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Effect of temperatures and residence time of calcinations on substitution process during enrichment of Tunisian phosphorites

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Abstract: The present study deals with the effects of temperature and residence time of calcinations on substitution process. The upgrading of sedimentary phosphorites coming from the Ras-Dhraa deposit which belongs to the Gafsa-Metlaoui basin (Tunisia) was conducted. The characterization of raw and calcined phosphorites and the evolution of rare earth elements and yttrium (REEs+Y) content and associated gangue were evaluated with different techniques (X-ray powder diffraction (XRD), scanning electron microscopy (SEM/EDX), Fourier transform infrared (FT-IR) and inductively coupled plasma mass spectrometry (ICP-MS)). The effect of increasing residence time and temperature of calcinations on phosphate structure were determined. FT-IR spectroscopy indicates that PO_4^{3-} was substituted by SiO_4^{4-} and SO_4^{2-} and these substitutions cause a worsening of phosphorites properties for sulfuric acid production. A temperature of calcination approximately of 900°C and a period of 30 minutes is sufficient, because higher temperature and longer residence time accentuate these substitutions. Indeed, in these conditions we obtain a phosphate with a better grade of P_2O_5. It permits to increase the phosphate content from 29.58% to 33.07%. Moreover, REEs+Y contents increased by 5%.

Keywords: Tunisian phosphorite; Calcinations; Substitution; Infrared spectroscopy; REEs+Y.

Introduction

Tunisian phosphorite is an essential element used in the process of phosphoric acid production. It consists mostly of carbonate fluorapatite and the major impurities are calcite and dolomite, while quartz and feldspar are present like traces[1]. Apatite with the formula $Ca_{10}(PO_4)_6F_2$ may have several substitutions in the structure[2,3].The most common substitutions in natural phosphates are Mg^{2+} and Na^+ for Ca^{2+}, CO_3^{2-} for PO_4^{3-} and OH^- for F^-.Substitutions modify the structure and often show marked effects on crystallinity, solubility and thermal stability[4]. The presence of carbonate in mineral phosphates requires a supplementary adding of sulfuric acid in the plants of production of phosphoric acid; and causes the formation of foams in the reactors during the addition of sulfuric acid. Also the presence of carbonates at high contents reduces the price value of phosphate rock. More studies have been carried out to reduce the calcium carbonate content of the phosphate rocks by flotation and/or calcination[5,6].

Enrichment of the ores by calcination is one of the well-known processes. It is based on the dissociation of the calcium carbonate by thermal treatment[7-9]. Calcination is the process of ore heating to a high temperatures ranging from 800° to 1000° C to decompose the $CaCO_3$ and $MgCO_3$ to CaO, MgO and gaseous CO_2. Then, after calcination, the formed CaO and MgO may be separated by slaking and washing. Several authors[8,10] have investigated the mineralogical effects of thermal treatment on sedimentary apatites. They showed that the main changes in the apatite structure are the structural CO_2 expulsion, cell parameter a increase and crystallite size variation. These transformations are accompanied by the formation of free CaO. There are several parameters that determine calcinations such as the residence time, the temperature and the physico-chemical properties of the phosphates[9,11]. Not enough investigations have been carried out to study the effect of calcinations parameters on substitutions. In the present study, the upgrading of Tunisian phosphorites by thermal treatment was conducted. The effects of temperature and residence time of calcinations on the substitution process were investigated. Calcinations tests as well as measurement techniques such as XRD, FT-IR, scanning electron microscopy (SEM), and ICP analysis were used to characterize and analyze the raw and calcined phosphorites.

Experimental Section

Samples selection and preparation

Phosphorite used in this investigation was provided from phosphate deposit in Ras-Dhraa

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(Tozeur). The 70-2000 µm grain size fraction was investigated. As published elsewhere in our paper[12], the chemical composition was determined as: 29.58% P_2O_5, 49.45% CaO, 6.48% CO_2, 3.58% SO_3, 2.84% F, 3.08% SiO_2, 1.39% Na_2O, 0.25% F_2O_3, 0.86 Al_2O_3, 0.054% K_2O and 0.7% MgO. The thermal behavior was studied to predict the optimal temperature for the phosphate rock enrichment. It was found[12] that calcination at 900°C removes humidity, organic matter and decomposes carbonates.

Equipment and instruments

XRD analyses were performed using an X'PERT Pro PAN Analytical diffractometer with CuKa radiation (λ=1.5418 Å). The samples were scanned in the diffraction angle range (2θ) varying from 5° to 80° with steps of 0.02° for 5 min. The crystalline phases have been determined by comparison of the registered patterns with the International Center for Diffraction Data (ICDD)-Powder Diffraction Files (PDF).

Infrared spectra were measured from 400 to 4000 cm^{-1} (wavenumber) by the standard KBr pellet method using a Fourier transform infrared spectrometer (Perkin–Elmer). The resolution of 4 cm^{-1} was used collecting 20 scans for each sample. The micromorphology of the phosphate ore samples before and after calcination was evaluated using scanning electron microscopy (QUANTA 200 microscope). In addition, SEM–EDX technique was used to identify the chemical composition of the products.

The rare earth elements concentrations were carried out at the Department of Earth Sciences, Università della Calabria, and were determined by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) using an Elan DRCe (Perkin Elmer/SCIEX).

Phosphorous was determined by spectrophotometric method using “Perkin-Elmer, model Lambda 20” Spectrophotometer, by measuring the color density of yellow complex phospho-vanado-molybdate at a wavelength of 430 nm.

Digestion procedure

For the ICP-MS analysis phosphorites samples were powdered in an agate mortar and then dissolved by microwave digestion using a Mars5 microwave apparatus (CEM technologies). About 100 mg (±0.01 mg) of powder was placed in a microwave vessel with a mixture of Merck “suprapur” quality hydrofluoric acid (6 ml HF), nitric acid (5 ml HNO_3) and perchloric acid (3 ml $HClO_4$), covered and sealed with a cap and subjected to an oven method that consisted of a 15min ramp to 200 °C and a pressure of 600 PSI, then held at temperature for 15 min and then a 15 min cool down. An unclear solution containing some residue was obtained. The content of the vessel was allowed to heat up to 200 °C. Before the acid complete evaporation, 3ml of pure $HClO_4$ were added and the mixture was heated up to 200°C. Before the complete evaporation, 5 ml of HNO_3 (5%) was then added. A clear, colorless solution was finally obtained. This latter, was left to cool down gently and made up to a standard volume in a 100 ml volumetric flask with Millipore water in order to prepare the mother solution. External calibration curves were prepared using Perkin Elmer “multi-element Calibration Standard 2 solution” to analyze rare earth elements. Standard reference materials Micaschist (SDC1) were prepared in the same way and were used as unknown samples during the analytical sequence. The elements concentrations were compared with certified values to evaluate accuracy and precision of analytical data.

Calcination experiments

Calcination was carried out in electric furnace. 2 g of phosphorite were putted in platinum crucible, then the temperature was raised gradually (10°C/min) from room temperature until reaching the required level and maintained for the predetermined time. A series of experiments were carried on the phosphorite covering the temperature 900, 1000 and 1050 °C for 30, 40, 60 and 90 minutes.

Results and Discussion

SEM and EDX of raw and calcined phosphorites

The scanning electron microscopy (SEM) observation of raw phosphorites reveals the irregular particle morphology, as shown in Fig.1.The dispersive analysis in energy of X-rays (EDX) (Fig.2) indicates high contents of Ca, P, O and impurity levels of Si, Mg, Na and S. This observation confirmed the results found by XRD, FT-IR and chemical analysis.

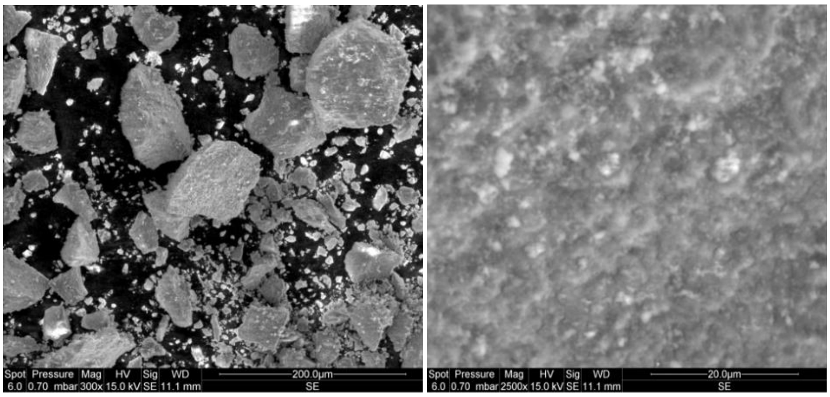


Figure 1. SEM images of raw phosphorites with two different resolutions

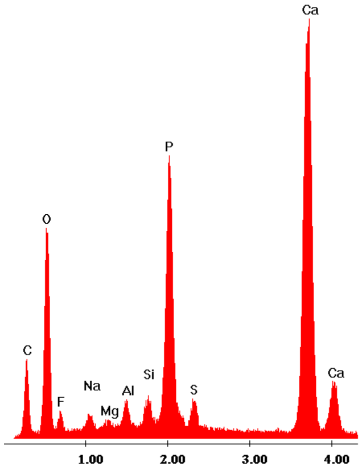


Fig. 2. EDX pattern of raw phosphorite

The SEM micrographs of phosphorites particles after calcinations at 900°C for 30 min (Fig.3) indicates that the calcined particles appear more compacted as well as the surface of particles becomes relatively smooth due to the sintering of the particles at high temperature. Also, SEM micrographs showed macropores occurrence in the phosphate after calcinations. In addition, the EDX results of calcined phosphorites are shown in Fig. 4. As it is clear, peaks of C, Al and O elements are present in addition to Ca, P, and Si. The high intensity of carbon and aluminum peaks can be explained by two reasons: In one hand, carbon and aluminum peaks are associated with the agents used to immobilize the particles for analysis. On the other hand, the carbon peak may depict the calcium carbonate presence after annealing for 30 min. Thus, it may imply the incomplete decomposition of $CaCO_3$.

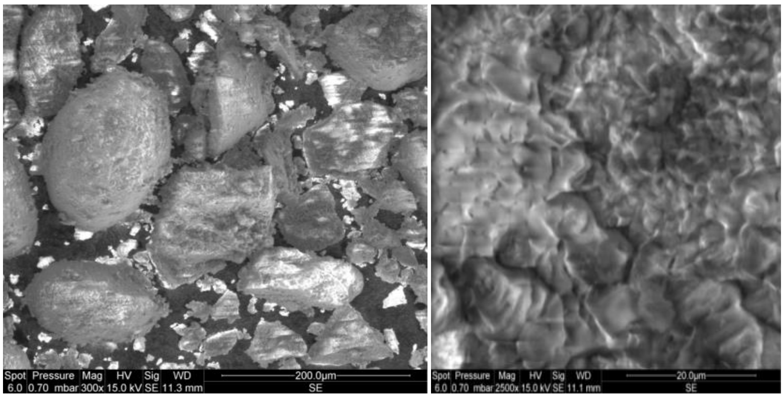


Figure 3. SEM images of phosphorites particles calcined for 30 min at 900°C with two different resolutions

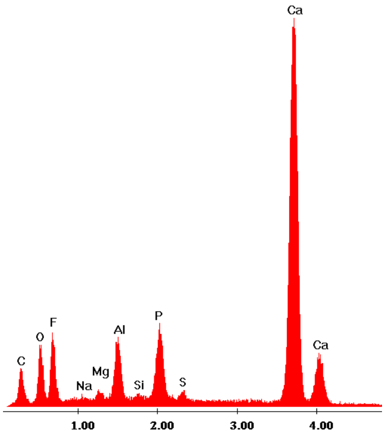
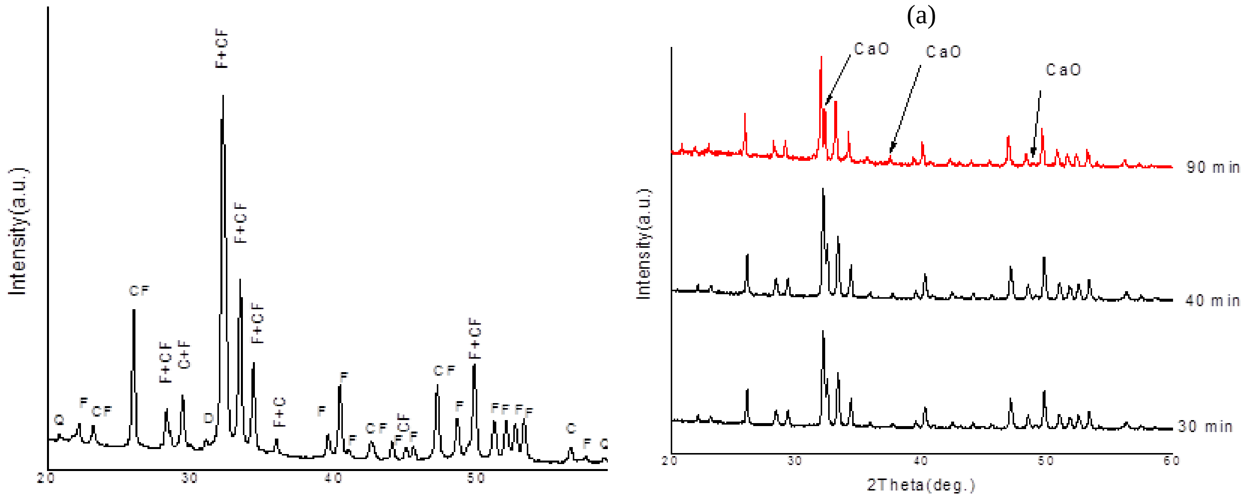


Figure 4. EDX pattern of phosphorites particles calcined for 30 min at 900°C.

XRD analysis of raw and calcined phosphorites

The XRD patterns of raw and calcined phosphorites are shown in Fig.5. XRD pattern of raw phosphorites (Fig.5.a) presents various reflections attributed to carbonate fluorapatite, fluorapatite, dolomite, calcite and quartz[12]. After calcination at 900°C, a slight modification of the reflection positions is noted. During calcinations carbonate fluorapatite changes to fluorapatite and carbonates decompose to form CaO. The relative intensities of the calcite, dolomite, and quartz reflections in the XRD patterns disappears and the lime reflections were formed and became clearly distinguishable (Fig.5.b).

As a result of CO_3^{2-} removement from phosphorite at temperatures above 900°C the unit cell parameter achieves almost the value of pure fluorapatite and the crystallinity improves again[13]. It is important to note that regardless of the residence time of calcinations; the obtained X-ray patterns of calcined phosphorites are similar suggesting that there is no significant structural difference between the phosphorites calcined 30 min or 90 min. As it is supposed, carbonate decomposition is the main process during calcination, and 30 min is long enough to complete the transformation.



(a)

(b)

Fig. 5. XRD patterns of (a) raw and (b) calcined phosphorites at 900° for 30, 40 and 90 min F:fluorapatite ; C:calcite ; D:dolomite ; Q:quartz ; CF: carbonate fluorapatite

FT-IR spectroscopy

The FT-IR spectroscopic study was conducted in order to check the following complex ions: PO_4^{3-}, CO_3^{2-}, SiO_4^{4-}, SO_4^{2-} and SiO_3^{2-}. Fig.6 shows infrared absorption spectrum of phosphorites before and after thermal treatment. The IR spectral analyses of Tunisian phosphorite examined in details in our previous publication[12] have evidenced the bands of PO_4^{3-}, SiO_2, CO_3^{2-}, OH^- referring to the apatite, quartz and calcite.

The effect of residence time of calcination on phosphorites was determined by calcinations of phosphate particles at 900°C for 30 min, 40 min, 60 min and 90 min. FT-IR spectra of calcined samples are shown in Fig. 6. It is quite worthy to note that no appreciable changes in phosphate matrix have been happening at rising residence time of calcinations. Bands characteristic of fluorapatite are not affected. The absorption bands assigned to the PO_4^{3-} group was detected at 1096, 1040, 962, 606, 577 and 474 cm^{-1} [14]. Most of the bands due to the phosphate vibrations of fluorapatite have largely increased in intensity after increasing time of calcination. This behavior has been described by other authors[15,16] as a consequence of the thermal treatment of apatites.

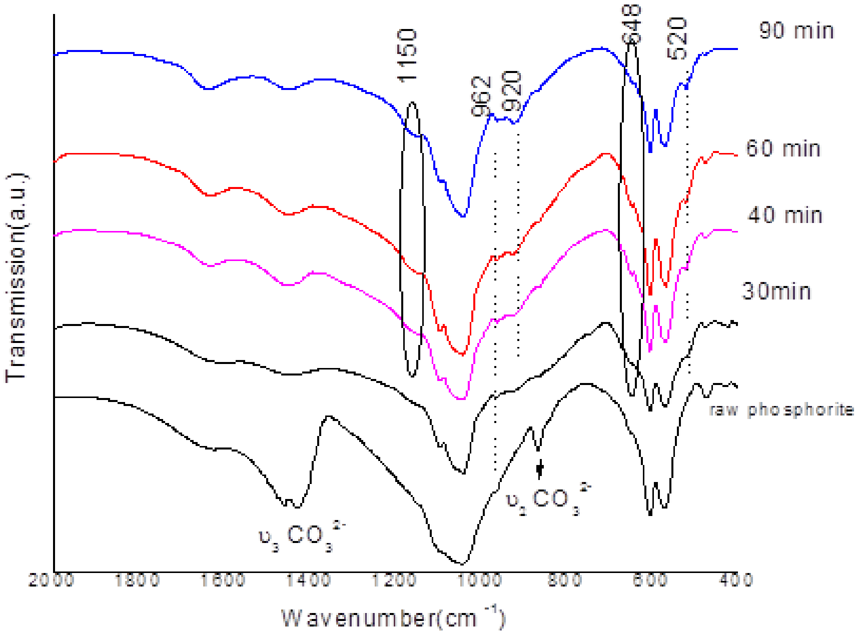


Figure 6. FT-IR spectra of raw and calcined phosphorites at 900°C for 30, 40, 60 and 90 min

FT-IR Spectra showed additional absorption bands at 520 cm^{-1}, 926 cm^{-1} and 647 cm^{-1}. These results resemble those found by Petkova[17] during thermal treatment of nanosized carbonate apatite from Syria. These bands are attributed to the bending and stretching modes of the SiO_4^{4-} and SiO_3^{2-}. The established change gives ground to assume that during calcinations quartz mineral present in raw phosphorites transform into structure of higher symmetry. Bands around 520 $cm^{-1}$and 926 cm^{-1}

indicate substitution of PO_4^{3-} by (SiO_4^{4-})[12]. The peak observed around 647 cm^{-1} was attributed to (SiO_3^{2-}) [17]. The intensity of this peak increases with increasing residence time of calcinations.

Previous study[18] on apatite-type lanthanum silicates showed an increase in the intensity of stretching and bending mode of the SiO_4 tetrahedra with firing temperature. These increases indicate increase of cation vacancies at high temperature. These vacancies were produced by the ousting of the carbonate.

Small band was observed at 1150 cm^{-1} in the FT-IR spectra of phosphorite calcined up to 40 min at 900°C. This band indicates substitution of PO_4^{3-} by SO_4^{2-}. Thermal oxidation and decomposition of organic matter occurs, sulfur is liberated, mainly as SO_2 and some of it enters the apatite structure as SO_4. The SO_4^{2-} and SiO_4^{4-} enter the apatite structure in the vacant orthophosphate positions produced by the ousting of the carbonate. Other workers [19] in this field argued that the presence of carbonate groups in the raw apatite played an important role in the incorporation of silicates during heating and observed that at low silicate content, the latter would substitute for carbonate during the heat treatment. Baumer et *al.*[20] argue for the occurrence of a coupled substitution ($2PO_4^{3-} \rightarrow SO_4^{2-} + SiO_4^{4-}$).

We note that increasing residence time increases the intensity of bands corresponding to the SO_4^{2-} , SiO_3^{2-} and SiO_4^{4-} substitutions. It is obvious that these bands have been intensified with increasing the degree of substitution.

On the other hand, we have raised temperature of calcinations (900; 950; 1050°C) to investigate the effect of temperature on substitutions. As it can be seen from Fig.7 the intensity of bands at 520, 920, 648 and 1150 cm^{-1} increases with increasing temperature of calcinations. An increase in the operating temperature was accompanied by an increase in the extent of calcination and sulfation[21].

Additionally, the typical bands of carbonate substituting for phosphate site (type B) in the apatite lattice (peak at 871 cm^{-1} and double band at 1410/1445 cm^{-1}) [12] are not observed at 1050°C. The calcination at higher temperatures (900-1200 °C) results in the complete removal of carbonate from the mineral[22]. Higher temperature is not desirable in spite of almost complete ousting of structural carbonate, because the reactivity of the calcined product was lowered by raising the calcination temperature[12].

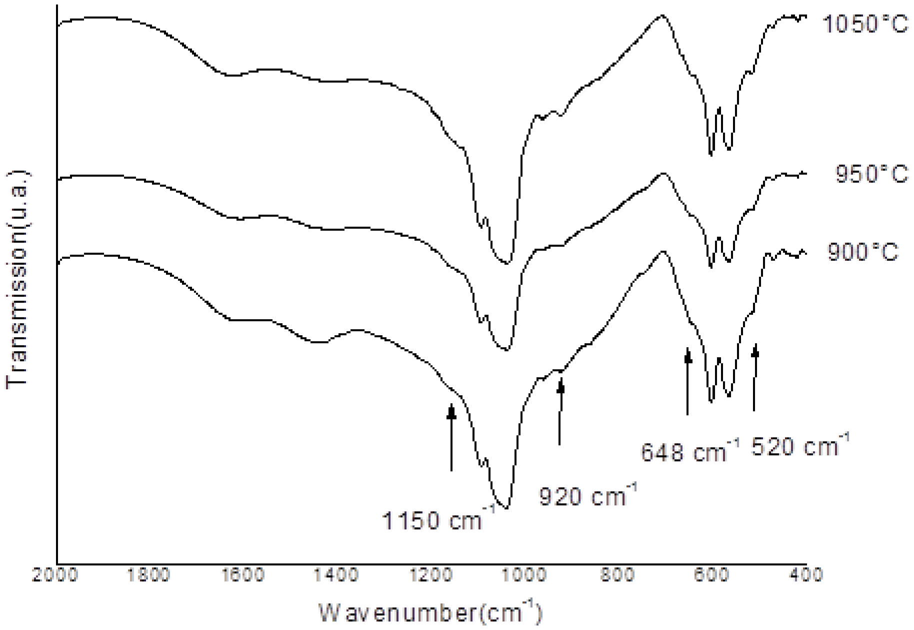


Figure 7. FT-IR spectra of phosphorites calcined at 900, 1000 and 1050°C for 30 min

Higher temperatures and longer residence times can accentuate the substitution of PO_4^{3-} by SO_4^{2-} and (SiO_4^{4-}) [23] and these substitutions cause a worsening of phosphorite properties for sulfuric acid production[24].

The obtained results show that calcination at 900°C for 30 min is sufficient to enrich phosphorites without accentuation of the substitution rate. In addition, these heating time and temperature were more economical. It was shown in another work[6] that increasing temperature and time of calcinations may result in the loss of phosphate grains but has not affected the P_2O_5 content significantly. Flash calcinations reduce the residence times at the high temperature[23]. In this calcination the entering of sulfur and silicon in the apatite structure practically takes place only at 950°C. Knubovets *et al.*[23] showed that flash calcination at 870° (residence time a few seconds) is enough for the beneficiation of phosphorites from the Nahal Zin deposit. This shows that use of flash for upgrading phosphorite is desirable because the samples are heated at a high temperature for a very short time (a few seconds).

REEs + Y contents in raw and calcined phosphorites

Rare earth elements are required for many different applications such as metal and glass additives, catalysts for petroleum refining and phosphors used in electronic displays [25-27].

Increased commercial demand for REEs has resulted in a research of new rare earth elements bearing minerals, as well as process required to separate lanthanides. Phosphorites ores are potential resource of REEs and it is important to determine the concentration of these elements for their recovering. Esmaeil *et al.*[28] have studied the extraction of REEs from apatite and they show that it is possible to extract REEs with a percentage of 80% for neodymium, cerium, lanthanum and yttrium. These elements are of significant industrial interest and even a small quantity could be extracted from phosphate.

The REEs+Y contents of raw phosphorites from Rhas-Dhraa deposit were presented in Table 1.

Table 1 Rare earth elements concentration (ppm) of raw and calcined phosphorites (30min/900°C) from Ras-Dhraa deposit.

Element	Raw phosphorites	Calcined phosphorites
La	54.63	58.56
Ce	67.63	62.64
Pr	10.53	10.57
Nd	56.44	60.41
Sm	7.69	7.43
ΣLREEs	**196.92**	**199.61**
Eu	1.91	1.87
Gd	8.7	8.34
Tb	1.38	1.32
Dy	8.99	8.67
Ho	2.02	1.97
Er	6.5	6.42
Tm	0.91	0.88
Yb	7.45	7.34
Lu	0.97	0.96
Y	92.17	107.99
ΣHREEs	**38.83**	**37.77**
ΣRREs+Y	**327.92**	**345.37**

Light REEs (LREEs: La to Sm), Heavy REEs (HREEs: Eu to Lu)

The sum of rare-earth elements concentration (ΣREEs+Y= 327.9 ppm) is lower than the average content in the phosphorite from Sra Ouertane phosphorites (ΣREE=570,56 ppm) and Jebel Jebs phosphorites (ΣREEs=547.79 ppm)[29] but Ras Dhraa phosphorites have higher REEs content compared to the Gafsa Metlaoui particles (ΣREEs=162.3 ppm)[29]. A significant concentration of yttrium, lanthanum, cerium and neodymium was observed in Rhas-Dhraa phosphorites samples. The concentration of the light rare elements is higher than the concentration of the heavy rare elements; the ionic radii of the light elements are very close to that of Ca^{2+}, which facilitates their substitutions in the crystal lattice of the francolite[30].

Phosphorites are composed of francolite as the main mineral and the asseccory minerals like silicates, carbonates and organic matter, which incorporate REEs+Y disproportionately and unpredictably**.** Such accessory phase must be ruled out in order to interpret properly REEs+Y content of phosphorites. After calcinations of phosphorites at 900°C for 30 min we note that the REEs content increases from 327.92 to rich 349.77 ppm. REEs+Y contents increased by 5% .Dolomite and quartz contain insignificant amount of REEs as compared to carbonate fluorapatite[31].The effect is not strong and may be attributed to total mass decrease due to CO_2 loss.

Effect of calcination on P_2O_5 content of phosphorites

Chemical analysis of calcined phosphorite show higher P_2O_5 grade in the phosphate product after calcinations 30 min at 900°C. The decomposition of adsorbed and combined water, burning of organic matter and most of the combined carbon dioxide increase the phosphate grade in the calcined product. It permits to increase the phosphate content from 29.58% to 33.07%. Many investigators[31] recommended that further increase in calcinations temperature has no detectable effect on P_2O_5 content.

Conclusion

In this study, the calcination of Ras-Dhraa phosphorite was conducted in terms of calcinations temperature and time .Chemical analysis; FT-IR spectroscopy and XRD analysis were used to investigate changes in the raw and calcined phosphorites. The elemental analysis of raw phosphorites verified the presence of many impurities such as S, Al, Si and Mg and the morphology of calcined phosphorite shows formation of macropores after calcinations. No significant effect of substitution in apatite structure was detected by XRD analysis. In addition, FT-IR spectroscopy results highlighted that increasing residence time of calcinations can accentuate SiO_4^{4-} and SO_4^{2-} substitutions and these substitutions cause a worsening of phosphorites properties for sulfuric acid production. It was also found that calcination at 900°C for a period of 30 min increase the phosphate grade by 10.5% and increase REE+Y content by 5%.

As a result, in the light of these observations, it can be concluded that the calcination of phosphorite at 900°C for 30 min minimize the rate of substitution and permit to obtain phosphorite with better phosphate grade and REEs +Y content and minimize calcite. This phosphorite will be suitable for the manufacture of clear green phosphoric acid with the possibility of recovering REEs.

Acknowledgments

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