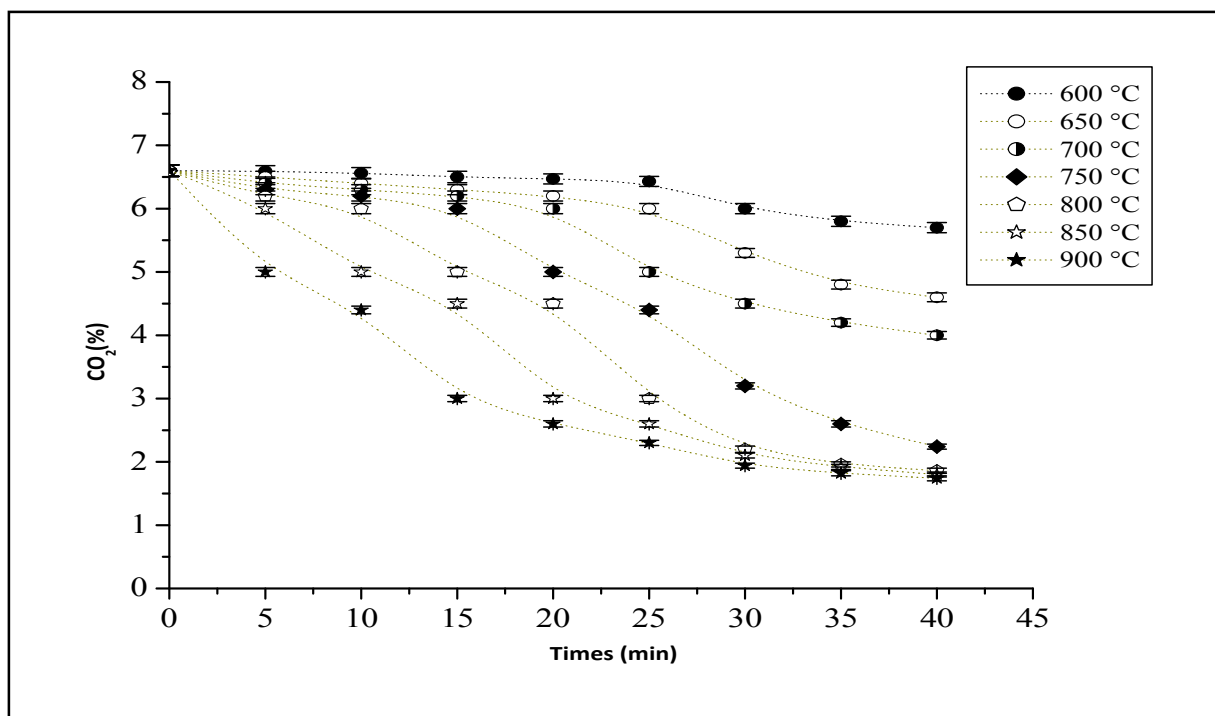


Fig. 7b. Variation of the CO_2 as a function of time at different temperatures

As we have seen previously, to a temperature of between 600 and 700°C the organic carbon content varies slightly depending on the time. This is from 700 °C as the burning of organic matter becomes measurable and accelerating with the raising the temperature. The content of organic carbon reaches a quasi-stationary 30-minute limit after roasting for higher temperatures at 800 °C, is about 0.15% (Figure 7a).

The figure 7b shows that the release of carbon dioxide is initiated from 600 °C with a remarkable speed up to 800 °C. Beyond 800 °C and from a holding time 30 min, the curves of variation are very close to 2%.

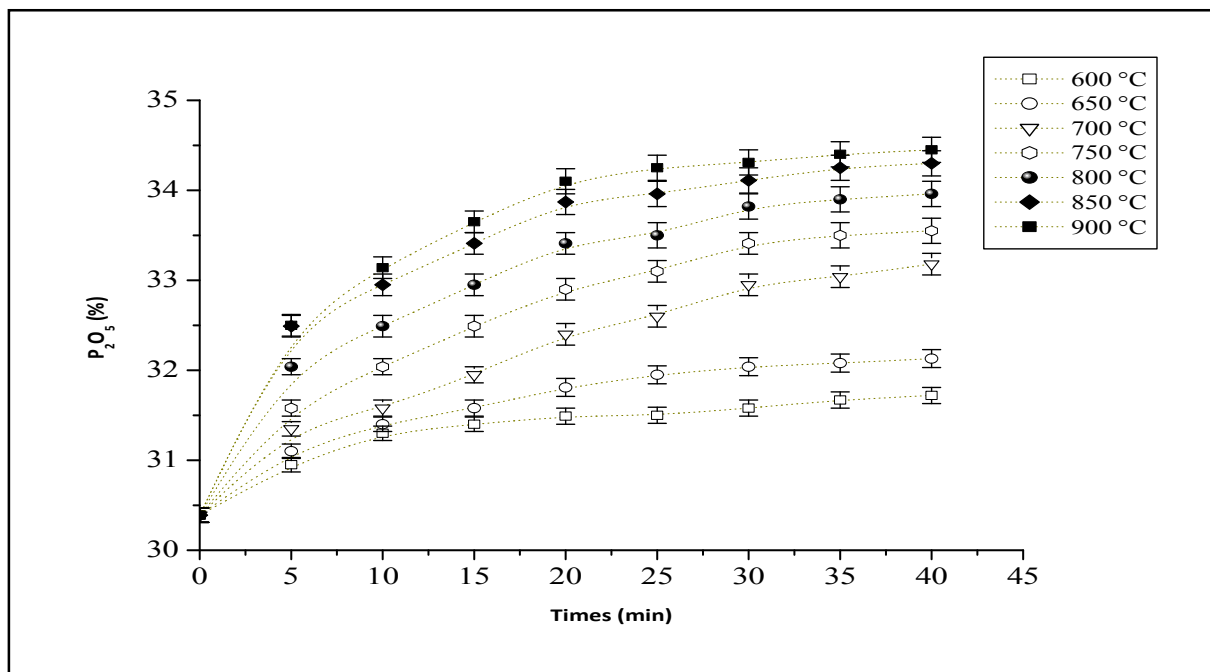


Fig. 7c. Variation of the P₂O₅ as a function of time at different temperatures

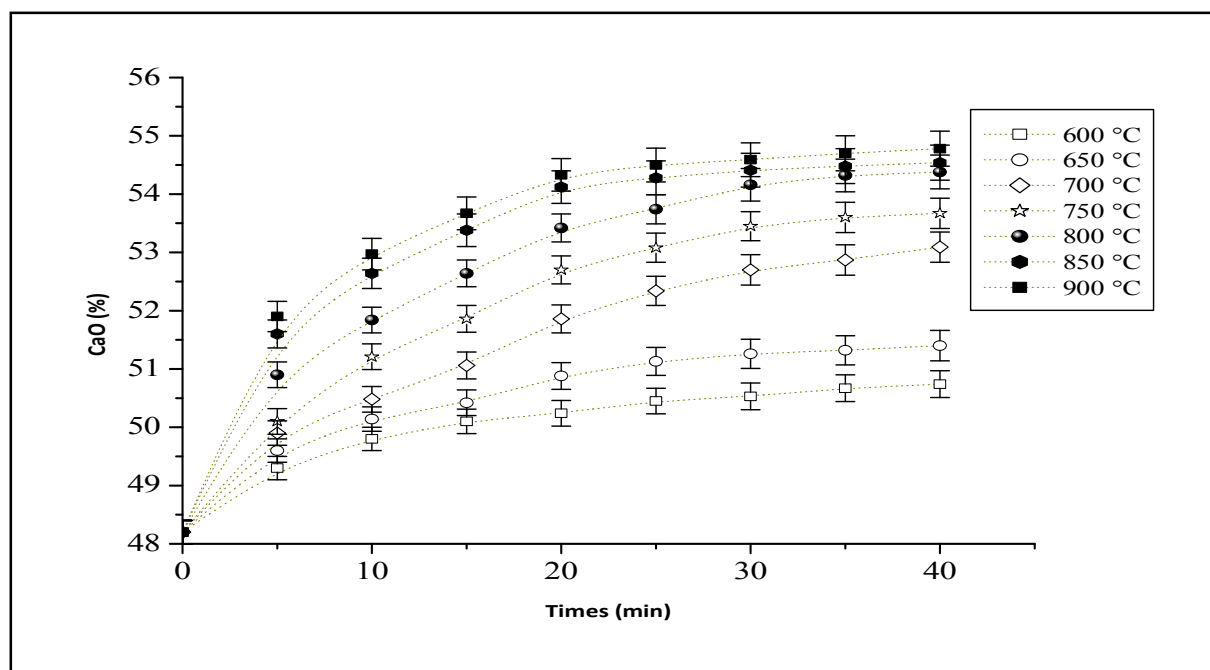


Fig. 7d. Variation of the CaO as a function of time at different temperatures

The percentages by weight of phosphorus pentoxide and lime vary in the same manner as a function of temperature and time (Figures 7c and 7d). They believe between 600 and 800 °C, after the roasting of organic matter and the decomposition of carbonates. Beyond 800 °C, these values are almost invariant and with 33.82 and 54.16% respectively.

3.3 THE RATE OF HEATING OF THE FURNACE

The electric furnace including a sample of approximately than 200 grams is maintained, in the intervals of temperature and time studied, to a variation in the rate of heating where the temperature rise is not linear (Figure 8).

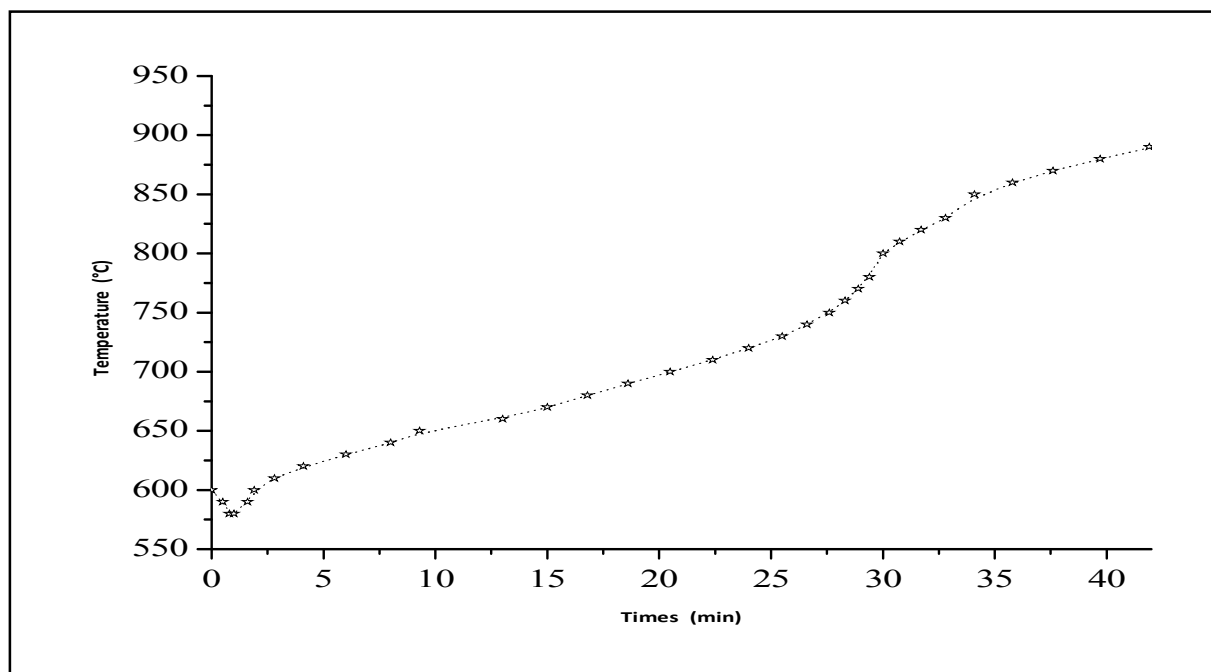


Fig. 8. Heating speed of the furnace

The speed of the heating of the furnace consists of three parts: (i) the first is the heating of the fixed bed and the sample. It requires a time of about 2.5 minutes. (ii) The linear velocity becomes to a temperature of 800 °C for 30 minutes. (iii) Beyond these conditions, the rate of heating increases. This tells us that the kinetics of thermal decomposition of the sample decreases as the content of organic matter and carbonates become weak. These remarks agree reasonably with results cited in the preceding paragraph.

4 BEHAVIOR OF ORGANIC MATTER AND CARBONATES OF CALCINED PHOSPHATE

We concluded that the calcination of phosphate requests a temperature of 800 °C and a residence time of 30 minutes. However, enrichment is never complete as it will be confirmed by studying the behavior of organic matter and carbonates of calcined phosphate, by differential thermal analysis coupled with the thermogravimetric analysis and the analysis of X-ray diffraction.

The ATG analysis revealed successive three losses masses, as in the case of crude phosphate, (Figure 4) in relation to the respective temperature ranges assigned, (i) the adsorption of moisture of the resulting hygroscopic equilibrium, (ii) to the dehydration of structural water and the roasting organic matter remaining after calcination and (iii) the decomposition of carbonates undissolved during calcination (Figure 9) [32]. The mass losses related to general reactions endothermic or exothermic nature that can followed by ATD. It follows that the endothermic peaks are due to the phenomena of dehydration and decomposition of carbonates. While, the exothermic peaks are due to the phenomena of roasting organic matter and recrystallization of the apatite phosphate.

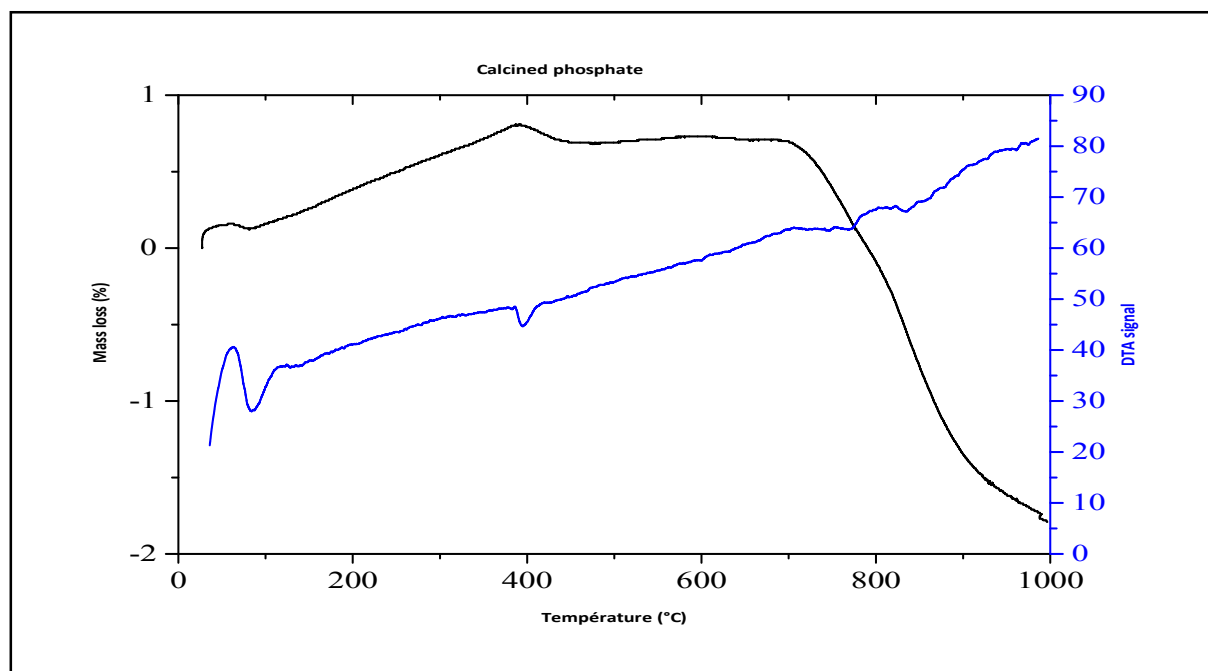


Fig 9. Curve DTA-TGA of a sample of Bouchane phosphate calcined

The peaks highlighted correspond to:

- The dehydration: This is an endothermic peak of low amplitude assigned from humidity related of adsorption phenomenon. It is observed from room temperature to 100 °C with a peak around 80 °C.
- The second mass loss: it is an endothermic peak starting around 400 °C due to the departure of the remaining amount of structural water. The exothermic reaction associated with the combustion of the organic material becomes low in the calcined phosphate is fully offset by the endothermicity.
- The third mass loss: It trigger from 750 °C. It is due to the decomposition of carbonates (calcite (CaCO_3) and dolomite ($\text{CaMg}(\text{CO}_3)_2$)) remaining in the calcined phosphate with the release of CO_2 .

The results of thermal analysis of the behavior of organic compounds and carbonates can be concluded that the almost total decomposition is effective only from 700°C. It is noted that the mass loss, the phosphate calcined under the conditions of 800 °C and 30 minutes, is the order of 1.8% (Figure 9). This value is incomparable relative to crude phosphate (9.2%) (Figure 4). It does not seriously affect the quality of calcined phosphate.

The diffraction pattern of the calcined phosphate reveals the presence of the following phases: the fluorapatite $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$ and the calcite CaCO_3 (Figure 10), the latter exists is of shape endogangue or exogangue. we note that, the interferences presented between dolomite, calcite and quartz with fluorapatite in phosphate rock are removed during calcination. The disappearance of the phases due to the decomposition of carbonates and quartz transformation of amorphous calcium silicate [42].

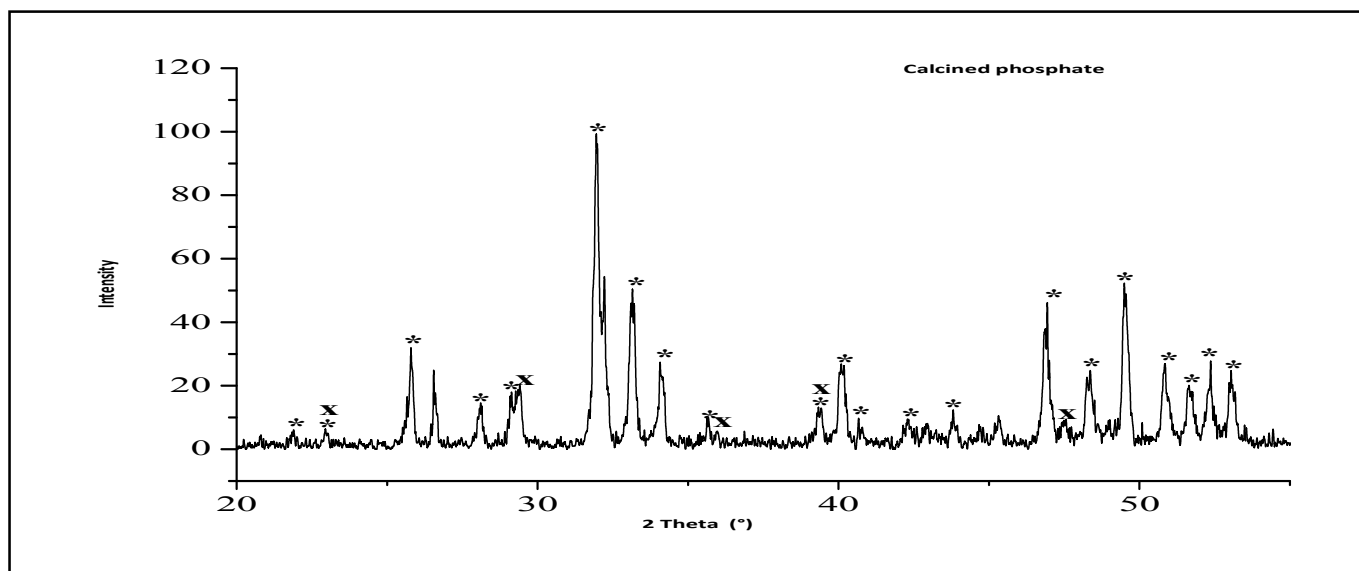


Fig. 10. Diffraction of X-ray of a sample of Bouchane phosphate calcined (*: Fluorapatite and x: Calcite)

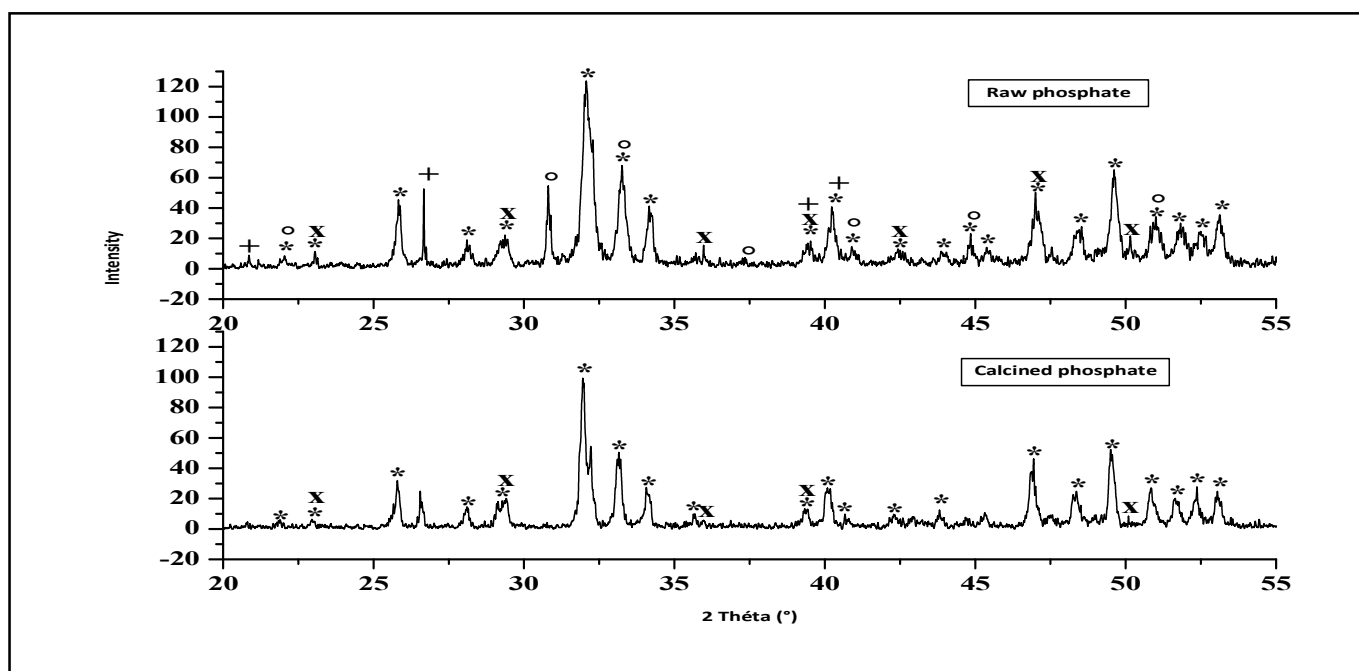


Fig. 11. Diffraction of X-ray of a sample of raw phosphate and calcined Bouchane (*: Fluorapatite, +: Quartz, x: Calcite and o: Dolomite)

The diffractograms, presented in figure 11, shows that crude and calcined phosphates are composed of phases with completely different intensities. Therefore, under the conditions of calcination, the temperature of 800 °C and a residence time of 30 minutes, the diffraction lines of the RX are refined and become resolved and less intense. The width at half height and background noise are lower in the calcined phosphate causing a good crystallinity. These findings are reflected in the thermal decomposition of carbonates that can be associated with some structural changes in the apatite. However, the improvement of the crystalline quality of calcined phosphate depends on the mass percentages of the remaining impurities, notably the fluorine, the calcite and the carbonates. We note that, the studies on other types of phosphate show that the crystallinity is only good for calcination temperatures above 700 °C [43].

5 BEHAVIOR OF THE MINERAL MATRIX DURING CALCINATION

5.1 EVOLUTION OF THE SURFACE AREA AND THE DENSITY AS A FUNCTION OF TIME AT DIFFERENT TEMPERATURES

During the calcination of phosphates, the combustion of organic matter and the decomposition of carbonates provoke a volumetric strain. This leads to a change in physical properties such as the size of the unit cell, the crystal size, surface area, density, porosity and chemical reactivity that are interdependent [16]. Therefore, it suffices to consider two or three parameters to predict the behavior of other physical properties.

The figures 12 and 13 illustrate, successively, the evolution of the specific surface area and the density as a function of time at different temperatures ($T = 600^{\circ}\text{C}$, $T = 700^{\circ}\text{C}$, $T = 800^{\circ}\text{C}$ and $T = 900^{\circ}\text{C}$).

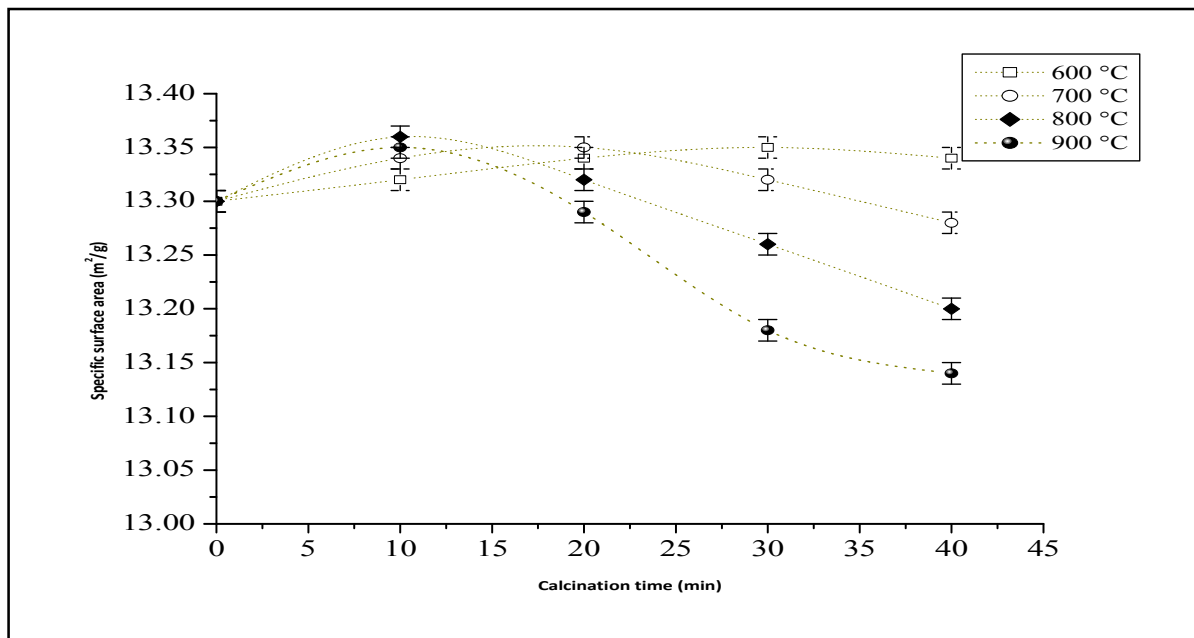


Fig. 12. Evolutions the specific surface area of phosphate as a function of time at different temperatures

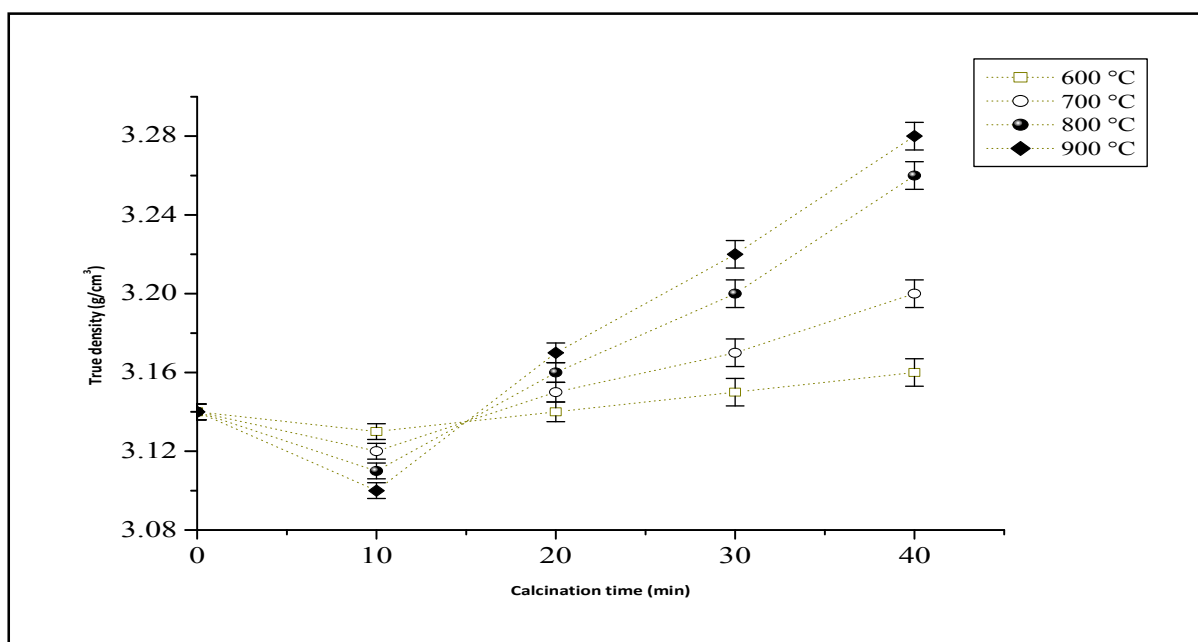


Fig. 13. Evolutions the density of phosphate as a function of time at different temperatures

It was found that the specific surface area and density of the phosphate are affected by two distinct phenomena:

While the first ten minutes, an increase is observed of the surface area and a decrease in density, as a function of calcination temperature. These variations are due to the degradation of unwanted materials, above all the mesh of the organic matter and decomposition of carbonates, which favor destruction of pores, following the breakdown of volatile gases, and therefore the increase in porosity.

Beyond the first ten minutes and 700 °C, we note a decrease in surface area and increase the density. Thus, the calcined phosphate becomes more mineral and denser. These changes become very significant with temperature due to the extent of the sintering phenomenon [44], [45].

As a result, in the first minutes of calcination and a temperature of about 700 °C, the density and the specific surface varies in the direction to increase the chemical reactivity of the phosphate. We note that, the solubility and chemical reactivity increases with decreasing density and increasing the specific surface [2]. Therefore, the organic matter and carbonates may cause slight variations on the measurement of physical properties after the calcination.

5.2 EVOLUTION OF THE SIZE DISTRIBUTION AS A FUNCTION OF TEMPERATURE

The particle size distribution of the phosphate, of between 40 and 500 μm , is requested in phosphoric workshops. Indeed, it promotes reactivity, and therefore the chemical yield. It appears therefore interesting to follow the evolution of the particle size distribution and grain size during calcination. We note that, the particles do not necessarily have spherical shapes. They may have several sizes and forms. For this, the mean diameter (d_m) which is defined as the diameter of the sphere having the volume of the particles are commonly used. This parameter is calculated by the following formula:

$$d_m = \frac{1}{\sum \frac{x_i}{d_{pi}}} \quad (6)$$

Where x_i is the weight fraction of particles having an average diameter d_{pi} .

Overall, it appears that the residence time (30 min) and calcination temperature (800 °C) are necessary to minimize the content of organic matter and carbonates of crude phosphate. These conditions depend on the particle size of the phosphate, the nature and amount of impurities and the manipulation itself.

The evolution of the particle size distribution as a function of calcination temperature, for a residence time of 30 minutes is illustrated in Table 3.

Table 3. Evolutions of the particle size distribution of the phosphate as a function of the temperature

refusal (μm) T(°C)	500 >	315 >	250 >	200 >	160 >	80 >	40 >	40 <	d_m (μm)
$T_{amb}^{(1)}$	0	37.66	24.75	15.85	9.98	9.88	1.88	0	188.44
600	0	36.96	24.25	15.45	10.20	9.94	2.16	1.04	170.77
700	0	36.60	23.85	15.30	10.65	10.30	2.40	0.9	167.11
800	0	32.27	26.21	20.20	11.30	8.56	1.43	0.03	191.15
900	1.40	32.40	26.38	20.30	11.34	7.56	0.60	0.02	202.41

⁽¹⁾ T_{amb} : ambient temperature

There is a decrease in particle size from 600 to 700 °C, above all refusal than 160 microns (decrease of the mean diameter). This change of the grain size is attributed roasting of organic matter and decomposition of carbonates and aggregation of fine grains with large grain and destruction of the structure of the pores in the coarse ore. Beyond 700 °C, there is a slight grain growth which resulted in the outbreak of the sintering phenomenon which intensifies from 800 °C (increase in average diameter), at this stage densification increases and pores begin to disappear. This is associated with a change in the microstructure of the phosphate [24].

This result confirms a correlation between the average grain diameter, the specific surface area and density. The evolution of these physical properties is improved in the direction of increasing the reactivity of phosphate during his attack, to a temperature below 800 °C. This led us to think about reducing the residence time of the calcination by reducing the cycle cooling by adjusting the cooling rate without affecting the final product.

6 CONCLUSION

The temperature, the time and the particle size are significant parameters to optimize the calcination of phosphate. In this study, we found that, the calcined phosphate meets the merchant profiles and the use requirements under the conditions of a temperature of about 800 °C and a time of 30 minutes. In these conditions, we observed a decrease of the organic carbon to 89.29% and carbon dioxide to 72.72% with an increase in weight of bone phosphate lime (BPL) to 12.63% without affecting the ratio of CaO/P₂O₅ which is equal to 1.6. However, under these conditions the calcination causes a volumetric strain, and consequently a textural evolution resulting from a different variation of physical properties which can affect the reactivity of product phosphate. The latter depends on the operating parameters and the cooling cycle of the calcination. This pushed us to think about reducing the time of the phase of cooling the calcined product.

REFERENCES

- [1] G. H. Mc Clellan, S. J. V. Kauwenbergh, "Mineralogical and chemical variation of francolites with geological time," *J. Geol. Soc.*, 148, pp. 809-812, 1991.
- [2] M. Gharabaghi, M. Irannajad, M. Noaparast, "A review of the beneficiation of calcareous phosphate ores using organic acid leaching," *Hydrometallurgy* 103, pp. 96-107, 2010.
- [3] A. M. Abouzeid, "Physical and thermal treatment of phosphate ores - An overview," *Int. J. Miner. Process*, 85, pp. 59-84, 2008.
- [4] J. Vermeulen, T. Grotenhuis, J. Joziase, W. Rulkens, "Ripening of dredged sediments during temporary upland disposal," *Journal of Soils and Sediments* 3, pp. 49-59, 2003.
- [5] L. El Himari, *Synthesis and physico-chemical studies of calcium phosphate porous grafts organic molecules*, Thesis, University of Rabat, 2007.
- [6] J. C. Elliott, "Structure and chemistry of the apatites and other calcium orthophosphates," *Elsevier, Amsterdam*, 1994.
- [7] A. Arafan, M. Benchanaa, A. Chik, J. Maghnouj, "Study of the thermal treatment of phosphate ores: Influence of chemical and mineralogical characteristics," *COVAPHOS II*, Marrakech 10-13, 2006.
- [8] S. Benalioulhaj, *Comparative series of Oulad Abdoun Basin phosphate and Basin oil shale Timahdit (Morocco). Implications in phosphatogenesis*, Thesis, University of Orleans, p. 242, 1989.
- [9] G. H. Mc Clellan, W.R. Clayton, "Francolite: The Commercial Phosphate Mineral," *IMPHOS*, pp. 21-25, 1980.
- [10] M. Cuney, "Factors controlling the nature and concentration of impurities in sedimentary phosphates," *COVAPHOS I*, Marrakech, pp. 11-14, 2004.
- [11] A. Bendada, "Experimental study and modeling of the removal of metal cations of phosphoric acid from the wet process. Application to the case of aluminum, iron and copper," Thesis of Algeria, 2005.
- [12] M. Ashraf, Z. I. Zafar, T. M. Ansari, "Selective leaching of low grade calcareous phosphate rock in succinic acid," 18(2), pp. 145-157, 2007.
- [13] S. Michael, "Wet Process Phosphoric Acid Production Problems and Solutions," *Industrial minerals*, 355, pp. 61-71, 1997.
- [14] P. Blazy, E. A. Jdid, "Calcination of calcareous sedimentary Akashat phosphate (Iraq) using a rotary kiln and a flash furnace," *C. R. Acad. Sci. Paris, série Ila* 325, pp. 761-764, 1997.
- [15] P. Blazy, E.A. Jdid, "Clinkering phenomena and sticking during calcination of limestone Akashat gangue phosphate (Iraq)," *C. R. Acad. Sci*, 324 Series Ila, pp. 79-86, 1997.
- [16] I. S. El-Jallad, *Investigations on the upgrading processes of the low grade phosphate*, Ph. D. Thesis, Cairo University, 1977.
- [17] T. Zoumis, A. Schmidt, L. Grigorova, W. Calmano, "Contamination in sediments: remobilisation and demobilization," *The science of the total Environment*, 266, pp. 195-202, 2001.
- [18] C. Caplat, H. Texier, D. Barillier, C. Lelievre, "Heavy metal mobility in harbour contaminated sediments: The case of Port-en-bassin," *Marine Pollution Bulletin*, 50, 504, 2005.
- [19] A. Battaglia, S. Ghidini, G. Campanini, R. Spaggiari, "Heavy metal contamination in little owl (*Athena noctua*) and common buzzard (*buteo buteo*) from northern Italy," *Ecotoxicol. Environ. Saf*, vol. 60, no. 61, 2005.

- [20] R. W. Canavan, P. Van Cappellen, J. J. G. Zwolsman, G. A. Van Den berg, C.P. Slomp, "Geochemistry of trace metals in a fresh water sediment: Field results and diagenetic modelling," *Science of The Total Environment*, 381, Issues 1- 3, 263, 2007.
- [21] S. J. Kowalski, "Toward a thermodynamics and mechanics of drying processes," *Chemical Engineering Science* 55, pp. 1289-1304, 2000.
- [22] Z. I. Zafar, M. M. Anwar, D.W. Pritchard, "Optimization of thermal beneficiation of a low grade dolomitic phosphate rock," *Int. J. Miner. Process.* 43, pp. 123-131, 1995.
- [23] H. E. Feki and I. Khattech, "Thermal decomposition of carbonated hydroxyapatite sodées," *Thermochimica Acta* 237, pp. 99-110, 1994.
- [24] J. Ramaroson, *Calcination of dredged sediments contaminated: Study of physico-chemical properties*, Thesis of INSA Lyon, 2008.
- [25] K. Souhila, *Organic matter decomposition and stabilization of heavy metals in dredged sediments*, Thesis of INSA Lyon, 2005.
- [26] I. Bisutti, I. Hilke, J. Schumacher, M. Raessler, "Anovel singleirun dual temperature combustion method for the determination of organic, in-organic and total carbon in soil samples," *Talanta*, 71, pp. 521-528, 2007.
- [27] L. Bilali, M. Benchanaa, M. El Harfi, K. Mokhlisse, A. outzourhit, *J. Anal. Appl. Pyrolysis* 73, pp. 1-15, 2005.
- [28] L. Bilali, A. Aouad, K. El harfi, M. Ben Chanâa and A. Mokhlisse, *J. Anal. Appl. Pyrol.* 65, p. 221, 2002.
- [29] L. Bilali, M. Kouhila, M. Benchanaa, A. Mokhlisse, A. Belghit, "Experimental study and modelling of isotherms of sorption of humid natural phosphate," *Energy Conversion and Management* 42, pp. 467-481, 2001.
- [30] A. Noubhani, "Selachii ponds Morocco phosphate (Maastrichtian - Lutetian): Systematics - Biostratigraphy - Evolution and dynamics of fauna," *PhD Montpellier II*, p. 73, 1986.
- [31] S. Bakkali, "Application of spatial filtering to the analysis of the contours of anomalous zones of fault of phosphate series Sidi Chennane: Morocco," *Africa Science* 02 (1), pp. 116-130, 2006.
- [32] M. El Ouardi, L. Saadi, M. Waqif, H. Chehouani, I. Mrani, M. Anoua, A. Noubhani, "Characterization of phosphate Bouchane (Morocco) and study the evolution of the main components of the control of its calcination," *Phys. Chem. News*, 54, pp. 68-75, 2010.
- [33] H. Azim, K. H. El Moselhy, "Determination and partitioning of metals in sediments along the suez canal by sequential extraction," *Journal of Marine Systems*, 56, pp. 363-374, 2004.
- [34] S. Elasri, *New materials apatite structure prepared from natural Moroccan phosphate environmental applications*, Thesis flap University Mohammed V - Rabat, 2009
- [35] H. D. Vosteen, R. Schellschmidt, "Influence of temperature on thermal conductivity, thermal capacity and thermal diffusivity for different types of rock," *Phys. Chem. Earth*, 28, pp. 499-509, 2003.
- [36] L. Bilali, M. Benchanaa, A. Mokhlisse, "Pyrolysis black Youssoufia phosphate by heating conventional," *COVAPHOS I*, Marrakech, pp. 34-37, 2004.
- [37] L. Rebiai, *Thermodynamic study of sintered materials-based kaolin tamazert*, Thesis, University Mentouri - Constantine, 2006.
- [38] M. Mouflih, A. Aklil, S. Sebti, "Removal of lead from aqueous solutions by activated phosphate," *J. Hazard. Mater. B* 119, pp. 183-188, 2005.
- [39] A. Aouad, M. Benchanâa, A. Mokhlisse, A. Ounas, "Thermal analysis of Moroccan phosphates Youssoufia in an oxidative atmosphere by TG and DSC," *Journal of Thermal Analysis and Calorimetry* 75, pp. 887-900, 2004.
- [40] A. Aouad, M. Benchanâa, A. Mokhlisse, A. Arafan, "Study of thermal behaviour of organic matter from natural phosphates (Youssoufia -Morocco)," *Journal of Thermal Analysis and Calorimetry* 70, pp. 593-603, 2002.
- [41] M. El Ouardi, H. Chehouani, M. Anoua, I. Mrani, "Thermic treatment of phosphate: drying – calcination," *Third international conference*, Marrakech, 7-10 December 2005, p 231;
- [42] F. Z. Boujrhah, *Study of the emanation of radon-222 and corresponding sedimentary phosphates phosphogypsum. Effect of temperature*, Thesis Rabat, 1993.
- [43] L. Sandrine, *Synthesis and thermal behavior (stability and sintering) of rare earth phosphates cerium or yttrium*, Thesis, University of Limoges, 2003.
- [44] X. Shu, X. Xu, H. Fan, S. Wang, D. Yan, "Application of TG - DTG analysis and centrifugal separation in the investigation of less combustible constituents in coals," *Thermochimica Acta*, 381 (1) , pp. 73-81, 2002.
- [45] D. Nicholson, "Variation of surface area during thermal decomposition of solids," *Trans Faraday Soc.*, 61, pp. 990-998, 1965.