

# Textural And Mineralogical Studies Of Two Tunisian Sedimentary Phosphates Or Carbonated Fluorapatite Used In The Process Of Production Of Phosphoric Acid

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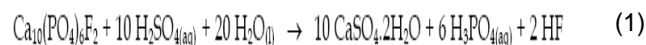
**Abstract:** Tunisian phosphate is a sedimentary rock and is the second major expense in producing phosphoric acid which is used mainly in fertilizer field. Phosphate is a mesoporous solid and has very large specific surface areas which often lead to greater activity due to increased dispersion of the active sites. The reaction between phosphate rocks and acids is essentially a surface reaction. Within the framework of valorization of Tunisian natural phosphate which is a carbonate fluorapatite or francolite and to establish the relations between the reactivity of phosphate rock and their physico-chemical properties. Two Tunisian's deposits of phosphate were selected. Several techniques were used such as the SEM, physisorption for textural study, X-ray diffraction technique and Infra Red Spectroscopy for the mineralogical study. From the textural study, we note that the two samples of phosphate have a mesoporous texture and all phosphate rocks contain many impurities. From the mineralogical study we note that the two main constituents of sedimentary phosphate rocks are apatite and calcium carbonate. The results obtained show a slight difference in physico-chemical properties between the two types of sedimentary phosphates and the dependence between the chemical reactivity and the structure of these phosphates.

**Index Terms:** Carbonated fluorapatite, Infra Red Spectroscopy, Physico-chemical characterization, Physisorption, Reactivity of the ore, SEM, Tunisian sedimentary phosphate, X-ray diffraction.

## 1 INTRODUCTION

Phosphate rock is the second major expense in producing phosphoric acid which is used mainly in fertilizer field. Phosphate is a mesoporous solid and has very large specific surface areas which often lead to greater activity due to increased dispersion of the active sites. Phosphate rock exists principally as the mineral francolite, a carbonate fluorapatite with the formula  $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2 \cdot \text{XCaCO}_3$ , and in minor amounts as chlorapatite  $3\text{Ca}_3(\text{PO}_4)_2 \cdot \text{CaCl}_2$ , and hydroxyapatite  $3\text{Ca}_3(\text{PO}_4)_2 \cdot \text{Ca}(\text{OH})_2$  [1]. Most of the phosphate rock used for phosphoric acid manufacture comes from sedimentary deposits formed by reprecipitation of dissolved phosphate from prehistoric sea [2]. Phosphates ore are intercalated with sedimentary stratus of other waste materials or similar ores interpenetrated by gangue minerals [3]. During this process the phosphate rock was subjected to an interaction with water of varying temperature and impurity content. A large number of these impurities became included in the rock by either coprecipitation or by incorporation in the apatite crystal lattice.

In this way phosphate rocks with a large variety in impurity composition and concentration were created [4]. Most sedimentary phosphate rocks are found to be more than a million years old [5]. The sedimentary phosphate rock mainly consists of fluoroapatite, in which part of the phosphate ions are replaced by fluoride and carbonate ions. This fluoroapatite is commonly referred to as francolite. Phosphoric acid is an important intermediate chemical product. It is mainly used for the manufacturing of fertilizers. Wet process phosphoric acid technology comprises essentially the sulfuric acid attack and the separation of the phosphoric acid produced from the calcium sulfate crystals resulting from the reaction. Both the attack and the separation, which is effected by filtration [4], are considerably affected by the nature of the ore and its impurities. Besides calcium phosphate, the phosphate ores contain 10-15 major impurities and another 16 or so trace elements. The ore also contains traces of heavy metal ions, as cadmium and radium are the most worrisome. They can cause serious environmental problems [6]. During the production of phosphoric acid from phosphate ore by acidulation with sulphuric acid, huge amounts of calcium sulphate are precipitated as a by-product. The main reaction in the wet process for producing of phosphoric acid is as follows [7]:



If phosphate ore is digested by phosphoric acid, the following reactions can take place [8].



The reaction between phosphate rocks and acids is essentially a surface reaction [9], in which the rate is largely controlled by the reaction temperature, hydrogen ion concentration, diffusion through liquid films at the surface, and the surface of the rock

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available for reaction. In wet-phosphoric acid processes, where sulfate ions are present, additional complications are introduced in that calcium sulfate may form on the rock surface. The objective of this study is to establish the relations between the reactivity of phosphate rock and their physicochemical properties in order to provide this reactivity starting from physicochemical analysis of the rock; we try to prove that the chemical reactivity and the structure of these phosphates are strictly dependant. The following properties were included in the studies which are the chemical composition, the specific surface and the structure of the ore. Two different phosphate rocks from southern Tunisia were physically and chemically characterized; we select the best phosphate compound which will be the subject, in another work, of a kinetic study [7].

## 2 EXPERIMENTAL PROCEDURE

### 2.1 Physisorption

The nitrogen is the appropriate gas to characterize the mesoporous texture of the phosphate particles. The apparatus used to determine the physical phosphates adsorption is called "QUANTACHROME AUTOSORB-1". Physical adsorption or physisorption is used to measure surface area and pore size. As more gas molecules are introduced into the system, the adsorbate molecules tend to form a thin layer that covers the entire adsorbent surface. Based on the well-known Brauner, Emmett and Teller (B.E.T) theory [10].

### 2.2. Microscopic Observations: SEM

The scanning electron microscope (SEM), "ZEISS DSM960A", was used for the morphological study of the phosphate particles. SEM is an analysis instrument providing rapid information on the morphology and chemical composition of a solid object.

### 2.3. FTIR Spectroscopy

The apparatus used in this study is Perkin Elmer Spectrum BX, infra-red spectrometer with transform of Fourier, assembled in transmission. The resolution of the apparatus is 2 cm<sup>-1</sup> and the studied spectral field extends from 4000 to 400 cm<sup>-1</sup>. The pellets were prepared according to the technique of Hannah and Swinehart [11], which consists in grinding only the product to be analyzed. The anhydrous potassium bromide (KBr) is then added to the resulting powder and the mixture was homogenized by a spatula and then pelletized.

### 2.4. X-ray diffraction

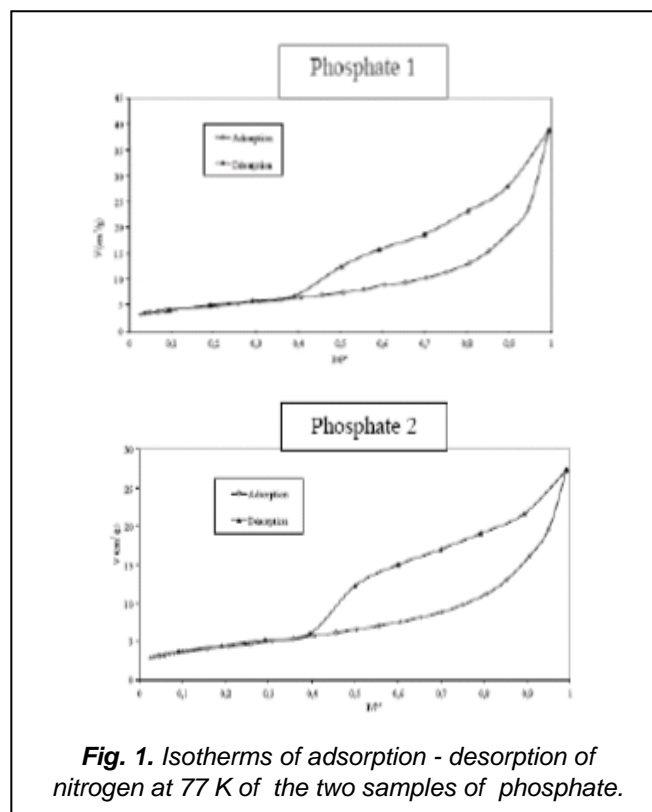
The used apparatus is a SIEMENS D5000 diffractometer with powder provided with an anticathode of copper. The radiation used is CuK $\alpha$  and the wavelength is  $\lambda = 1,541 \text{ \AA}$ .

## 3. RESULTS AND DISCUSSION

### 3.1 Study of textures

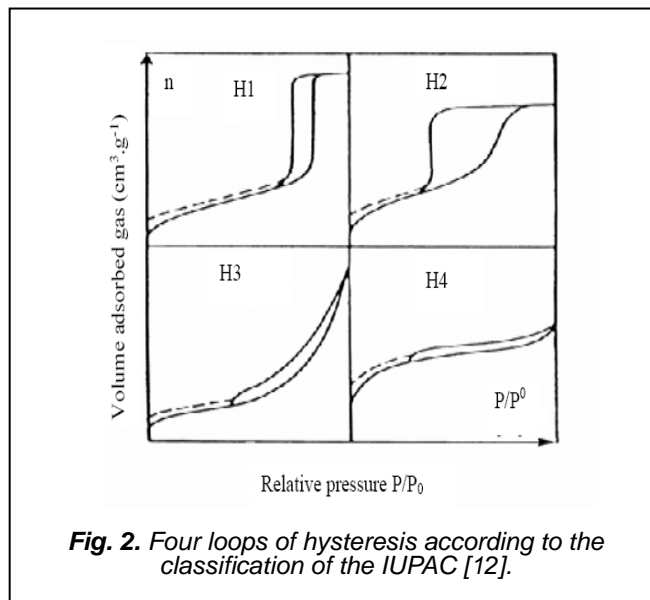
#### 3.1.1 Physisorption

Two textural parameters of the samples of phosphates are determined these are the specific surface and the average diameter of pores. The isotherms of adsorption-desorption are schematized on figure 1.



**Fig. 1.** Isotherms of adsorption - desorption of nitrogen at 77 K of the two samples of phosphate.

We notice that all the isotherms present loops of hysteresis of the H3 types in accordance with the classification of the IUPAC [12] (IUPAC 1985), given on figure 2.



**Fig. 2.** Four loops of hysteresis according to the classification of the IUPAC [12].

The H3 type present a vertical branch of adsorption to the strong relative pressures, and a branch of desorption which is closed again with an average relative pressure between 0,4 and 0,5. This is characteristic of the broad pores commonly called "ink bottle". These pores are sufficiently narrow to allow a capillary condensation with a phenomenon of hysteresis. Specific surfaces ( $S_{BET}$ ) and the average diameters of the pores ( $(D_p)_{\text{moy}}$ ) of two phosphates were determined by the experimental isotherms. The results are given on table 1.

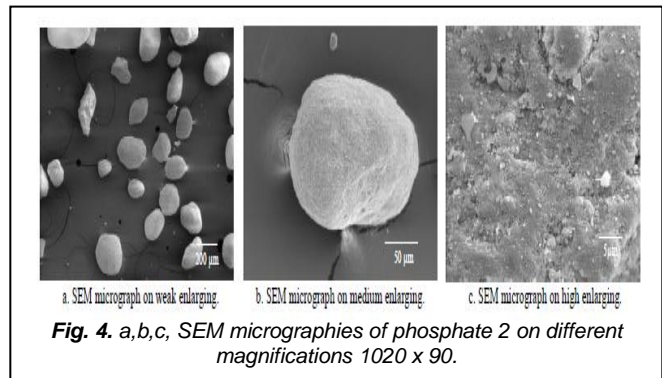
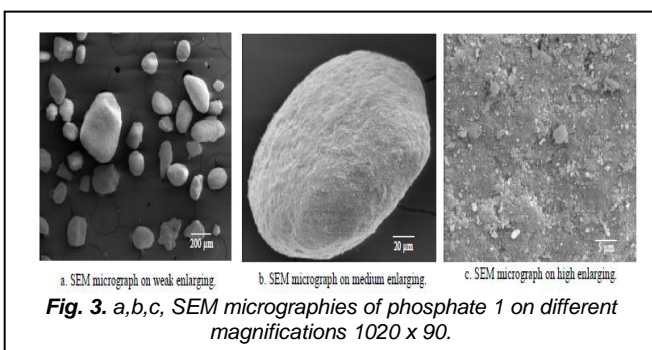
**TABLE 1**  
SPECIFIC SURFACE AREA AND MEAN-SIZE DIAMETER OF THE TWO SAMPLES OF TUNISIAN PHOSPHATE.

Symbol	Quantity	Phosphate 1	Phosphate 2
$S_{ext}(m^2/g)$	Specific surfaces	17,48	15,34
$(D_p)_{moy}(\text{Å})$	Average diameters of the pores	139,62	108,96

The porous average diameters are then all located in the range of mesopores. The existence of mesopores whose diameters are between 2 nm and 50 nm, is at the origin of the hysteresis loops observed on the isotherms of adsorption - desorption of the two phosphate samples. The main advantages of mesoporous solids are their very large specific surface areas which often lead to greater activity due to increased dispersion of the active sites, high adsorption capacities and the ability to induce a selective of size in the reaction. The reaction between phosphate rocks and acids is essentially a surface reaction [2]. Janikowsky et al. found that reactivity of phosphate rock evaluated by citric acid extraction does not correlate with the conditions of wet-phosphoric acid manufacture [13]. This is because the fine pores may become blocked calcium sulphate and their large surface area thereby prevented from entering into the reaction. Solution entering into the pores at the first contact reacts, but as the diffusion of the ions of reaction products is hindered, calcium sulphate and eventually other calcium salts crystallize with in the pores and prevent additional internal attack [2], [13]. It is essential that any comparison of the reactivities of different rocks with sulfuric acid be made under continuous operating conditions. Only under such conditions can the sulfate ion concentration be kept at a sufficiently low level. It has been suggested that the external surface area, is the main factor determining reactivity [2], [9], [14], [15]. We note that the specific surface area of phosphate 1 is greater than that of phosphate 2, because of this the surface of contact with the  $H^+$  ions of phosphate 1 is more important than that of phosphate 2 thus phosphate 1 is more reactive.

**3.1.2 Microscopic Observations: SEM**

To complement the textural study and in order to determine qualitatively the chemical composition of the ore, we made a morphological study using the observations with a scanning electron microscope (SEM) on particles of the two phosphate samples on various magnifications. The micrographs are schematized in figure 3 and figure 4.

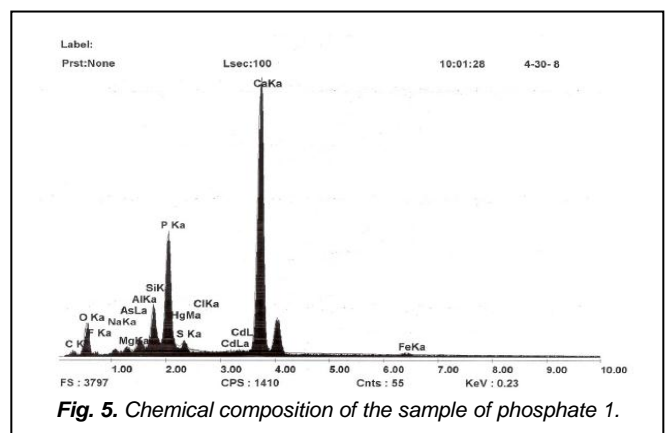


The chemical composition is given quantitatively according to standard analytical methods used for phosphates [4] and whose results given in weight percentages appear in table 2 [4].

**TABLE 2**  
Chemical Analysis of the Samples of phosphate [4].

Symbol	Quantity	Phosphate 1	Phosphate 2
% $P_2O_5$	Phosphorus pentoxide Percentage	29,76	30,66
% CaO	Calcite Percentage	49,87	49,63
% $Al_2O_3$	Aluminum oxide Percentage	0,43	0,46
% $Fe_2O_3$	Iron oxide Percentage	0,18	0,19
% F	Fluorine Percentage	3,14	3,21
% MgO	Magnesium oxide Percentage	0,62	0,69
% $SO_3$	Sulfur oxide Percentage	3,34	3,39
% $CO_2$	Carbon dioxide Percentage	6,56	6,47
% $SiO_2$	Silicon dioxide Percentage	3,96	2,51
% $Ca_3$	Carbon Percentage	0,22	0,24
Organic matter (%)	Organic matter Percentage	0,51	0,53
Cl (ppm)	Chlorine parts per million	947	918
Cd (ppm)	Cadmium parts per million	10	11

The chemical compositions are given qualitatively and schematized in figure 5 and figure 6.



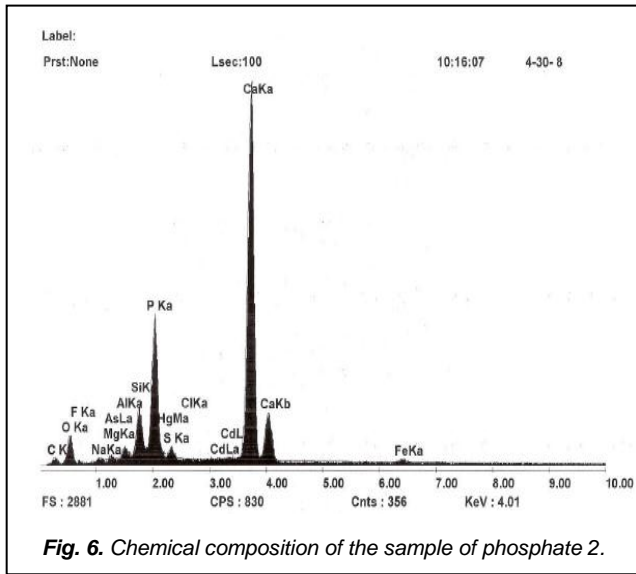


Fig. 6. Chemical composition of the sample of phosphate 2.

On weak magnification, we notice that all phosphate rocks contain many impurities. These include organic matter ; iron and aluminum oxides ; silica ; clay; carbonates; sulfates; and chlorides of lime and magnesium; and small quantities of sodium, potassium, titanium, zinc, copper, manganese, arsenic, chromium, vanadium and uranium [16]. On a medium magnification, the figures show that the particles of the two phosphate samples are constituted of nodules of phosphate, these nodules are presented in oval form and its surface is rather smooth. Phosphorite nodules of considerable size have been founding the continental shelf in many regions; these nodules contain 28-32 % P<sub>2</sub>O<sub>5</sub> and offer potentially rich new source pf phosphorus [2], [17]. On a greater magnifications, roughness as well as porosity becomes clear, surfaces appear porous. The pores observed which cover all the surfaces are of different sizes.

3.2 Mineralogical study

3.2.1 FTIR Spectroscopy

The samples of phosphates analyzed by infra-red spectrometry are characterized normally by the presence in their absorption spectra of the absorption bands relating to CO<sub>3</sub><sup>2-</sup>, PO<sub>4</sub><sup>3-</sup> and OH<sup>-</sup> groups. Other absorption bands Characteristics of several other atomic groupings may be present in samples to be analyzed. The location and the identification of characteristic bands of functional groups are done through the existing tables in the literature [18], [19], [20], [21], [22]. The infra-red spectra are given on figure 7.

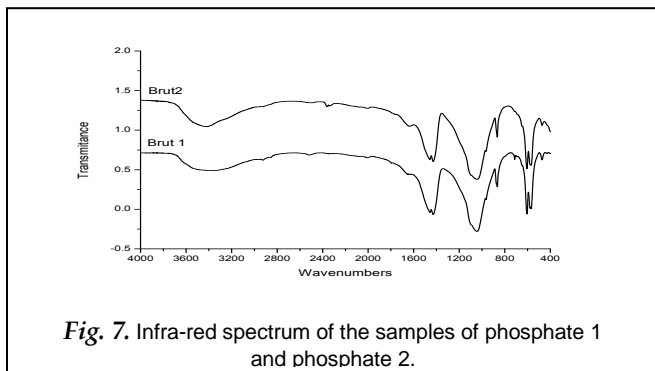


Fig. 7. Infra-red spectrum of the samples of phosphate 1 and phosphate 2.

From the infrared spectra of the two samples of crude phosphate 1 and 2, we notice a great similarity through the existence of the 4 modes of vibration of the groups of PO<sub>4</sub><sup>3-</sup> reported to 565, 600, 1045 and 1096 cm<sup>-1</sup> and the groups for CO<sub>3</sub><sup>2-</sup> which are of the type B observed around 865, 1430 and 1459 cm<sup>-1</sup>. In the case of the two samples of phosphate, there are three bands of low intensities relating to OH<sup>-</sup> groups differently surrounded. Indeed, one band is observed around 715 cm<sup>-1</sup> relating to the mode of vibration of the OH<sup>-</sup> groups bordering by OH<sup>-</sup> ions. Another band is observed at around 690 cm<sup>-1</sup> relating to the mode of vibration of OH<sup>-</sup> group bordering by F<sup>-</sup> ions. The third and last band is observed at around 645 cm<sup>-1</sup> relating to the mode of vibration of the OH-group bordering CO<sub>3</sub><sup>2-</sup> groups. Finally, we note the presence of a broad band around 3400 cm<sup>-1</sup> relating to the mode of vibration from H<sub>2</sub>O group.

3.2.2. X-ray diffraction

The X-ray diffractograms are shown in figure 8.

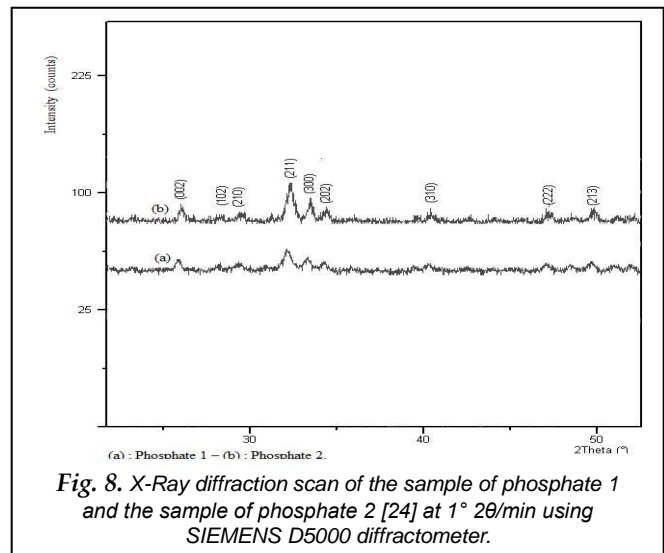


Fig. 8. X-Ray diffraction scan of the sample of phosphate 1 and the sample of phosphate 2 [24] at 1° 2θ/min using SIEMENS D5000 diffractometer.

The diffractograms of phosphates presents fine lines. The analysis of this diagram by isotopy with the charts of reference [23], [24] show that the solids crystallize in the hexagonal system and have P63/m symmetry. It consists of a carbonate fluorapatite or francolite, as main constituent, together with calcite in large quantity and amount of quartz well expressed mineralogically. The crystallographic parameters of phosphate rocks and those of references [23], [24], [25] are shown in table 3.

TABLE 3

Crystallographic parameters of phosphate rocks and those of references.

Symbol	Crystallographic parameters	Phosphate 1	Phosphate 2	Hydroxy Apatite	Fluoco Apatite	Francolite
Angstrom (Å)	a	9.325	9.330	9.421	9.372	9.360
Angstrom (Å)	b	9.325	9.330	9.421	9.372	9.360
Angstrom (Å)	c	6.895	6.905	6.882	6.888	6.890

Apatites have the general formula,  $\text{Ca}_{10}(\text{PO}_4)_6\text{X}_2$  where X is typically F (fluorapatite,  $\text{F}_{\text{Ap}}$ ), OH (hydroxyapatite, OHAp), or Cl (chlorapatite, ClAp). The apatite lattice is very tolerant of substitutions, vacancies and solid solutions, for example, X can be replaced by  $\frac{1}{2}\text{CO}_3$  or  $\frac{1}{2}\text{O}$ ; Ca by Sr, Ba, Pb, Na or vacancies; and  $\text{PO}_4$  by  $\text{HPO}_4$ ,  $\text{AsO}_4$ ,  $\text{VO}_4$ ,  $\text{SiO}_4$  or  $\text{CO}_3$  [26]. Adlèn and Lindqvist [27] suggest that the structure may correspond to some regular type of overgrowth, which leads to compounds of the composition  $\text{Ca}_5(\text{PO}_4)_3\text{OH}\cdot x\text{CaF}_2\cdot y\text{CaCO}_3$  where x and y are simple fractions [27]. Such compounds could have sub-structures corresponding to hydroxyapatite exhibiting the observed variations in a and c lattice parameters [1]. (Slack 1968). Some of the calcium carbonate is present as discrete particles. Thus there is as yet no definitive conception of the structure of carbonate fluorapatite [2].

#### 4. CONCLUSION

From the characterizations performed previously, we can conclude that the two main constituents of sedimentary phosphate rocks are apatite and calcium carbonate. The calcium carbonate content of a phosphate rock determines to a great degree the reactivity of the ore. The pore structure and the surface area of the apatite are one of the most important factors determining the reactivity of the ore; Phosphate rocks are a mesoporous solid and have large specific surface areas which often lead to greater activity. We notice the strictly dependence between the chemical reactivity and the structure of these two phosphates. According to the textural study, the quality of phosphate 1 is better than the quality of phosphate 2. Thus, phosphate 1 is more favourable to be studied on the kinetic level.

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