



Characterization of crude and calcined phosphates of Kef Essennoun (Djebel Onk, Algeria)

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Received: 6 August 2019 / Accepted: 4 August 2020 / Published online: 15 September 2020
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Abstract

Rock phosphate is the fundamental component for the manufacture of phosphoric acid and phosphate fertilizers. The aim of this study is to predict how sample preparation of Kef Essennoun phosphate responds to heat treatment and to estimate the purity of the raw and calcined phosphates. The influence of temperature (600–900 °C) was evaluated. The evolution of thermal treatment and the characterization of the Kef Essennoun ore (Djebel Onk mine, Algeria) were carried out by various analytical techniques including X-ray diffraction (XRD), wavelength-dispersive X-ray fluorescence, Fourier-transform infrared spectroscopy, thermogravimetric analysis/differential thermal analysis, and scanning electron microscopy (SEM). The results showed that the raw phosphate is a mixture of six phases, of which carbonate hydroxyapatite [Ca₁₀(PO₄)₃(CO₃)₃(OH)₂] is the dominant phase. With heat treatment, at 700 °C, a fluorapatite [Ca₅(PO₄)₃F] phase appeared, as confirmed by XRD analysis, with good crystallization indicated by SEM. The P₂O₅ content was increased from 28.389% in raw phosphate to 31.085% in the calcined product. The dissolution of the calcined phosphate at 900 °C was completed by HNO₃ acid attack, and occurred rapidly at ambient temperature. The results show that the production of phosphoric acid by Ca₅(PO₄)₃F was more easily achieved with optimized consumption of the acid attack.

Keywords Phosphates · Phosphoric acid · Environment · Calcination · Characterization · Thermogravimetry

Introduction

The Djebel Onk deposit in Algeria is a significant phosphate reserve. Djebel Onk is located approximately 100 km southwest of Tébessa, near the Tunisian border, with a capacity of about 2 billion tons of 53–61% tri-calcium phosphate (TPL) [1]. The current annual production is about 2.3–2.5 million tons of high-grade ore (25–26% P₂O₅). Organic matter is usually present in the phosphates in very small quantities, from 0.25 to 1%. Despite this low content, it hinders the purification of phosphoric acid. The main constituents of the organic matter in phosphate sediments include aliphatic and polynuclear aromatic hydrocarbon, lipids, fatty acids and humic compounds [2, 3]. The presence of organic matter in the phosphates is a major drawback because of the formation of foam that causes difficulties in separating phosphoric

acid and calcium sulfate [4, 5], and it hinders the recovery of uranium. Among the processes proposed in the literature, the calcination process has very interesting advantages in terms of eliminating organic matter and also decomposing the gangue minerals (carbonate) to form CaO and MgO, which can be separated after calcination by extinction and washing [6].

In the present work, we consider calcining the natural phosphate in order to achieve both elimination of organic matter and changes by heat treatment, as considered by many authors [7–9]. The calcination of Kef Essennoun phosphate is studied in the temperature range of 600–900 °C. The evaluation of the calcination process is followed by characterization of the raw and calcined phosphate by various analysis techniques including X-ray diffraction (XRD), wavelength-dispersive X-ray fluorescence (WDXRF), Fourier-transform infrared spectroscopy (FTIR), thermogravimetric analysis/differential thermal analysis (TG/DTA), and scanning electron microscopy (SEM). This process is necessary to obtain a suitable phosphate material for the production of light-green phosphoric acid, which in turn is used for the production of ultrapure phosphoric acid.

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Experimental

Sample preparation

Phosphates used in this study came from the Djebel Onk deposit (Fig. 1), part of a succession of sedimentary layers formed at the end of the Cretaceous–Eocene. Djebel Onk is a limestone mountain range, about 20 km long. Phosphates are milled and sieved at a diameter of 80 μm .

Thermal treatment and characterization

Calcination was used to pretreat Djebel Onk phosphates. Traditionally, the heat treatment of phosphate ore involves heating the ore to a certain temperature in order to obtain a product with specific properties. The calcination method in this study was carried out by introducing samples of phosphate into a muffle furnace at fixed temperatures of 600 °C, 700 °C, 800 °C and 900 °C. The sample was then analyzed by XRD, WXRf, FTIR, and SEM, and %CaCO₃ was calculated by determination of total limestone (Bernard calcimeter).

Simultaneous thermogravimetric (TG) and differential thermal analysis (DTA) of crude phosphate sample was carried out on a Setaram Labsys TM TG-DTA16 instrument. The sample is introduced into a furnace in an inert nitrogen environment at a heating rate of 10 °C min⁻¹. The temperature range employed was from ambient to 900 °C. The phase identification and the related properties of the calcined phosphates were investigated by XRD using a PANalytical X'Pert (Philips) instrument operated at 45 kV and 40 mA. All the

data were processed by X'Pert HighScore Plus software with commercial databases [full width at half maximum (FWHM) deduction and peak identification]. The infrared spectra were recorded in the range of 400–4000 cm⁻¹ with a Nicolet 380 FT-IR spectrometer.

Results and discussion

Composition of raw phosphate

The composition of the Djebel Onk phosphate is presented in Table 1. Chemical analysis as determined by WXRf shows that the content of P₂O₅ is 28.389% and CaO is 41.346%. The CaO/P₂O₅ mass ratio is a common measure of rock quality. The mass ratio for the raw phosphate was 1.456, which was increased to 1.784 for phosphate calcined at 900 °C. It is important that this value does not exceed the percentage required on the phosphates market [10]. The effect of temperature shows that the grade (P₂O₅ at.%) of phosphate ore increased for calcination at 900 °C, with MgO < 1%. Iron (Fe₂O₃) and aluminum (Al₂O₃) form phosphate sludge as the acid is concentrated to commercial concentrations, contributing to P₂O₅ losses and maintenance requirements (Fig. 2). As P₂O₅ concentrations increase, high iron content contributes to increased acid viscosity. Aluminum enhances the crystal properties; high aluminum content is associated with good filtration rates. Aluminum also reacts with fluoride ions to form aluminum fluoride complexes. Above a certain concentration, magnesium is linked to increased product acid viscosity and to the formation of struvite (MgNH₄PO₄·6H₂O) when making ammonium phosphates

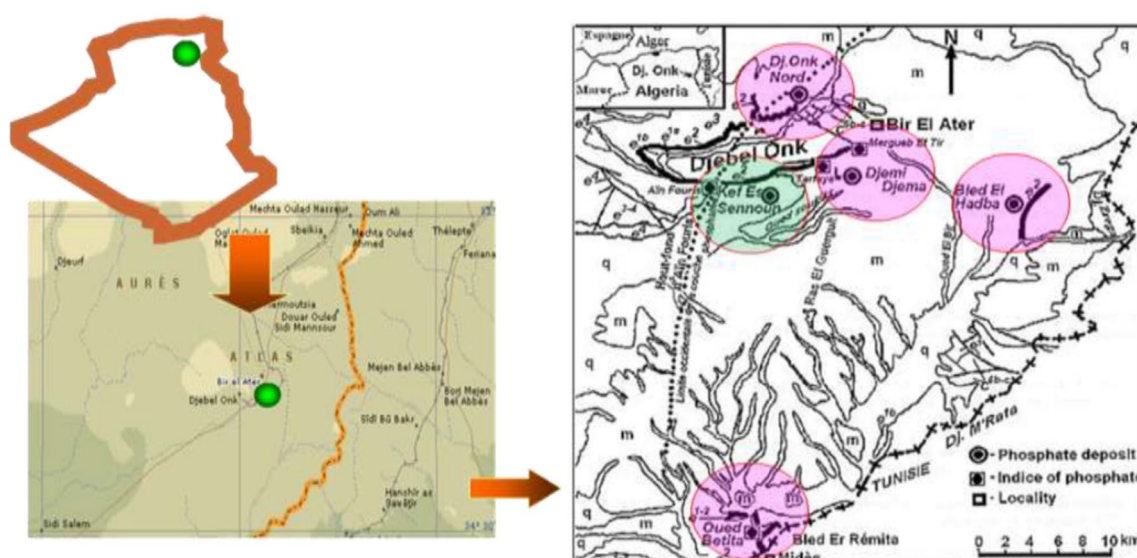


Fig. 1 Location of Djebel Onk (Tebessa), Algeria

Table 1 Chemical composition of raw and calcined phosphate

Formula	Composition/%		
	Raw phosphate	Calcined at 800 °C	Calcined at 900 °C
F	3.726	3.833	4.317
Na ₂ O	1.441	1.998	1.356
MgO	0.913	1.565	1.539
Al ₂ O ₃	0.580	0.561	0.606
SiO ₂	2.189	2.164	1.942
P ₂ O ₅	28.389	31.089	31.085
SO ₃	3.184	3.873	3.328
Cl	0.086	–	0.052
CaO	41.346	53.382	55.479
Fe ₂ O ₃	0.378	0.611	0.600
K ₂ O	0.153	0.076	–
CaO/P ₂ O ₄	1.456	1.700	1.784

(human kidney stones can also comprise struvite). In the industry, two ratios are used to describe these impurities, the iron–aluminum (I&A) ratio and the minor element ratio (MER): the lower the ratio, the purer the rock. I&A and MER are defined in the following equations:

$$I\&A = \frac{\%Al_2O_3 + \%Fe_2O_3}{P_2O_5} = 0.08 \text{ to } 0.10 \tag{1}$$

$$MER = \frac{(\%Al_2O_3 + \%Fe_2O_3 + \%MgO)}{P_2O_5} = 0.08 \text{ to } 0.20 \tag{2}$$

The results in Table 2 show that the two values of I&A and MER calculated for the raw and calcined phosphates at 900 °C are very low, in the range of 0.036–0.038 and 0.070–0.078, respectively.

Thermal analysis

Many studies on natural phosphates have shown that when these materials are subjected to heat treatment, different mass loss as a function of temperature occurs [11]. A Lab-sys™ TG-DTA16 was used to sample 10–20 mg nacelle compound while also utilizing a high-precision micro-balance. The nacelle is introduced into a furnace in an inert nitrogen environment with a heating rate of 10 °C min⁻¹. The temperature range employed is from ambient to 900 °C. The results (Fig. 3) revealed three main successive mass losses. The first mass loss of 1.4% is observed between room temperature and 150 °C and is attributed to the loss of water (moisture). The second mass loss is observed between 220 and 550 °C, which can be considered as roasting [12]. It is attributed to the simultaneous loss of structural water and the decomposition of organic matter. [13]. It should

Table 2 Variation in I&A and MER

	Raw phosphate	Calcined phosphate (900 °C)
I&A	0.038	0.038
MER	0.070	0.087

Fig. 2 Composition of Djebel Onk beige phosphate

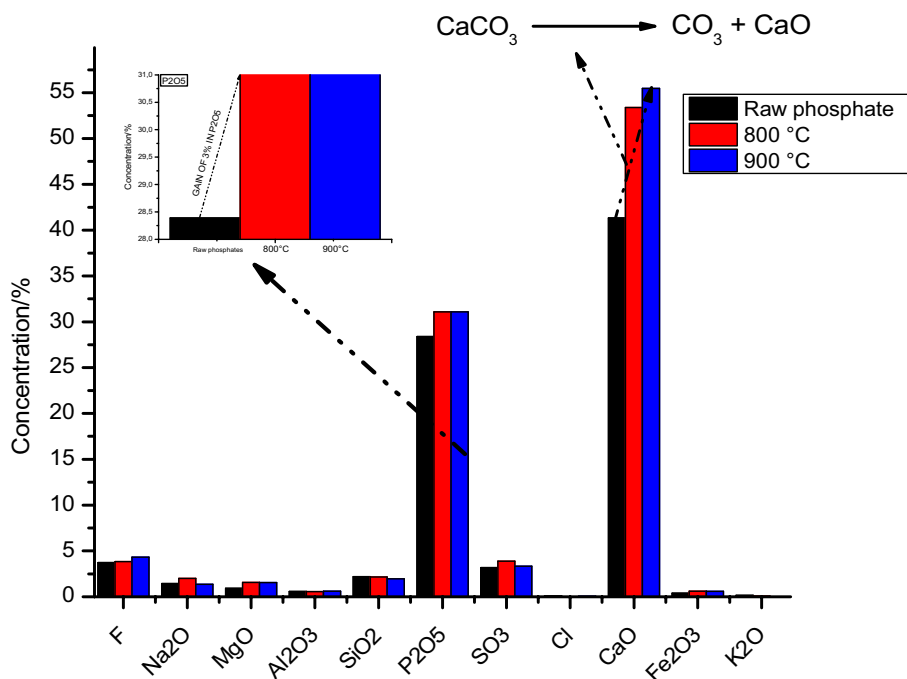
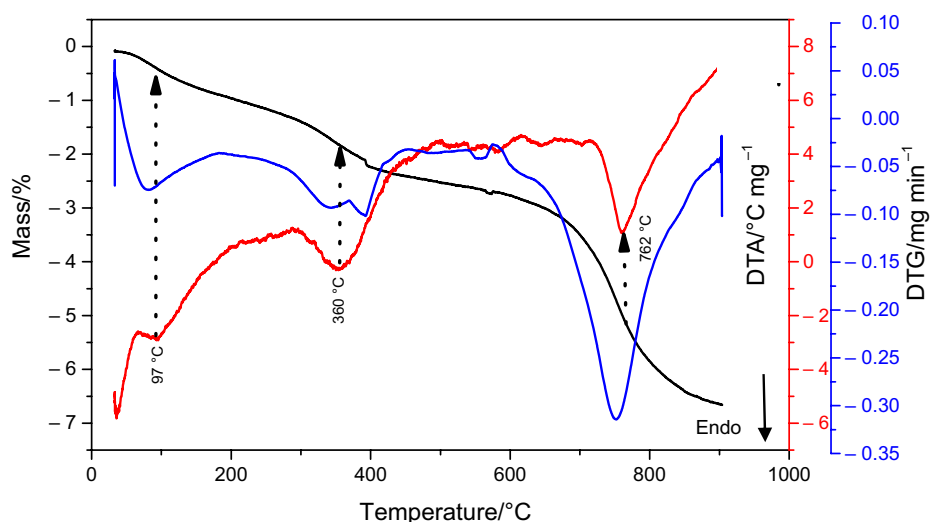


Fig. 3 TG/DTA curve of beige Djebel Onk phosphate



be noted that it is 2.116% for the studied phosphates. The third mass loss, the most important, is recorded between 600 and 900 °C. It corresponds to the decomposition of calcite releasing CO₂ and H₂O. The importance of this loss is related to the abundance of dolomite cement (carbonated), estimated to be 6.123%. In the DTA curve, it was possible to observe three endothermic peaks at 97, 360 and 762 °C. They are respectively related to evaporation, melting and decomposition of organic matter, and the decarbonation reactions of endogane (Fig. 3).

Structural characterization

XRD mineralogical analysis

Figure 4 shows the XRD recorded at room temperature for the raw phosphate powder and for the powder calcined at different temperatures. The identification of the mineral phases of the samples showed the presence of the apatite mineral class, including hydroxyapatite [Ca_{9.74}(PO₄)₆(OH)_{2.08}],

carbonate-hydroxyapatite [Ca₁₀(PO₄)₃(CO₃)₃(OH)₂] and carbonate-fluorapatite [Ca₁₀(PO₄)₅CO₃F_{1.5}(OH)_{0.5}]. Apatite mineral class phases are known by their non-neutrality due to the presence of carbonates in their structure and those of the matrix such as dolomite [CaMg(CO₃)₂], quartz (SiO₂) and calcite (CaCO₃) for raw phosphates [14, 15]. Carbonate-hydroxyapatite [Ca₁₀(PO₄)₃(CO₃)₃(OH)₂] is the dominant phase in raw phosphate. The ionic crystal belongs to the space group *P63/m*, and diffraction patterns are indexed according to JCPDS card 19-0272 [16, 17]. The spectra are similar and have the same hexagonal structure regardless of the temperature. We also note that the intensity is proportional to the temperature increase. This is due to the crystallization of phosphate calcined in the temperature range of 600–900 °C and the appearance of a very stable phase that is fluorapatite [Ca₅(PO₄)₃F], as shown in Fig. 5. The results confirm the structural rearrangement and the decomposition of the carbonates included in the phases. However, with the presence of carbonate, the 211 and 112 reflections are superimposed in the raw phosphate and the phosphate calcined at 600 °C.

Fig. 4 X-ray diffraction patterns of the raw phosphate

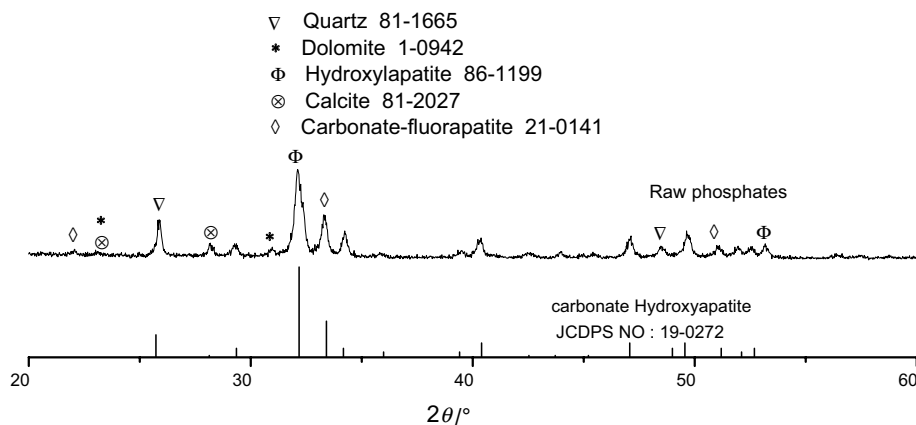
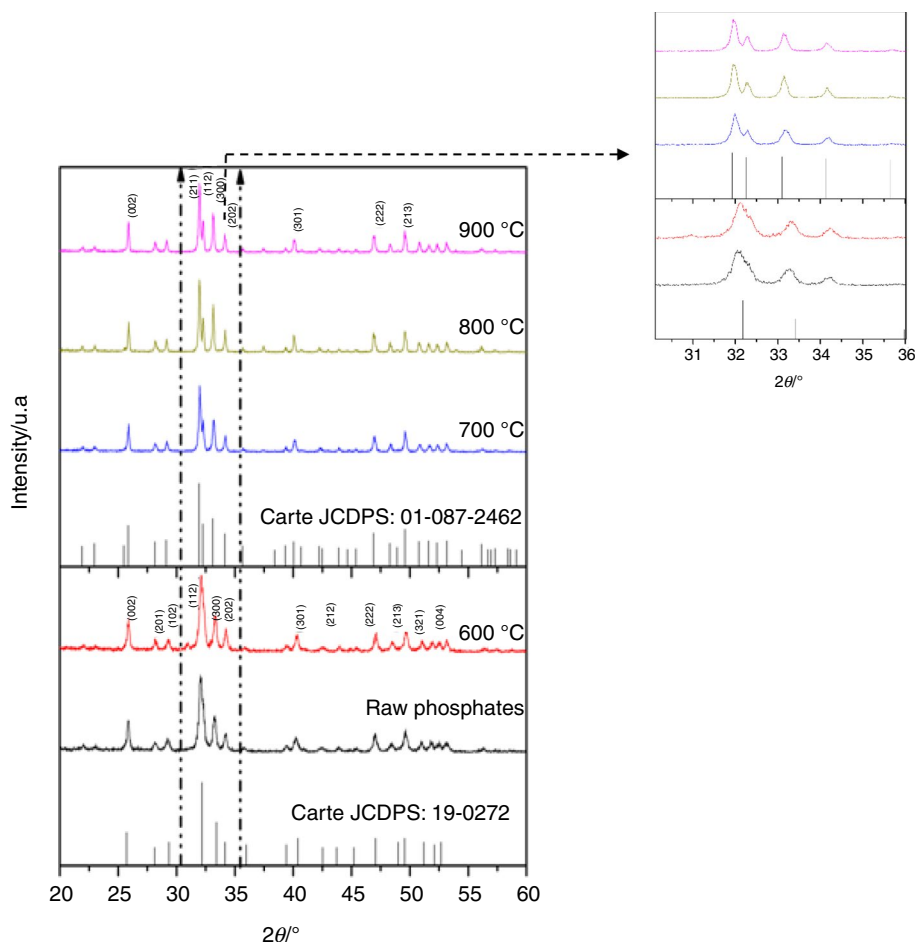


Fig. 5 X-ray diffraction patterns of phosphate calcined at different temperatures



The diffractograms of the phosphates show fine lines. In order to obtain more detailed structural information, the crystallite sizes (*D*) of fluorapatite at different temperatures were calculated from the full width at half maximum (FWHM) of all the diffraction peaks in the XRD patterns using the Scherrer formula [18, 19] as given below:

$$D = K\lambda / \beta_{\text{sample}} \cos \theta \tag{3}$$

Here *K* is the Scherrer constant, which is its good approximation value is 0.9, λ ($= 1.54059 \text{ \AA}$) is the wavelength of CuK α radiation, $\beta_{\text{sample}} = \sqrt{\beta_{\text{exp}}^2 - \beta_{\text{ins}}^2}$, β_{exp} is the FWHM

in all (*hkl*) reflections, β_{ins} is the correction factor for instrument broadening and θ is the diffraction angle.

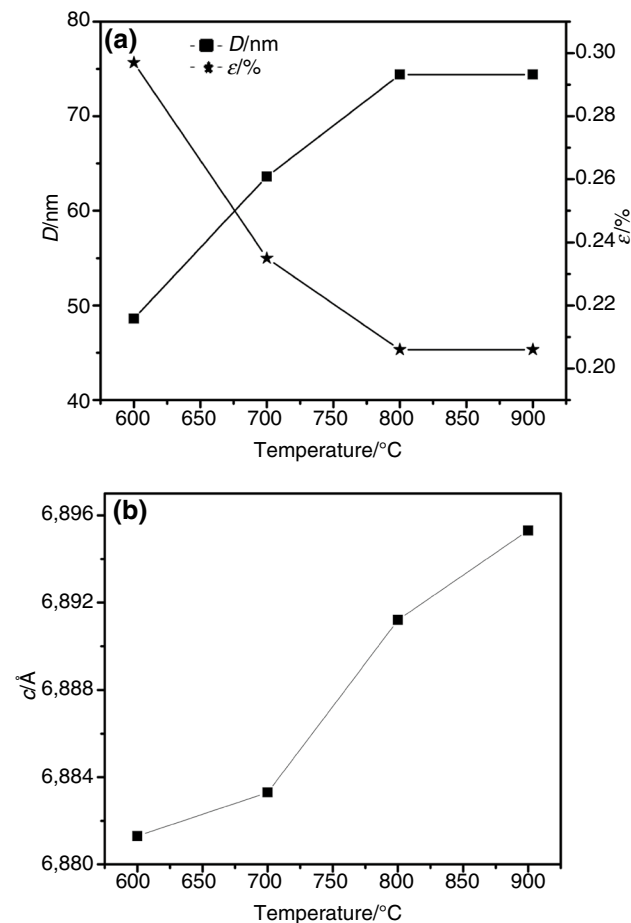
The crystallographic parameters of the phosphate rock and of phosphate calcined at different temperatures are presented in Tables 3 and 4. The crystallite size increases with the increase in temperature from 48.6 nm at 600 °C to 74.4 nm at 800 °C and then remains constant. It was also found that the strain decreased with the increase in temperature (Fig. 6). The results confirm the rearrangement among the $\text{Ca}_{9.74}(\text{PO}_4)_6(\text{OH})_{2.08}$, $\text{Ca}_{10}(\text{PO}_4)_3(\text{CO}_3)_3(\text{OH})_2$ and $\text{Ca}_{10}(\text{PO}_4)_5\text{CO}_3\text{F}_{1.5}(\text{OH})_{0.5}$ to give the fluorapatite

Table 3 Crystallographic parameters of raw phosphate

Phases	Mineral	Reference code	Parameters		
			<i>a</i> /Å	<i>b</i> /Å	<i>c</i> /Å
$\text{Ca}_{9.74}(\text{PO}_4)_6(\text{OH})_{2.08}$	Hydroxyapatite	01-086-1199	9.4150	9.4150	6.8790
CaCO_3	Calcite	01-081-2027	4.9910	4.9910	17.0620
$\text{Ca}_{10}(\text{PO}_4)_3(\text{CO}_3)_3(\text{OH})_2$	Carbonate-hydroxyapatite	00-019-0272	9.3090	9.3090	6.9270
$\text{Ca}_{10}(\text{PO}_4)_5\text{CO}_3\text{F}_{1.5}(\text{OH})_{0.5}$	Carbonate-fluorapatite	00-021-0141	9.3460	9.3460	6.8870
$\text{CaO}\cdot\text{MgO}\cdot 2\text{CO}_2$	Dolomite	00-001-0942	4.8330	4.8330	15.9350
SiO_2	Quartz	01-081-1665	5.0300	5.0300	5.6200

Table 4 Structural parameters of phosphate calcined for different temperature

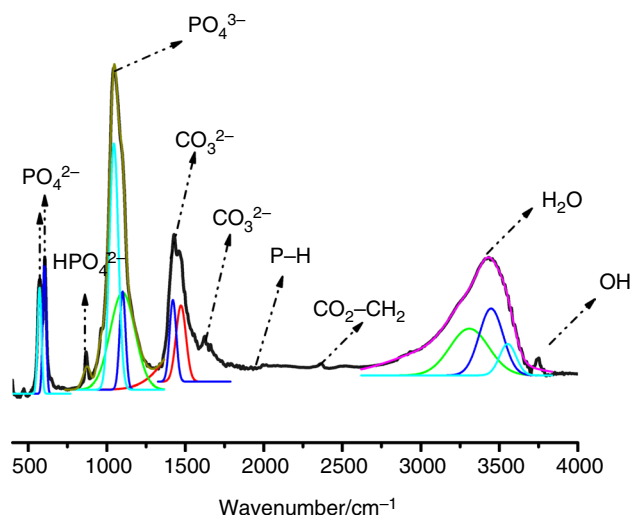
Parameters	Temperature/°C			
	600	700	800	900
$a/\text{Å}$	9.3313	9.3533	9.3622	9.3642
$b/\text{Å}$	9.3313	9.3533	9.3622	9.3642
$c/\text{Å}$	6.8813	6.8833	6.8912	6.8953
D/nm	48.6	63.6	74.4	74.4
$\varepsilon/\%$	0.297	0.235	0.206	0.206

**Fig. 6** Evolution of the crystallite size (D) and strain according to the temperature (a) and the crystallographic parameters according to temperature (b)

$\text{Ca}_5(\text{PO}_4)_3\text{F}$. For the latter component, several applications in different areas are known [20].

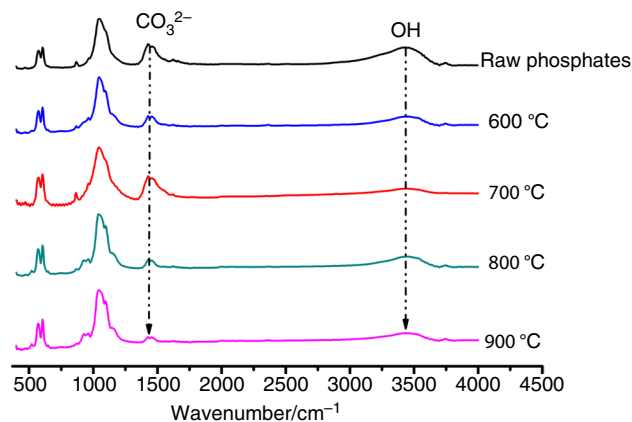
FTIR methods

FTIR spectroscopy analysis reveals several bands (Fig. 7), in particular those due to phosphates, carbonates and hydroxyapatite ions [21, 22]. The bands due to PO_4^{3-} ions

**Fig. 7** FTIR spectra of raw phosphate

are observed at 1045.7 cm^{-1} . The symmetric and antisymmetric adsorption bands of PO_4^{3-} groups lie between 1100 and 950 cm^{-1} , and those of strain are between 571 and 607 cm^{-1} [23]. The peak obtained at 1428.5 cm^{-1} is the same observed for the fluorapatite phosphate carbonates, as indicated by Bonel [24]. The peak at 868.3 cm^{-1} corresponds to elongation of P-OH (HPO_4^{2-}), and that at 3409 cm^{-1} is attributed to the vibration of hydroxyl ions OH^- .

After heat treatment of phosphate at different temperatures from 600 to 900 °C , the characteristic bands of hydroxyapatite disappeared (Fig. 5), which indicates the change in its internal structure of the apatite phases. In addition, the band intensity for carbonate at $1400\text{--}1500 \text{ cm}^{-1}$ becomes wider, and the carbonate peak at 873 cm^{-1} decreases dramatically, which indicates that a small amount of carbonate is retained in the sample.

**Fig. 8** FTIR spectra of raw and calcined phosphates

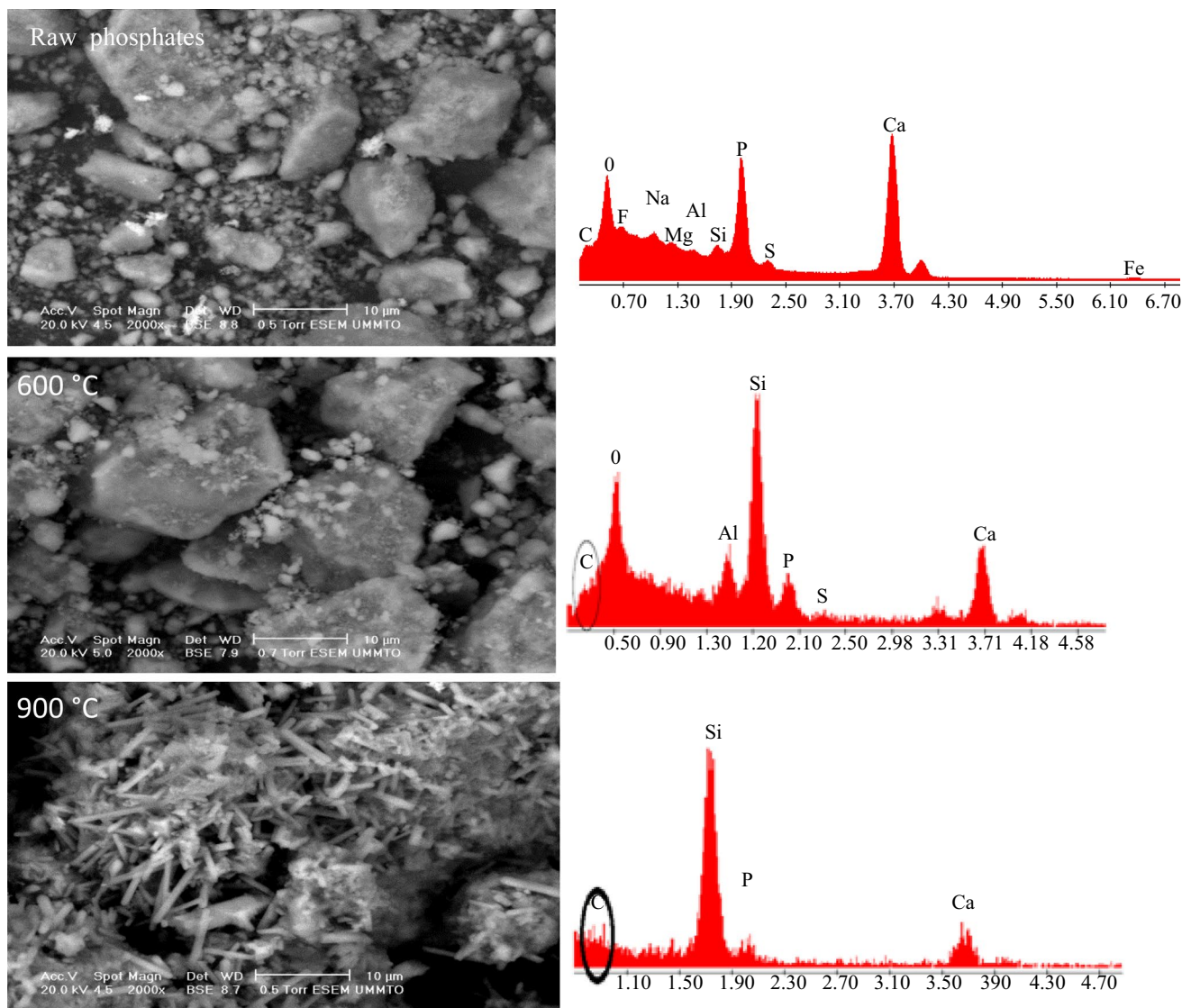


Fig. 9 SEM micrographs of raw beige phosphate and calcined phosphate (left) and EDAX (right)

Figure 8 shows the FTIR spectra of the phosphate samples heated at different temperatures of 600, 700, 800 and 900 °C for 4 h.

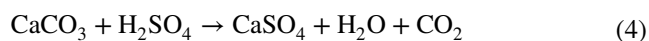
SEM analysis

SEM was utilized to investigate the morphology of the phosphate. At a scale of 10 μm, the crude beige phosphate is in the form of grains surrounded by a matrix (Fig. 9). The thermal effect on the calcined phosphates gave a well-defined morphology by way of example, and at 900 °C, phosphates become aggregates of rods. Thus, monitoring the organic matter contained in the phosphates before and after calcination at temperatures of 600 and 900 °C clearly shows the results found by energy dispersive X-ray analysis (EDAX), confirming the

thermal effect on the removal of organic and inorganic material. This confirms the results of the thermogravimetric analysis on the one hand, and on the other hand the appearance of the elements which form the phases of the phosphate. The elemental mapping of phosphates calcined at 900 °C (Fig. 10) shows the distribution of elements including P, Ca, Si and O, confirming the results of XRD.

Bernard calcimeter

During the production of phosphoric acid by the wet process, carbonates react with sulfuric acid according to the following reaction:



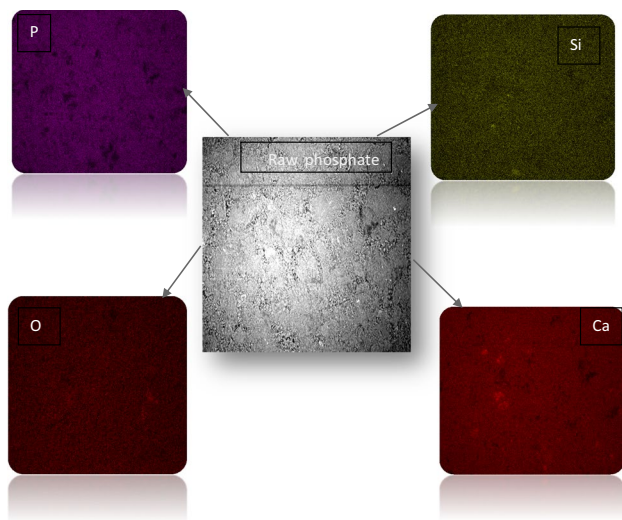


Fig. 10 Elemental mapping of phosphates calcined at 900 °C

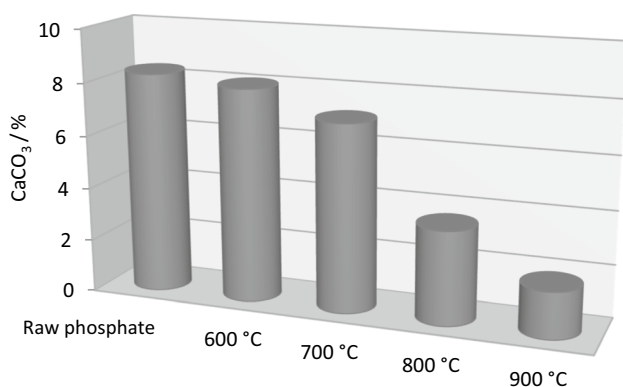


Fig. 11 Percentage of CaCO₃ for raw phosphates and phosphate calcined at different temperatures

During the reaction, the carbon dioxide produced is responsible for the foam and the production of small gypsum crystals, which can cause binding of the filter downstream, and consequently the production of phosphoric acid of low quality [25]. The volume of gas in the slurry must be controlled in order to control the reaction, which is achieved with antifoaming agents. In turn, these agents can cause problems downstream in solvent extraction units. Thus, the prior removal of this compound is an important step. The dissociation of the carbonates is an endothermic reaction, which requires high heat consumption. The proposed cleavage reaction [26] is as follows (5):



The dosage of calcite in raw phosphate and phosphate calcined at different temperatures for 4 h was assessed using a Bernard calcimeter according to the French standard NF P

Table 5 Decomposition temperatures of some carbonates [29]

Carbonate	Decomposition temperature/°C	Results
Calcite (CaCO ₃)	675	90% decomposes in 4 h
Aragonite (CaCO ₃)	645	–
Dolomite [CaMg(CO ₂) ₂]	450	Only 20% is degraded in 16 h
Magnesite (MgCO ₃)	425	80% decomposes in 4 h
Siderite (FeCO ₃)	425	93% decomposes in 15 min

94-048 [27]. The results obtained are shown in Fig. 11. We note that the percentage of CaO gradually decreases with increasing temperature. We obtain the best results for the removal of CaCO₃ at a temperature of 900 °C. This result supports the fabrication of phosphoric acid by the wet process, as it enables reduced consumption of sulfuric acid to produce phosphoric acid of high quality. Phosphoric acid is considered the second mineral acid produced after sulfuric acid. The bulk of phosphoric acid production (90%) is dedicated to chemical fertilizers [28]. According to the literature, carbonates degrade differently during heat treatment. Degradation temperatures of some carbonates are shown in Table 5.

Tests of dissolution of calcined phosphates

The acid attack of phosphates has been the subject of several studies [30, 31]. In this study, the dissolution of 0.5 g of calcined phosphates at 900 °C with nitric acid attack carried out at ambient temperature and under stirring showed total dissolution. These results have important implications for the production of phosphoric acid by eliminating the problems caused by organic matter and carbonates, and also for optimization of phosphoric acid production conditions.

Conclusions

This study of the calcination of Kef Essennoun phosphate allowed several conclusions to be drawn:

- Kef Essennoun raw phosphate is a mixture of six phases, of which the predominant phase is carbonate-hydroxyapatite. XRD analysis of the calcined phosphates showed the effect of temperature on the phase structures of the phosphates.
- The formation of fluorapatite Ca₅(PO₄)₃F was very stable initially at 600 °C. The disappearance of the secondary phase improved the crystallinity of the Ca₅(PO₄)₃F, and the increase in the crystallite size of Ca₅(PO₄)₃F with temperature.

- TG/DTA analysis confirmed the results obtained by EDAX and by the Bernard calcimeter. The elimination of organic matter and calcite in response to future challenges in the phosphate industry will greatly assist the economical production of high-quality phosphoric acid with low consumption of acid. The process consists of optimizing the acid attack of phosphates using the $\text{Ca}_5(\text{PO}_4)_3\text{F}$ formed.

Acknowledgements The authors are grateful for the financial support of this project by the Nuclear Research Center of Algiers (CRNA).

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