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Physicochemical and mineralogical characterization of natural phosphate from Tapoa (Niger)

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Abstract: This work is a contribution to the development of the natural phosphates of Tapoa (Niger). To do this, a physicochemical and mineralogical study of the raw ore was carried out using different analytical techniques (particle size analysis, density, pH, XRF chemical analysis, X-ray diffraction, scanning electron microscopy, TDA-TGA). The results obtained by particle size analysis indicate that the best P_2O_5 content (19.72%) is found in the slice between 200 and 125 µm. The chemical analysis indicates a high content of P_2O_5 (18.20%), a large ferral mass (%Fe_2O_3 +%Al_2O_3) of 30.12%, silica at 17.30%, a low oxide content calcium (9.50%) and low levels of heavy metals such as copper, arsenic and lead. The density of the ore (2,73) is of the same order of magnitude as that of a synthetic vivianite and is close to that of natural apatite. The pH of phosphate ore is 5.27 at 31.7°C. The SEM image presents a blunt aspect of the grains reflecting the alteration effect. The black spots observed correspond to the intergranular porosity of the rock. Quantitative and qualitative X-ray analysis show that the natural phosphate of Tapoa contains mainly quartz (48.71%), apatite (28.91%), vivianite (17.25%) and turquoise in a minor proportion (5.11%). The thermal behavior of the ore indicates a mass loss of 11.67% at 910°C.

1. Introduction

Phosphorus is one of the three major chemical elements used for soil fertilization (Isil *et al.*, 2009, Bagayoko *et al.*, 2011, Ettoumi *et al.*, 2020), the main source of which is apatitic phosphates. But the low water solubility of the latter does not allow their direct use for soil fertilization due to the accessory minerals or gangue impurities present in the phosphate deposits (El mokhtar *et al.*, 2008). The chemical or biological treatment of the ore makes it possible to obtain mineral and/or organo-mineral phosphate fertilizers containing phosphorus available to plants (McClellan *et al.*, 2004, Koriko *et al.*, 2010, Ousmane *et al.*, 2016 & 2017, Zanguina *et al.*, 2018). However, the physicochemical characterization of phosphate rock provides data on the composition of apatite, gangue minerals and the relative quantities of mineral species present (Zapata *et al.*, 2004, Boughzala *et al.*, 2015). Several difficulties due to the diversity of physical properties and characteristics chemical and crystallographic, arise when we study phosphates. Moreover, the composition of the phosphate rock particularly depends on the type and origin (Moursalou *et al.*, 2021). Tapoa natural phosphate from Niger is a sedimentary phosphate. The geological and mining research campaign in Niger carried out in the 1980s by the geological and mining research office made it possible to identify significant phosphate deposits in the west of the country (Tapoa) (Natatou *et al*., 2005). The characterization of the product must make it possible to propose appropriate treatments with a view to valorizing the ore, hence the aim of this work. This involves studying the physicochemical and mineralogical properties of phosphate rock using different analytical techniques (XRF, SEM, DRX, ATD-ATG…). This will make it possible to suggest possible ways of enriching the ore and to make a preliminary evaluation of the adaptation of natural phosphates to the different fertilizer production processes and/or their suitability for direct application. Moreover, the recovery of this ore will make it possible to develop a phosphate product of good marketable quality, making it possible to remedy the problem of phosphorus deficiency in general on agricultural land in the Sahel and in particular in Niger (McClellan *et al*., 2004, Garba *et al*., 2023).

2. Material and methods

2.1 Phosphated material

These are phosphate samples taken at the Tapoa in old boreholes drilled in the 1980s by the Bureau of Geological and Mining Research of Niger. The GPS coordinates of the sampling site are 2°20'33" E and 12°26'0" N. In the laboratory, the representative sample of the phosphate ore (**Figures 1**) has previously undergone mechanical treatment (homogenization, grinding, sieving). Then, it was subjected to physico-chemical and mineralogical characterization tests by different quantitative and qualitative analysis methods.

Figure 1. Photo of raw samples of natural phosphates from Tapoa

2.2 Particle size analysis

A quantity of ore samples undergo mechanical processing in a ball mill for 30 minutes. A dimensional classification by dry process was carried out with a series of mesh sieves in geometric regression (> 400; 400-315; 315-200; 200-125 and < 125 µm). The P_2O_5 rate according to the grain size slices was determined by the colorimetric method through the formation of the phosphomolybdate complex after mineralization with nitric acid and sulfuric acid according to the modified protocol of Dabin (Mathieu & Piettain. 2003).

2.3 pH and density

The determination of the hydrogen potential is carried out on aqueous suspensions according to the AFNOR NF ISO 10-390 standard (Belyaeva *et al.* 2009). A suspension of the ore was prepared by mixing 5 g of the powder and 25 mL of distilled water. The suspension is homogenized by stirring for 10 minutes. After 30 minutes of rest, the pH is read directly using a HANNA-type pH meter. In addition, the density of the ore was determined by the pycnometer method. it consists in weighing the weight of the empty pycnometer (P1), the weight of the pycnometer + water (P2), the weight of the pycnometer + ore (P3) and the weight of the pycnometer + water + ore (P4). The application of **Eqn. 1** (1) makes it possible to determine the density (Zanguina, 2011):

$$d = \frac{(P_3 - P_1)}{(P_2 - P_1) - (P_4 - P_3)} \qquad \textbf{Eqn. 1}$$

2.4 Chemical analysis by X-ray fluorescence (XRF)

In order to determine the chemical composition of the raw samples, a chemical analysis was carried out on 5 g of raw powder using an energy dispersive X-ray fluorescence spectrometer (Minipal 4 model). The filters selected were "kapton" for major oxides and "Ag/Al-thin" for trace elements and rare earths. The measurement time for each sample was 100 seconds.

2.5 Mineralogical analysis by X-Ray Diffraction (XRD) and scanning electron microscopy

For X-ray diffraction, the diffractometer used is of the X'pert Pro MRD type from the PANalytical company of the PHILIPS brand, equipped with a copper anticathode (monochromatic radiation CuKα λ=1.54056 A°) operating at a voltage of 40 kV and an emission current of 40 mA. The scanning speed is 0.02 °/s. A 2SBU brand scanning electron microscope (SEM) was used to study the ore morphology.

2.6 Thermo gravimetric analyse-Differential thermic analyse (TGA-DTA)

Thermogravimetric (ATG) and thermo-differential (ATD) analyzes were carried out using an A 5c 1000c apparatus under air.

3. Results and Discussion

3.1 Particle size analysis

The percentages of partial refusals and cumulative refusals are collated in **Table 1**. These results show that the weight percentage is greater in the slice below 125 µm (31.44%) followed by the slice between 200-125 µm (26.27%). The results of the analysis of the phosphoric anhydride rate (%P_2O_5) according to the particle size slices obtained by the colorimetric method are collated in **Table 2**. It is noted that the best P_2O_5 content is found in the slice between 200 and 125 µm. In this tranche, the ore has a grade of about 19.72% P_2O_5. This P_2O_5 content is close to that found by XRF chemical analysis of the ore, which is 18.20% (see **Table 3**).

Table 1. Granulometry by sieving of the sample studied

Diameter (µm)	Partial refusal (%)	Cumulative refusal (%)
> 400	27,57	27,57
400-315	7,50	35,07
315-200	11,67	46,74
200-125	22,90	69,64
< 125	30,36	100

Moreover, an increase in the P_2O_5 content is noticed when the diameter of the mesh sieve decreases from 400 to 125 µm. This would result in a release of phosphate elements due to grinding. Moreover, a slight decrease in the rate of P_2O_5 is noted when the diameter is less than 125 µm (18.32%). This decrease could be caused by the presence in significant quantity, in this last slice, of minerals such as silica (SiO2) and ferral mass (Al_2O_3 + Fe_2O_3) considered as impurities (see **Table 3**).

Table 2. Analysis of P_2O_5 rate by particle size range

Diamètre (µm)	**%P_2O_5**
>400	15,09
400-315	15,43
315-200	18,77
200-125	19,72
<125	18,32

Table 3. Chemical composition of Tapoa phosphate ore

Major Elements	**%**	**Trace elements**	**(ppm)**
SiO_2	17.30	V	200
CaO	9.50	Cr	0.4
MgO	0.84	Cu	561
K_2O	0.85	Zr	980
Na_2O	ND	Zn	97
TiO_2	1.43	Ce	ND
SO_3	ND	Pb	ND
P_2O_5	18.20	CO_3^{2-}	NA
MnO	ND	Sb	200
Fe_2O_3	3.22	Ga	ND
BaO	0.89	As	ND
SrO	4.01	Y	96
Al_2O_3	26.90	Ni	ND
LI	16.60	F^-	<0.01

LI = Loss of Ignition, ND = Not Detected, NA= Not Applicable

3.2 Density and pH

The density of the ore determined by the pycnometer method is 2.73. This density is of the same order of magnitude as that of a synthetic vivianite (2.78) (Fejdi *et al.*, 1980) and is close to that of apatitic phosphate from Tahoua (Niger) which is 2.98 (Zanguina, 2011). In addition, this density is high and could reflect a low permeability of the phosphate rock. Indeed, the higher the density, the less porous the rock and the lower the permeability (Dieudonné *et al.*, 2022). On the other hand, the pH of Tapoa phosphate ore is 5.27 at 31.7°C. Which means that this ore is acidic.

3.3 XRF and chemical analysis

Table III gives the results of the X-ray fluorescence analysis of the raw sample. It can be seen that the P_2O_5 content of 18.20% is lower than that of a francolite (38.21%) which is a carbonated apatite generally well crystallized (Zapata *et al.*, 2004). Also, this P_2O_5 content shows that this phosphate ore is intermediate grade. Indeed, it is indicated in the literature that phosphate ores are divided to three groups according to their P_2O_5 content: low-grade ores (12-16% P_2O_5), intermediate-grade ores (17-25% P_2O_5), and high-grade ores (26-35% P_2O_5) (Sengul *et al.*, 2006). The CaO content (9.50%) is low while the silica content SiO_2 (17.30%) is high. The CaO/(P_2O_5) ratio is of 0.52. This ratio is lower than that of a fluorapatite which is 1.31 according to the literature (Natatou *et al.*, 2005). Also, this ratio could show the existence of the replacement of Calcium by Al, Fe, Cu… and the substitution of phosphate groups by $CO_3^{2-}$and SiO_4^{4-} ions in the crystal lattice (Jabri *et al.*, 2013). The very high ferral mass (%Fe_2O_3 +%Al_2O_3) of 30.12% suggests that upgrading the product by acid leaching is not the most appropriate process. The titanium oxide (TiO_2), Magnesium (MgO) and barium (BaO) oxide contents are very low. The low content of the ore in heavy metals such as arsenic, chromium is a guarantee of the quality of the product on the environmental and industrial plan and lead for the use of the crushed ore as a phosphorus contribution to agricultural soils.

3.4 X-ray diffraction analysis (XRD)

The diffractogram of the raw sample is shown in **Figure 2**. The qualitative identification of the peaks made it possible to detect the presence of quartz, vivianite, turquoise and apatite. The quantitative mineralogical composition is given in **Table 4**. We note the dominant presence of quartz (48.71%) followed by apatite (28.91%) and vivianite (hydrated iron phosphate) at 17.25%. Turquoise (hydrated copper and aluminum phosphate) is in a minor proportion (5.11%). These results are in agreement with those of the X-ray fluorescence which indicates a very varied chemical composition on the one hand, and on the other hand high contents of SiO_2 (Quartz), of P_2O_5, of AL_2O_3 as well as a low proportion of copper.

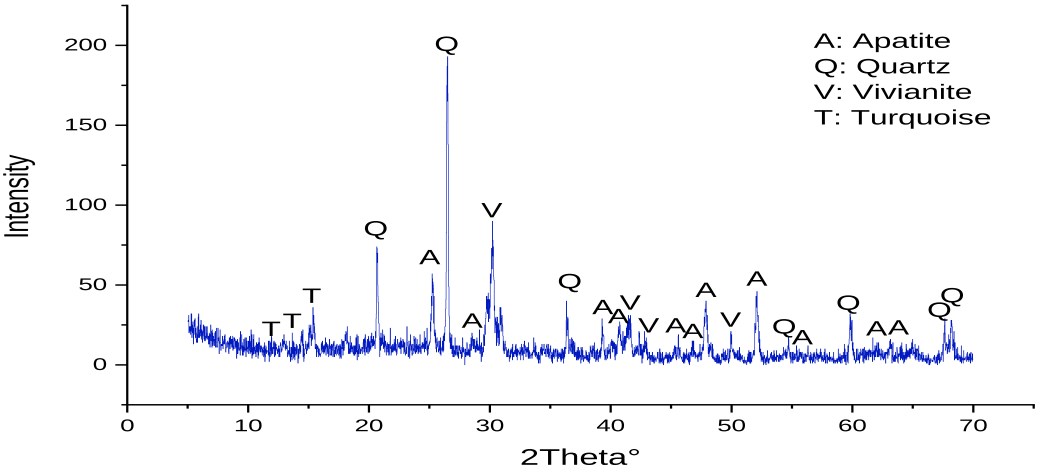

Figure 2. Diffractogram of the raw sample of the phosphate studied

Table 3. Quantitative mineralogical composition of the raw phosphate sample

Minerals	Turquoise : $CuAl_6(PO4)_4(OH)_8.4H_2O$	Vivianite : $Fe_3(PO4)_2.8H_2O$	Quartz	Apatite
%	5,119814366	17,25594609	48,71260914	28,9116304

3.5 Scanning Electron Microscope (SEM)

SEM images (**Figure 3**) show a granular structure of phosphates under a scanning electron microscope (SEM). The blunted appearance of the grains reflects the weathering effect that has affected this rock. The black spots correspond either to the intergranular porosity of the rock, or to oxides such as Al_2O_3, Fe_2O_3, CaO, SrO, MgO in agreement with the chemical composition of the ore in metallic oxides.

3.5 Thermal analysis

Studies on natural phosphates have indicated that when these products are subjected to heat treatment different mass losses are recorded. Thus, the departure of adsorption or wetting water is observed for a temperature between ambient temperature and 150°C. In addition, from 150°C to 500°C, a loss of mass corresponding to the desorption of structural water (constitutional water) and organic matter is observed. When the temperature exceeds 500°C, a release of hydrogen gas, methane and carbon dioxide is observed (Natatou *et al.*, 2005, El Ouardi *et al.*, 2009, Bilali *et al.*, 2000). The thermal behavior of Tapoa rock phosphate ore has been studied. Thermogravimetric (TGA) and differential thermal (DTA) analyzes were performed from room temperature to 910°C with a heating rate of 10°C/min (**Figure 4**).

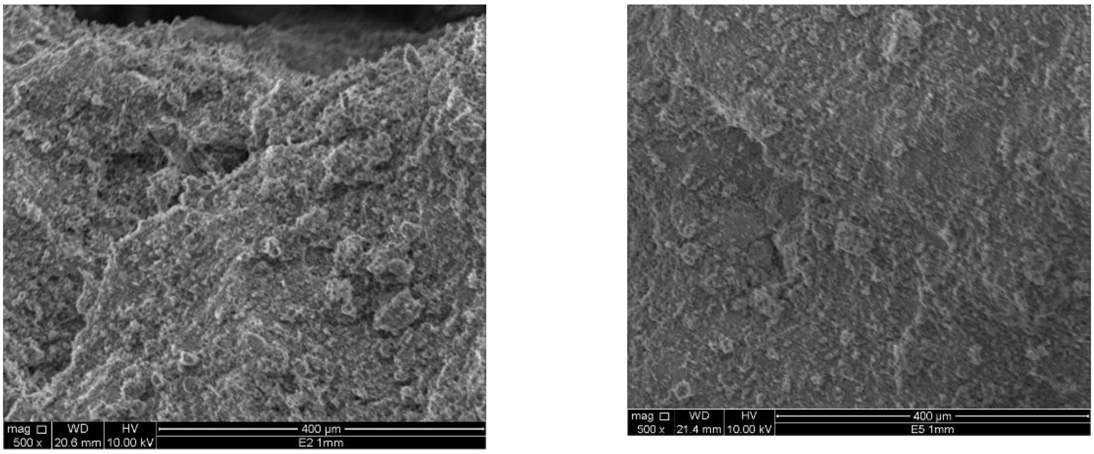

Figure 3. SEM of raw samples of the phosphate studied

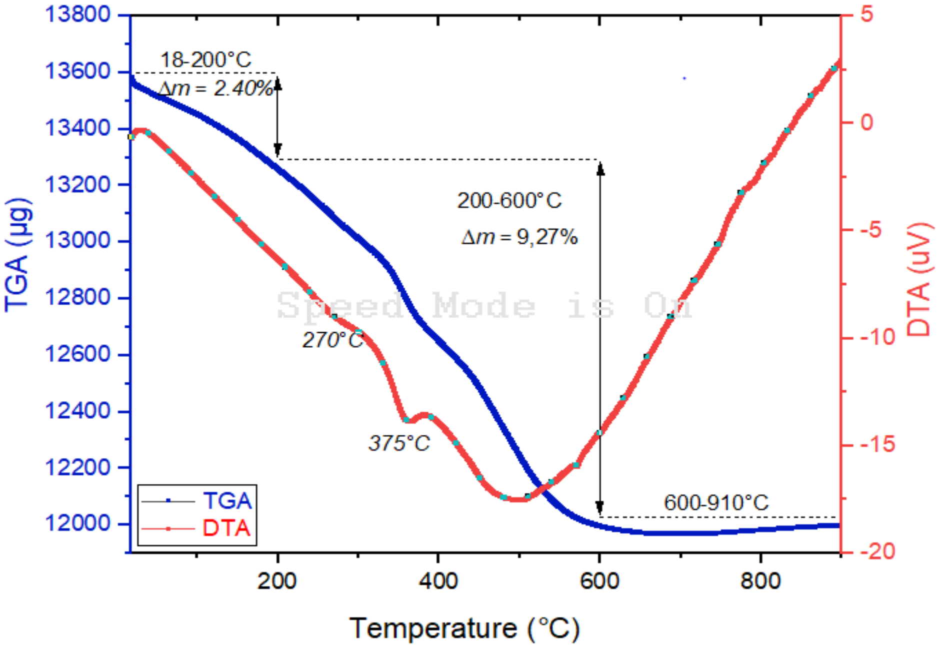

Figure 4. ATD-ATG curve of the raw sample of the phosphate studied

Differential thermal analysis shows two endothermic peaks between room temperature and 500°C followed by a change in slope from 500°C. Thermogravimetric analysis reveals two mass losses:

- between 18°C and 200°C, a loss of 2.40% by mass corresponding to the departure of adsorption water is observed. This transformation is not significant and does not lead to a modification of the crystalline structure of the network;

- a second loss in mass which is between 200°C and 600°C is observed (9,27%). This loss is associated with two endothermic peaks, the first peak of which is due to the desorption of structural water and the second peak to the decomposition of volatile organic matter;

- Above 600°C, no mass loss was practically observed.

Note that the overall mass loss observed at 910°C is 11.67%. This mass loss more or less confirms the loss on ignition (LI) obtained during the XRF chemical analysis which was 16.60% at 1000°C.

Conclusion

The study of the physicochemical and mineralogical characterization of the phosphate rock of Tapoa made a contribution to the valorization of the ore. The different analytical techniques applied made it possible to highlight the mineral phases, the chemical composition and the particle size distribution of the phosphate studied. Qualitative and quantitative analyzes by X-ray diffraction have established that the phosphate rock studied is essentially made up of phosphate mineral phase (apatite in major proportion, vivianite and a low proportion of turquoise) on the one hand, and quartz on the other hand. The chemical analysis showed a dominant proportion of silica, phosphoric anhydride (%P_2O_5), a large ferral mass (%Fe_2O_3 +%Al_2O_3) and traces of heavy metals. Chemically, the best P_2O_5 content is located in the slice between 200 and 125 µm where the mesh for releasing phosphate elements is located. Thermal analysis of the ore reveals that the overall mass loss observed at 910°C is 11.67%. In view of the results obtained, Tapoa phosphate ore is of intermediate grade to be used in the production of phosphate fertilizer. Which suggests that phosphate ore requires processing by some means of beneficiation to reduce the content of accessory minerals including quartz and ferral mass. Which would make it possible to obtain a high grade phosphated product.

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Compliance with Ethical Standards: This article does not contain any studies involving human or animal subjects.

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