International Journal of Advanced Chemistry, *2 (1) (2014) 24-26*

International Journal of Advanced Chemistry

Journal home page: www.sciencepubco.com/index.php/IJAC
doi: 10.14419/ijac.v2i1.1664
Research paper

Study the effects of calcinations and evolution of crystallographic parameters of two Tunisian natural phosphates

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Abstract

Tunisian natural phosphate is a highly form of fluorapatite, carbonate fluorapatite, also known as “francolite”. The presence of carbonate in mineral phosphates influences their reactivity overlooked acid attack, but their presence requires a supplementary adding of sulfuric acid in the plants of production of phosphoric acid; and causing the formation of foams in the reactors during the addition of sulfuric acid. The presence of carbonates in high contents reduces the price value of phosphate rock.
We propose in this work to study thermally the decomposition of two carbonated fluorapatite in a range of temperature between ambient and 1000°C; and the variation of the value of crystallographic parameters of the two samples of phosphate. The X-ray diffraction technique is used for this mineralogical study.
By referring to the crystallographic parameters of the lattice of phosphate, we note that the increase in temperature decarbonated the francolite which is transformed largely to a fluoroapatite. In addition, it was reported that the first decarbonation is around 650°C translated the kinetics of decomposition of the carbonate ions of the type B associated with a vaccum, while the second decarbonation is around 1000°C and related to the thermal decomposition of the entity of CO_3F, generated by the decomposition of carbonate ions of type B and A. The presence of these ions would be the result of a reorganization of the crystal lattice.

Keywords: *Carbonated fluoroapatite, effect of calcinations, mineralogical study, Tunisian natural phosphate, x-ray diffraction.*

1. Introduction

Tunisian natural phosphate is an essential element used in the plants of production of phosphoric acid. It is a highly form of fluorapatite, carbonate fluorapatite, also known as “francolite” (CHAABOUNI et al. 2013, Jahnke 1984, McConnell 1973). The structure of apatite can be described in terms of an approximate hexagonal close packed set of spheres in which each sphere represents a tetrahedral PO_4^{3-} ion. It is well established that carbonate substitution has a destabilizing effect on the apatite structures resulting in increased solubility (CHAABOUNI et al. 2013, Chien et al. 1976, Jahnke 1984). In addition, the presence of carbonates in the mineral phosphates greatly influences their reactivity towards acid attacks (Lehr et al. 1972). The presence of carbonates requires a supplementary add of sulfuric acid during the production of phosphoric acid; in addition to it causes foaming which inhibits the cooling of the reaction. Accordingly an increasing in temperature and viscosity of the phosphoric slurry; which leads to the formation of the hemihydrate phosphogypsum, it results a bad filtration which affects the quality of the phosphoric acid product and decreases the chemical yield (Becker 1989, SLACK 1968, Waggaman 1953).

Apatites have the general formula, $Ca_{10}(PO_4)_6X_2$ where X is typically F (fluorapatite, FAp), 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 $½CO_3$ or ½O; Ca by Sr, Ba, Pb, Na or vacancies; and PO_4 by HPO_4, AsO_4, VO_4, SiO_4 or CO_3 (Elliott 1994).

Beneficiation by calcinations is one of the well known processes. It is based on the dissociation of the calcium carbonate by thermal energy. Depending on the efficiency of the process, calcinations may lead to almost complete disposal of the carbonates present in the phosphate rock (Kumar 1980, Memminger et al. 1930, Ozer 2003).

There are two types of carbonate apatite:

The carbonate apatite of type A in which CO_3^{2-} ions are fixed along the senaire helical axis where usually located the monovalent anions (Bonel 1972, Trombe et al. 1967).

The carbonate apatite of type B in which CO_3^{2-} ions occupied the sites of phosphate ions (Bonel 1972, Legeros 1967, Legeros et al. 1964, Vignoles 1973) with creation for each substitution, a lacuna in a calcium site and the other in oxygen site and the third in the tunnels site.

It is noted that the crystallographic parameter "a" of carbonated hydroxyapatites containing sodium ions increases by adding carbonates content, while parameter "c" decreases (Bonel 1972, Memminger et al. 1930, Ozer 2003, Trombe et al. 1967).

In this work, we studied the temperature of calcinations and its effects on two sedimentary phosphates in a range of temperature between ambient and 1000°C and the effect of this increase on the crystallographic parameters “a” and “c” of these two samples.

2. Materials and methods

The tests are performed on the laboratory scale in an adjustable furnace in temperature on the Tunisian phosphate. The study of the time of calcinations is carried out by introducing samples of phosphate in the furnace for a period of 60 minutes at a fixed temperature (250°C, 650°C and 1000°C).

The powders were characterized by X-ray diffraction (DRX). The diffractograms are acquired with the radiation Kα of Copper (CuKα and the wavelength is λ = 1,541 Å) using a diffractometer SIEMENS D5000. Besides, the structural information was obtained starting from a powder diagram collected in the angular field 5–110 in 2h with an angular step of 0.04° (2h) and counting time of 5 s. The refinement of the lattice parameters is achieved by WPF method (Whole Pattern Fitting or Le Bail method) using Fullprof Suite software version 1.10.

3. Results and discussion

The X-ray diffractograms are shown in fig. 1 and Fig. 2.

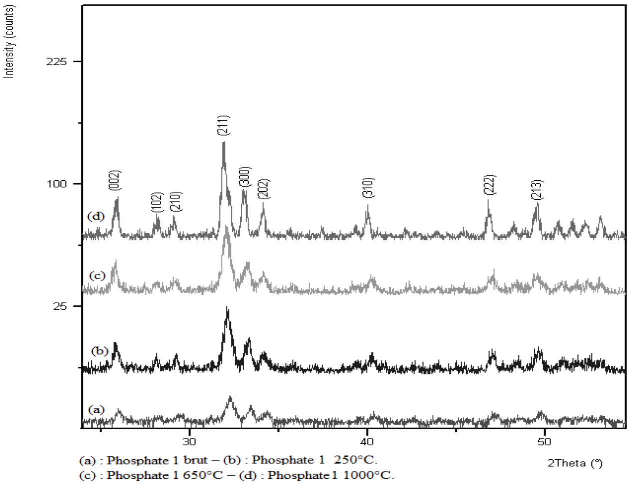

Fig. 1: X-Ray diffractograms of the sample of phosphate 1 at different temperatures (ambient temperature, 250°C, 650°C and 1000°C).

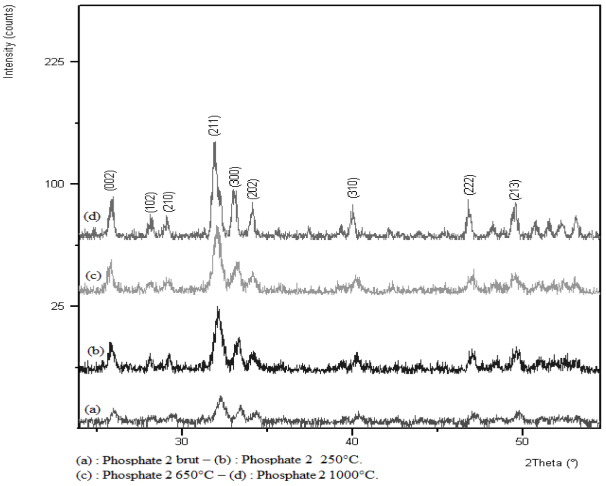

Fig. 2: X-Ray diffractograms of the sample of phosphate 2 at different temperatures (ambient temperature, 250°C, 650°C and 1000°C).

The diffractograms of phosphates presents fine lines. The analysis of this diagram by isotopy with the charts of reference (Trombe 1973, Young 1973), show that the solids crystallize in the hexagonal system and have $P6_3/m$ symmetry. The crystallographic parameters of phosphate rocks and those of references (Trombe 1973, Young 1973) are shown in table 1.

Table 1: Crystallographic parameters of phosphate rocks and those of references (Trombe 1973, Young 1973).

	Parameter a	Parameter b	Parameter c
Phosphate 1	9.327	9.327	6.894
Phosphate 2	9.337	9.337	6.909
Hydroxy-Ap	9.421	9.421	6.882
Fluoro-Ap	9.372	9.372	6.888
Francolite	9.360	9.360	6.890

At room temperature, by comparison between the crystallographic parameters of the two samples of phosphates and those of references (a = 9,327 Å for the sample of phosphate 1, and a = 9,337 Å for the sample of phosphate 2) and those hydroxyapatite (a = 9.421 Å), fluoroapatite (a = 9.372 Å) and the francolite (a = 9.360 Å). This proves that our fluorapatite is carbonated and it is a francolite (Trombe 1973, Young 1973).

The calculation of the crystallographic parameters of each sample at various temperatures and which are recapitulated in table 2 and table 3, shows that the volume of the crystallographic mesh of the crude phosphate 2 (V = 521,733 Å^3) is larger than that of crude phosphate 1 (V = 519,294 Å^3); this is explained by the presence of much more OH^- ions than of F^- ions in the crude phosphate 2 than in the crude phosphate 1, knowing that the ionic F^- ray (1,33 Å) is smaller than the ionic ray of OH^- (1,43 Å).

Table 2: Evolution of crystallographic parameters according to the temperature of the sample of phosphate 1

	Crude phosphate	Phosphate 250°C	Phosphate 650°C	Phosphate 1000°C
Temperature (°C)	25	250	650	1000
a (Å)	9,327	9,3507	9,2912	9,3809
b (Å)	9,327	9,3507	9,2912	9,3809
c (Å)	6,894	6,927	6,8571	6,8868
α (degrees)	90	90	90	90
β (degrees)	90	90	90	90
γ (degrees)	120	120	120	120
Symetry	Hexagonal	Hexagonal	Hexagonal	Hexagonal
Space group	$P6_3/m$	$P6_3/m$	$P6_3/m$	$P6_3/m$
Volume (Å^3)	519,294	524,523	512,643	524,852
Bragg R-Factor	0,353	0,148	0,0969	0,364
RF-Factor	0,188	0,19	0,163	0,543

Table 3: Evolution of crystallographic parameters according to the temperature of the sample of phosphate 2

	Crude phosphate	Phosphate 250°C	Phosphate 650°C	Phosphate 1000°C
Temperature (°C)	25	250	650	1000
a (Å)	9,33740	9,31680	9,33810	9,3858
b (Å)	9,33740	9,31680	9,33810	9,3858
c (Å)	6,9098	6,90110	6,90240	6,8954
α (degrees)	90	90	90	90
β (degrees)	90	90	90	90
γ (degrees)	120	120	120	120
Symetry	Hexagonal	Hexagonal	Hexagonal	Hexagonal
Space group	$P6_3/m$	$P6_3/m$	$P6_3/m$	$P6_3/m$
Volume (Å^3)	521,733	518,779	521,252	526,057
Bragg R-Factor	0,762	0,811	0,779	0,284
RF-Factor	0,643	0,39	0,656	0,573

The representations of the crystallographic parameters according to the temperature are indicated on fig. 3 and fig. 4.

Calcinations are primarily intended to decarbonise and dehydration an ore with a high grade in carbonates. During the heat treatment of mineral materials. Two solids capable of reacting giving to a monomolecular layer of the reaction product. The elements of the crystal lattice are in oscillatory motion whose intensity increases with increasing temperature. It is for this, the elements of the crystal lattice become able to overcome the force of attraction and change positions.

We note that there are fluctuations in parameters between ambient temperature and 250°C. This is explained by a departure of the water of hydration and intercrystalline water (LABARTHE et al.1973, Vignoles 1984).

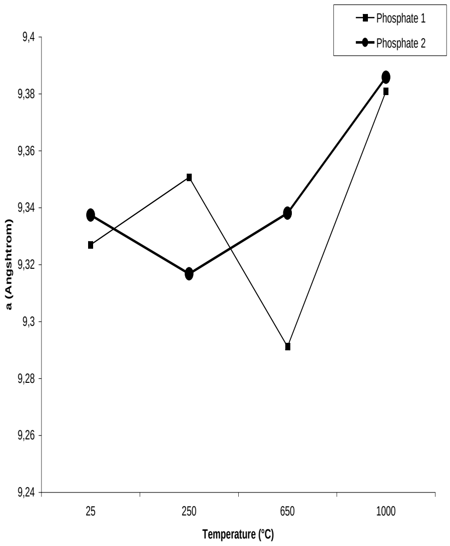

Fig. 3: Evolution of the crystallographic parameter “a” according to the temperature.

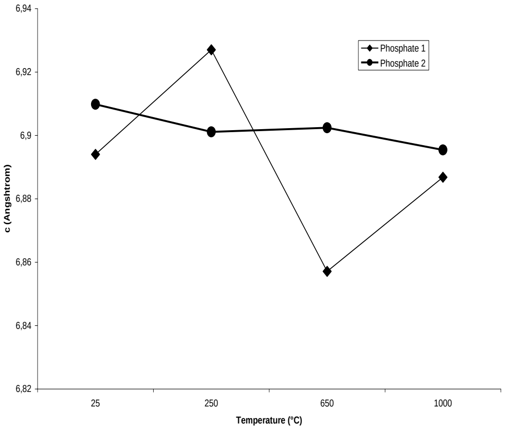

Fig. 4: Evolution of the crystallographic parameter “c” according to the temperature.

At the temperature 650°C, there is a carbon dioxide emission that begins to volatilize from 600°C to 800°C. This is a type B decarbonation which translates the kinetics of decomposition of the carbonate ions type B associated with a vaccum (EL FEKI et al. 1994, EL FEKI et al. 1991, EL FEKI et al. 1991, Lafon et al. 2002).

There is an emission of CO_2 around 700°C that corresponds to the decomposition of $CaCO_3$ presents in this powder of phosphate (Lafon et al. 2002).

At the temperature 1000°C, there is a carbon dioxide emission that begins to volatilize from 800°C to 1050°C (EL FEKI et al. 1994, EL FEKI et al. 1991, EL FEKI et al. 1991). This is a type A and B decarbonations. This is a result of thermal decomposition of the entity CO_3F generated by the decomposition of carbonate ions type A and B (EL FEKI et al. 1994, EL FEKI et al. 1991, EL FEKI et al. 1991). decarbonation of sites B which is accompanied by the appearance of CaO due to the restructuring of the crystal lattice (EL FEKI et al. 1994, EL FEKI et al. 1991, EL FEKI et al. 1991). At 1000°C, by comparison between the crystallographic parameters of the two samples of phosphates (a = 9, 3809 Å for the sample of phosphate 1, and a = 9, 3858 Å for the sample of phosphate 2) and those hydroxyapatite (a = 9.421 Å), fluoroapatite (a = 9.372 Å) and the francolite (a = 9.360 Å). This proves that after decarbonation, our francolite is similar to the fluoroapatite (Trombe 1973, Young 1973).

4. Conclusion

The heat treatment, in general and in the phosphate industry particularly is used in order to the valuation of raw ores, in their transformation into useful products, or even to transform raw materials into products directly.

The crystallographic parameters change depending on the temperature, which is the result of dehydration, and decarbonation type A or type B.

Calcinations decrease the content of Carbonates in the samples of phosphate. Accordingly it allows decreasing the consumption of sulphuric acid (H_2SO_4) during the production of phosphoric acid. Calcination gives therefore a product that fulfils the requirements of its use.

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