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Research Paper

Qualitative and quantitative analysis of phosphate rock from Hazm Al-jalamid area, northern Saudi Arabia

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Abstract

Four samples of phosphate rock were collected from Hazm Al-Jalamid region (North of Saudi Arabia). These samples were treated and characterized using X-ray diffraction pattern XRF analysis, thermal analysis (DSC-TG), IR spectroscopy, scanning electronic microscope (SEM), and elemental analysis (ICP-OES). Crystallographic analysis showed that phosphate rock of this region consist of four principle inorganic phases with concentration varies from sample to another.

In addition to calcium, elemental analysis verified the presence of other metals such as Fe, Al, Cd, Si and Mg. Infrared spectroscopy of the phosphate rocks reveals the presence of vibration bands characteristic of identified phases. The results of thermal analysis, essentially the mass loss were related to the variation of calcite and dolomite concentration in the phosphate rock.

Keywords: *Inorganic Phases, Phosphate Rock, Thermal Analysis.*

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1. Introduction

Phosphate rock is the main raw material for the production of soluble phosphate fertilizers (PF). In fact, approximately 90% of the phosphate product is used in the manufacture of fertilizer, which is available in a wide variety of products to both liquids and dry granular form [1].

Phosphate rock contains a great variability of heavy metals and trace elements, which upon dissolution in the soil may be harmful at certain concentration. Special concern is given to contents of Cd, Pb, Sr, As, Th [2-6]

Beneficiation or upgrading of the phosphate rock (PR) has required for a number of different techniques. In some favorable cases, only screening and drying is necessary to reach a commercial grade of about 30% P_2O_5. However, in most cases the ore quality needs removal of impurities. For sedimentary rock, suitable techniques for economic ore concentration are crushing and screening or grinding, followed by pneumatic particle size selection and washing by hydrocyclones or classifiers. These techniques are based on particle size selection [7].

Most conventional commercial phosphate fertilizers are made by reacting phosphate rock with sulfuric acid to produce phosphoric acid. The phosphoric acid is further reacted with ammonia (ammoniation) to produce ammonium phosphate fertilizers such as diammonium phosphate (DAP) and monoammonium phosphate (MAP). Production of ammonium polyphosphate fertilizer (APP) requires dehydration and polymerization of phosphoric acid prior to ammoniation [8-10].

Different types of phosphate rocks have widely differing mineralogical, chemical and textural characteristics. While there are more than 200 known phosphate minerals, the main mineral group of phosphates is the group of apatite. Calcium-phosphates of the apatite group are mainly found in primary environments (in sedimentary, metamorphic and igneous rocks) but also in weathering environments [11], [12].

This study aims to characterize quantitatively and qualitatively the phosphate rock of Hazm Al-Jalamid in the north of Saudi Arabia to know the chemical composition and the different crystallographic phases existing. In the other hand, the sequential separation of principles fractions of phosphate rock will be tested in a separate project. Along this work, the four samples of phosphate rock are named respectively PR_1, PR_2, PR_3 and PR_4.

2. Material and methods

2.1. Experimental

Three samples of phosphate rock abbreviated as PR_1, PR_2 and PR_3 were collected from different locals in the mine of Hazm Aljalamid. The sample number four was prepared to exportation by treatment and purification and it's called PR_4. All samples were grinded and dried calcined at 120°C for 2 hours. After draying, pure samples were characterized by FTIR spectroscopy using a Bruker vertex 70-DTGS transmission equipped with a diamond ATR setup in the range from 400 to 4000 cm^{-1}. X-ray powder diffractograms were performed at room temperature on a PANalytical X'Pert PRO MPD equipped with copper anticathode tube. Phase's identification was carried out by the mean of MATCH program [13]. The chemical element contents were obtained by ICP-OES on a Horiba Jobin Yvon Model Activa. The powder morphology as well as the microstructure of samples was obtained using a scanning electronic microscopy (SEM) FEI mark, model QUANTA 200 FEG. The thermal measurements DSC-TG were performed in Helium gas with a heating rate of 10°C/minute, from room temperature to 1000 °C. The apparatus used is Setaram Labsys Evo (DSC-TG 1600°C).

3. Results and discussion

3.1. XRF and elemental analysis

The results of XRF analysis are grouped in Table1. All the samples were analyzed for their major elements (CaO, P_2O_5, SiO_2, Al_2O_3, MgO and Fe_2O_3). Elemental analysis of phosphate rock samples (Table 2) reflected the presence of fluorapatite with other accessory minerals such as calcite, dolomite…

Table 1: XRF Analysis of Phosphate Rocks PR_1, PR_2, PR_3 and PR_4.

Sample	P_2O_5%	CaO%	MgO%	SiO_2%	Al_2O_3%	Fe_2O_3%	CaO/P_2O_5
PR_1	27.68	50.89	0.58	1.24	0.40	0.04	1.83
PR_2	30.96	51.94	1.22	0.97	0.28	0.05	1.69
PR_3	24.73	48.9	3.61	1.23	0.40	0.09	1.97
PR_4	33.20	54.57	0.39	1.38	0.28	0.04	1.64

The high P_2O_5 and CaO values (24.73 to 33.20% and 48.90 to 54.57 wt%) respectively are also indicative of high apatite content. The CaO/P_2O_5 ratio varies from 1.64 to 1.89 which indicates the high content of carbonate in all phosphate rocks analyzed. For the PR_4 sample (1.64) the value is closer to carbonato-fluorapatite CFA (1.58) than to pure fluorapatite (1.317) [14]. According to Cd concentrations in PR_1 and PR_4 samples (Table 2), the concentrations were low enough and were not considered as threat on either health or environment. In fact, according to the International Agency for Research on Cancer [15] and the World Health Organization [16], cadmium is classified as a class 1 human carcinogen (Group B1).

Table 2: Chemical Composition of Phosphate Rocks PR_1, PR_2, PR_3 and PR_4.

Sample	Ca%	P%	Na%	Mg%	Fe(ppm)	Pb(ppm)	Cd(ppm)
PR_1	36.35	12.09	0.15	0.35	355.02	LQ	2.04
PR_2	37.10	13.52	0.27	0.74	499.78	LQ	LQ
PR_3	34.94	10.80	0.17	2.19	852.84	LQ	LQ
PR_4	38.98	14.50	0.24	0.08	355.45	LQ	2.29

LQ: Low Quantity

3.2. XRD analysis and phases identification

The diffractograms shown in Fig. 1 were carried out by X-ray powder diffraction at room temperature with the assistance of a PANalytical X'Pert PRO MPD equipped with copper anticathode tube. This characterization informs about the structural state of the powders and the identification of the present phases.

The diffractogram, presented in Fig. 2, shows that phosphate rocks (PRs) are composed of different phases with different intensities. For each sample, the quantitative analysis of its diffractogram using MATCH program reveals the presence of the following phases: fluorapatite $Ca_{10}(PO_4)_6F_2$ (2θ : 25.82° 32.10°; 33.24°; 33.87° ; 46.96° ; 49.57), calcite $CaCO_3$ (2θ : 29.42°; 35.99°; 39.43°), dolomite $CaMg(CO_3)_2$ (2θ : 30.96° ; 41.17°) and quartz SiO_2 (2θ: 26.65° ; 40.17°) [17], [18].

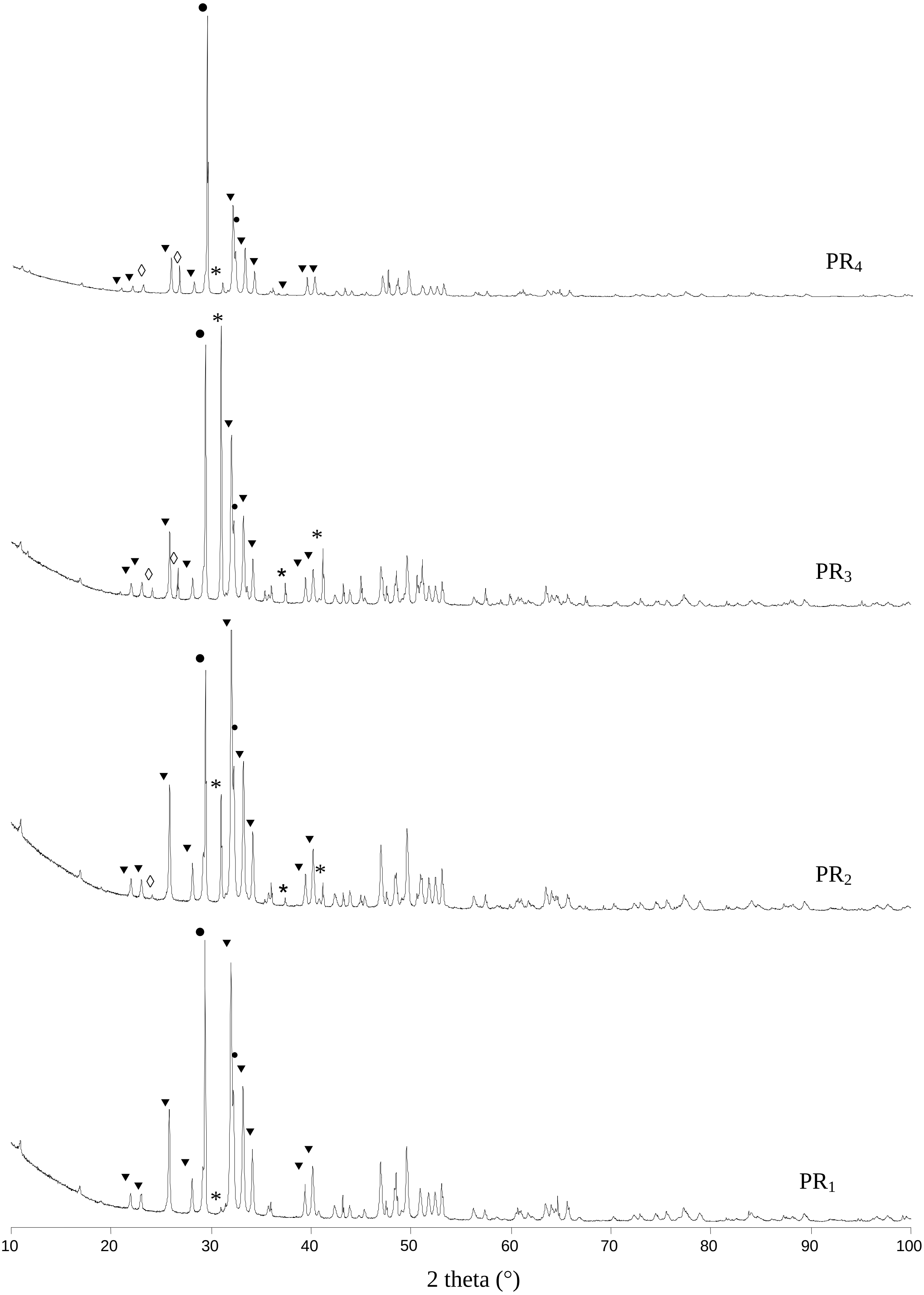


Fig. 1: X-Ray Diffraction Pattern of Phosphate Rock Samples PR$_1$, PR$_2$, PR$_3$ and PR$_4$ (▾: Fluorapatite; •: Calcite; *: Dolomite and ◊: Quartz).

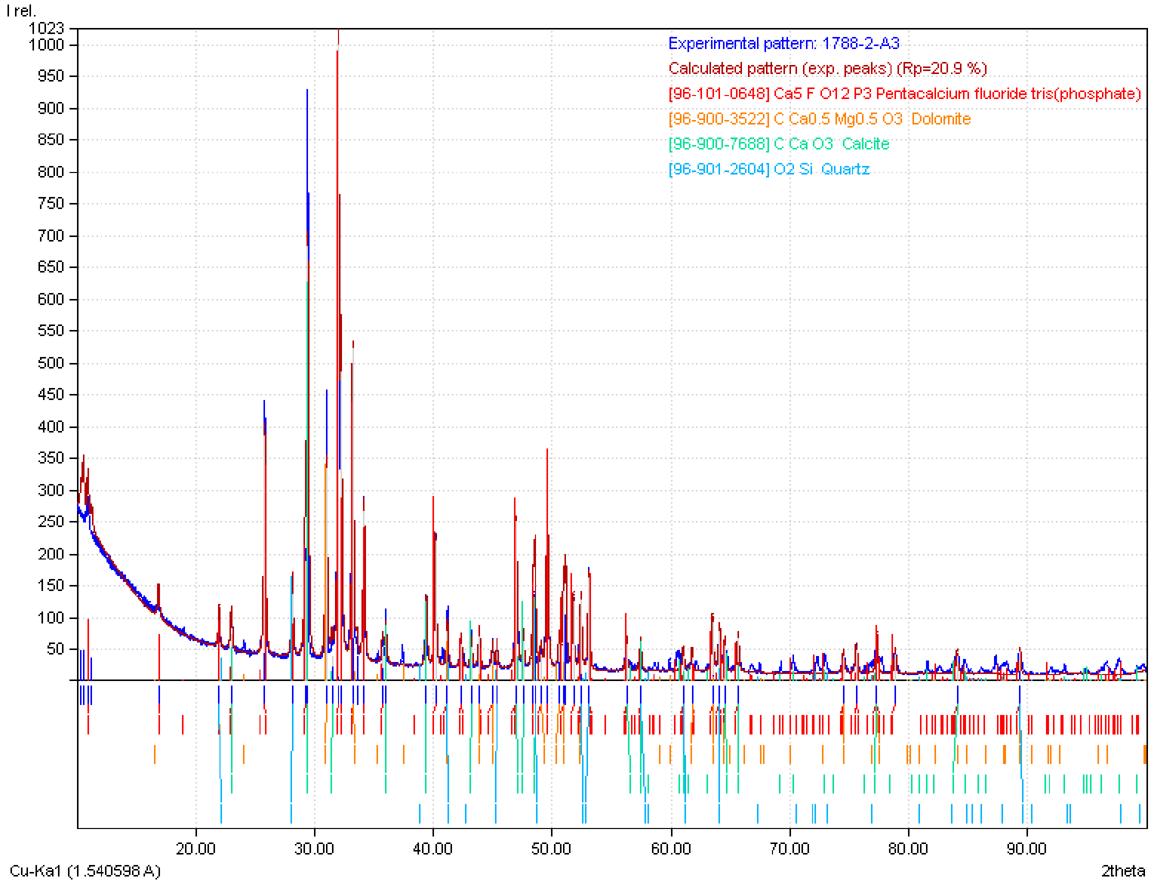
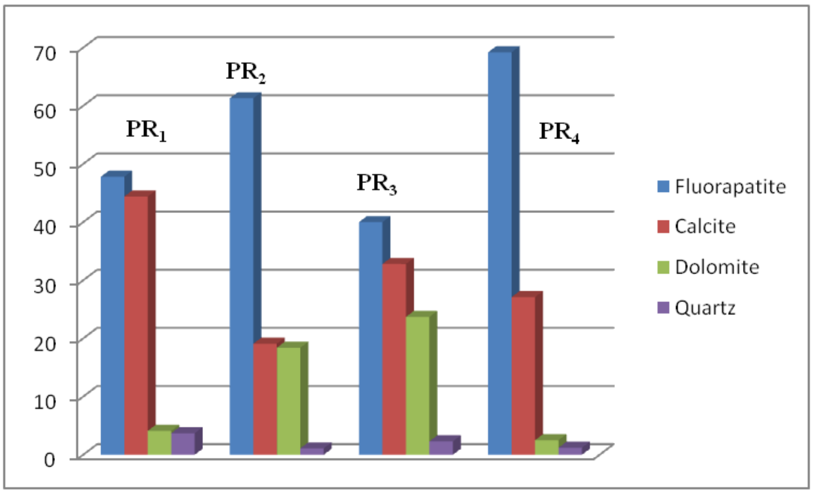


Fig. 2: Phases Identification of Phosphate Rock Sample PR_3

It appears that the recorded dolomite, calcite and quartz phases due to their nature exogangue, while the interference of these phases with fluorapatite are due to their natural endogangue. They constitute the francolite [19]. However, the concentration of each phase varies from sample to another (Table 3). The PR_3 mineral contains the higher percentage of dolomite (23.7%), according to the chemical analysis which reveals a concentration of 2.29% for magnesium. The different percentages of mineralogical phases determined by Match program were illustrated in Fig. 3.

Table 3: Phases (%) In the Phosphate Rock Calculated From MATCH Program.

Phosphate rock (PR)	PR_1	PR_2	PR_3	PR_4
Phase (%)				
Fluorapatite: $Ca_5(PO_6)F_2$	47.8	61.3	40.0	69.2
Calcite: $CaCO_3$	44.4	19.1	32.8	27.1
Dolomite: $CaMg(CO_3)_2$	4.1	18.4	23.7	2.5
Quartz: SiO_2	3.7	1.1	2.3	1.2



DSC-TG analysis

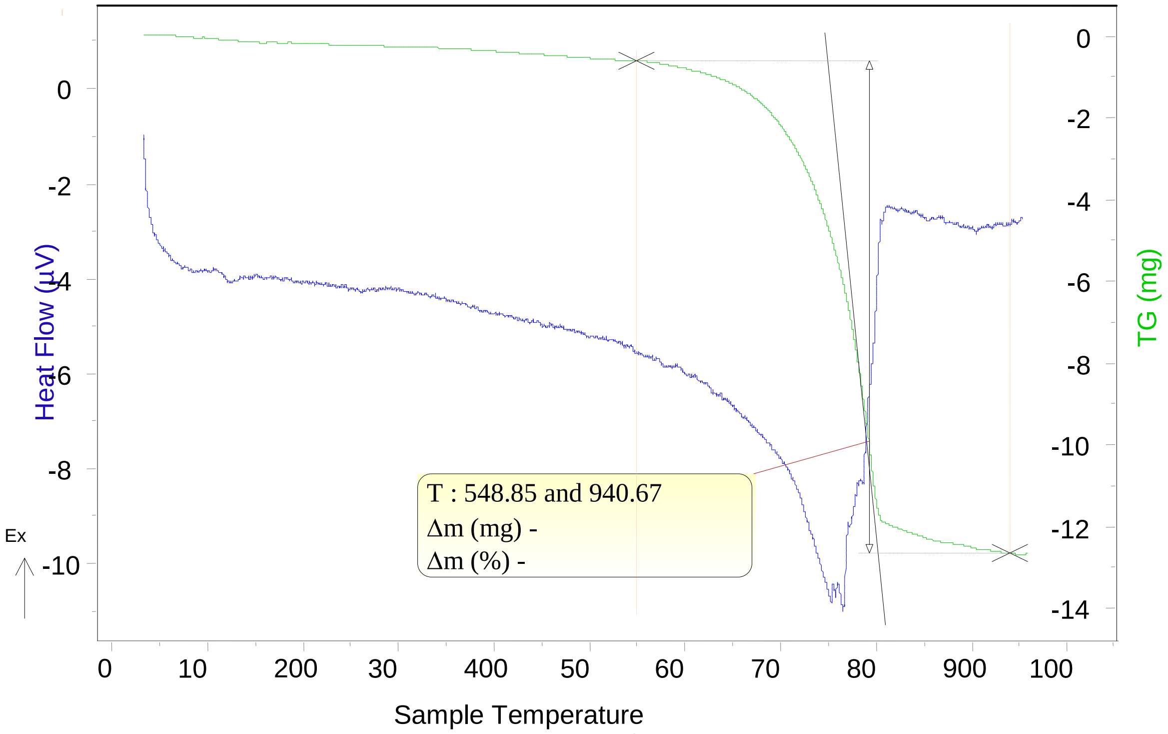
The DSC-TG data of phosphate rock for the four samples are represented in Fig. 4. Two endothermic peaks were detected:

The dehydration represented by endothermic peak of low amplitude appears at about 160°C, accompanied by a weight loss up to 0.12% which corresponds to the dehydration of ions HPO_4^{2-} according to the following reaction [20].

$2HPO_4^{2-} \rightarrow P_2O_7^{4-} + H_2O$

According to El Ouerdi and al [21] a second low mass loss (2 at 3%) starts around 200 °C and which lasts up to 550 °C. This result comes from the superposition of an endothermic reaction (from structural water) and an exothermic reaction (combustion of organic matter). In our case, the second mass loss is too lower and it was not be observed never in the case of PR_3 nor in the case of the purified phosphate rock PR_4, this can be explained by a very small organic moiety linked to the used phosphate.

The second mass loss starts from 550 °C represented by an area of strong endothermic due to the decomposition of carbonates (calcite ($CaCO_3$) and dolomite ($CaMg(CO_3)_2$) with release of CO_2 [21]. For the sample PR_3, this obtained peak was divided into two components which certainly due to the decomposition of two different phases calcite and dolomite. Thus, on the TG curve we note a sharp increase in the rate of mass loss between 700 and 900 °C which is due to the increase in the thermal decomposition kinetics of carbonates. The total mass loss obtained is about 15.6 %. This value is higher than that obtained for the purified phosphate PR_1 (9.81%) corresponding to only one endothermic effect. This phenomenon is in a good agreement with XRD analysis which confirms the presence of low quantity of dolomite up to 5% in purified phosphate. In addition, the total value differs between minerals according to the level of impurities [22]. The last mass loss was related to the sum of phase's percentage of calcite and dolomite determined by MATCH program. According to table 4 the removed mass from phosphate rock samples in the range 700-900 °C is proportional to the obtained values of % ($CaCO_3$+$MgCa(CO_3)_2$.



T : 548.85 and 940.67
Δm (mg) -
Δm (%) -

Fig. 4: Curve DSC-TG of Phosphate rock Sample PR_3

Table 4: Relationship between Mass Losses (%) In the Range 700-900 °C and (Calcite + Dolomite) %

Sample	Mass loss (%)	($CaCO_3$+$MgCa(CO_3)_2$) %
PR_1	11.64	48.5
PR_2	10.52	37.5
PR_3	15.60	56.5
PR_4	9.81	29.6

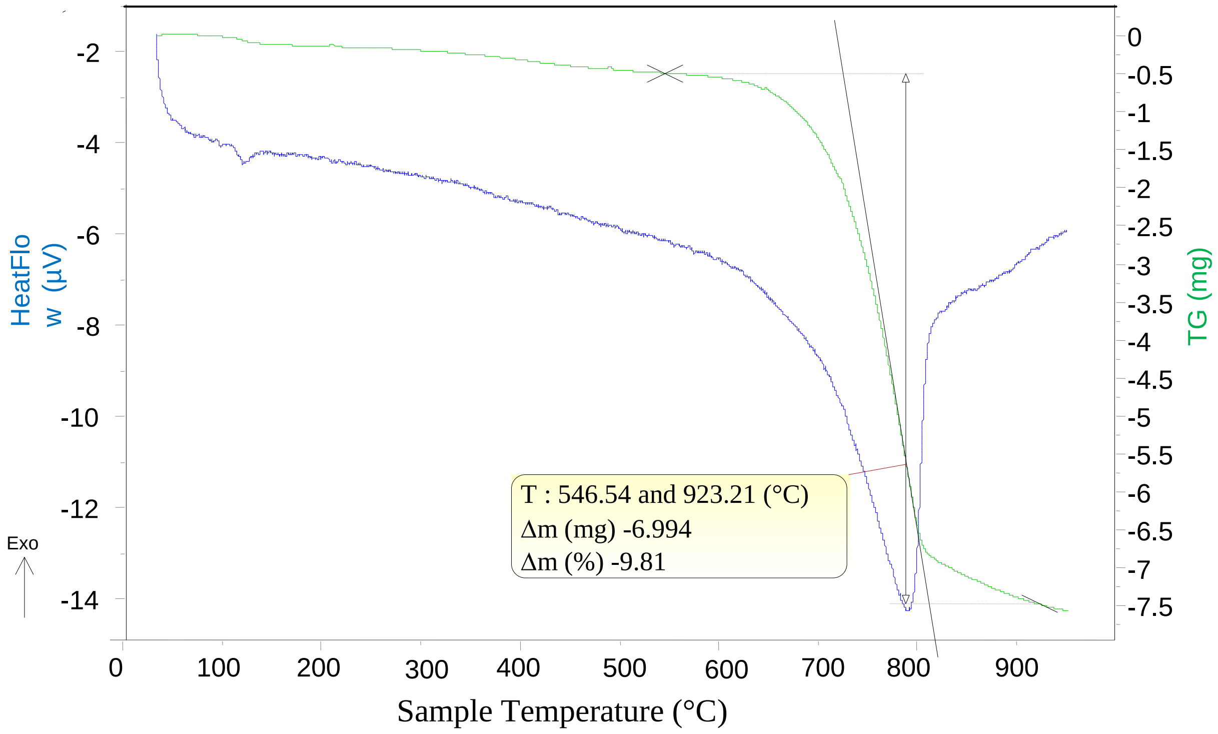


Fig. 5: Curve DSC-TG of Phosphate Rock Sample PR_4

3.3. Infra-red spectroscopy

The IR spectra of all characterized samples were illustrated in Fig. 6. All of them showed that vibration bands of PO_4^{3-} group of the apatite structure are detected: (ν_s) (963 cm^{-1}), (δ_s) (477 cm^{-1}), (ν_{as}) (1040–1095 cm^{-1}) and (δ_{as}) (568– 604 cm^{-1}) [23], [24]. However, the spectra show the absence of stretching (ν_s) and liberation (ν_L) bands characteristic of the hydroxyl ion in the apatitic structure. This gave convince evidence that the present phase was fluoroapatite and not a hydroxyapatite as the XRD analysis confirmed. A large peak with low intensity was observed around 3500 cm^{-1}. It was attributed to the molecules of water adsorbed on the surface of the phosphate ore. The last result confirms the low mass loss corresponding to the water eliminated during the thermal analysis.

The peaks observed toward 1454 and 1429 cm^{-1} were attributed to the anti-symmetrical vibration of the CO_3^{2-} group, while the peak observed around 865 cm^{-1} was assigned to the symmetrical vibration of same group. These bands are characteristic of calcite and dolomite phases [25]. The intensities of these bands are mostly higher for PR_2 and essentially for PR_3 sample than those of purified phosphate PR_4. This can be related to the diminution of the total amount of calcite and dolomite after purification of phosphate raw confirmed by chemical analysis and phase identification. These results are showed in Fig 7. Moreover, the vibration bands characteristic of the quartz phase essentially in the range 1200-1000 cm^{-1} are certainly masked by that of the apatitic phase.

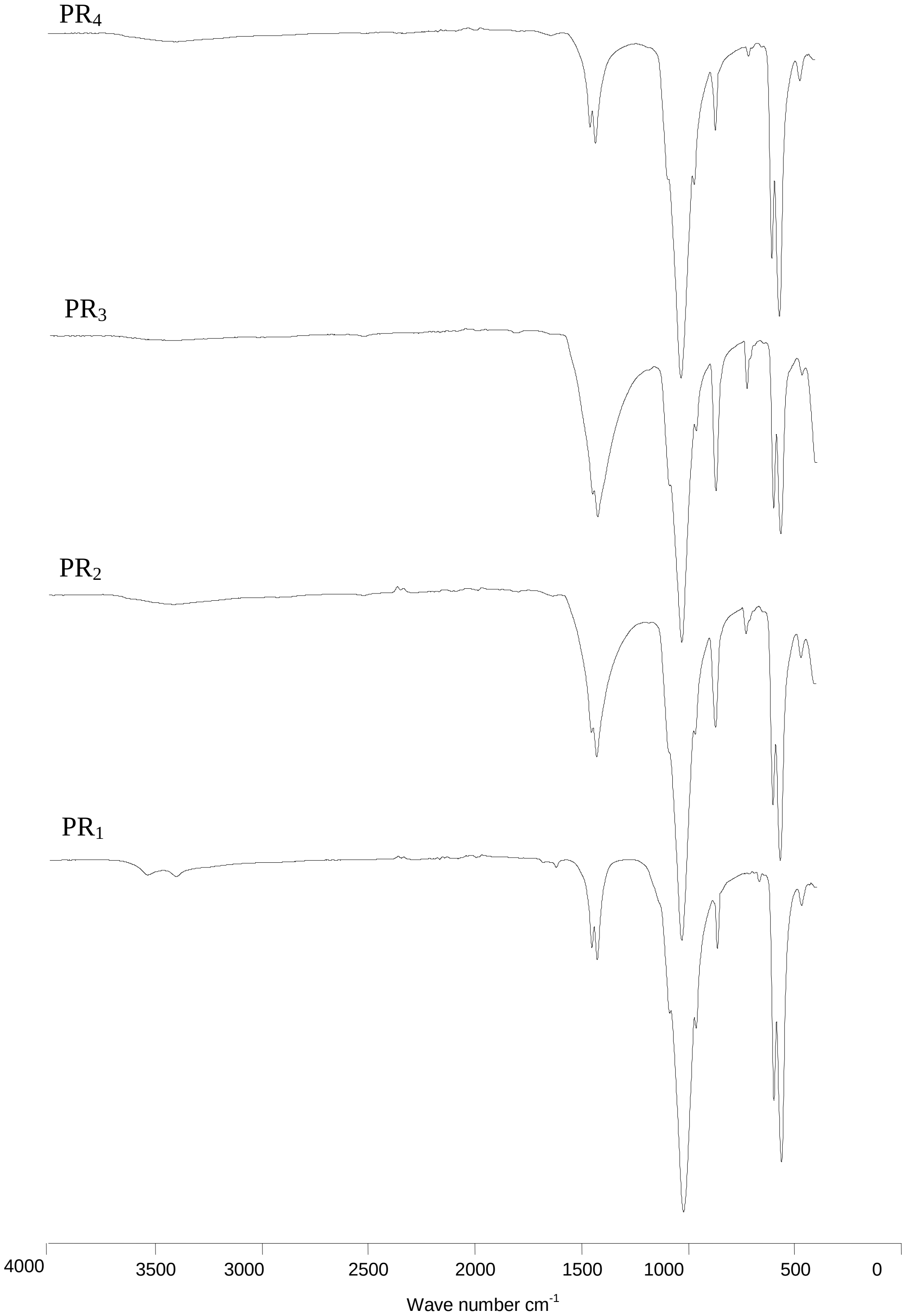


Fig. 6: Infrared Spectra of Phosphate Rocks Illustrated In the Range 400-4000 cm^{-1}.

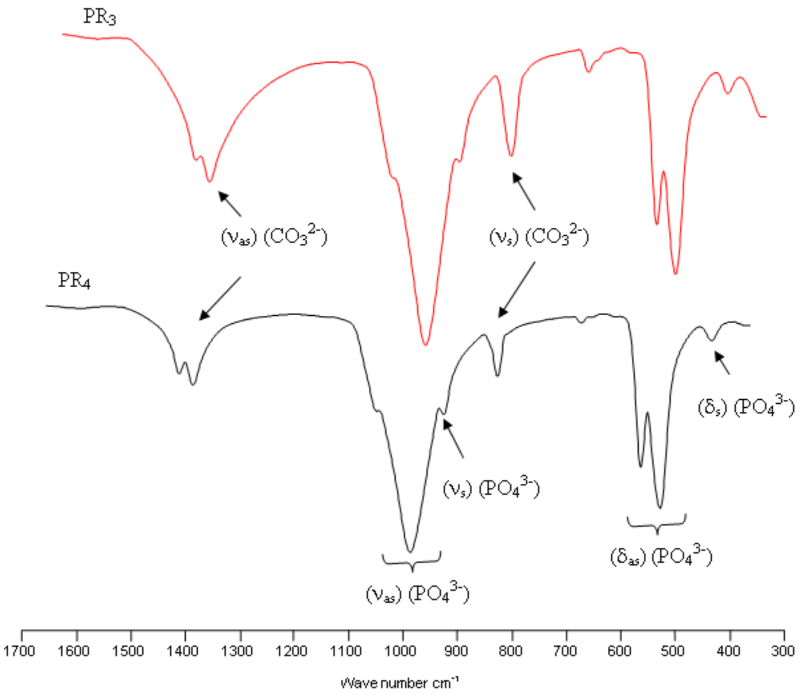


Fig. 7: Infrared Spectra of PR_3 and PR_4 Represented in the Range 300-1700 cm^{-1}

3.4. SEM spectroscopy

Fig. 8 shows the SEM micrographs of the powder PR_1, PR_3 and PR_4. Fig. 8 (a, c and e) shows a heterogeneous microstructure for these analyzed samples. Moreover, the observations achieved by SEM show that the powders of the different samples are strongly agglomerated. This agglomeration is clearly observed in the case of PR_4 which contains different phases with great difference between percentages shown by XRD analysis (Fluorapatite: 69.2%, Calcite: 27.1%, Dolomite: 2.5% and Quartz: 1.2%). For the PR_3 sample, when the percentages of the major phases are substantially closer (Fluorapatite: 40%, Calcite: 33%, Dolomite: 23.7% and Quartz: 2.1%), the powder has a lower agglomeration. The present pictures acquired by SEM permitting to confirm the presence of different phases in the phosphate rocks. This last reveals the presence of more than three essential colors, a black, a white and the gray color that indicates the presence of more than two mineralogical phases in the powder. These colors appear clearly when we use the scale bar 5 µm. This affirmation is in good agreement with the results of X-ray diffraction patterns.

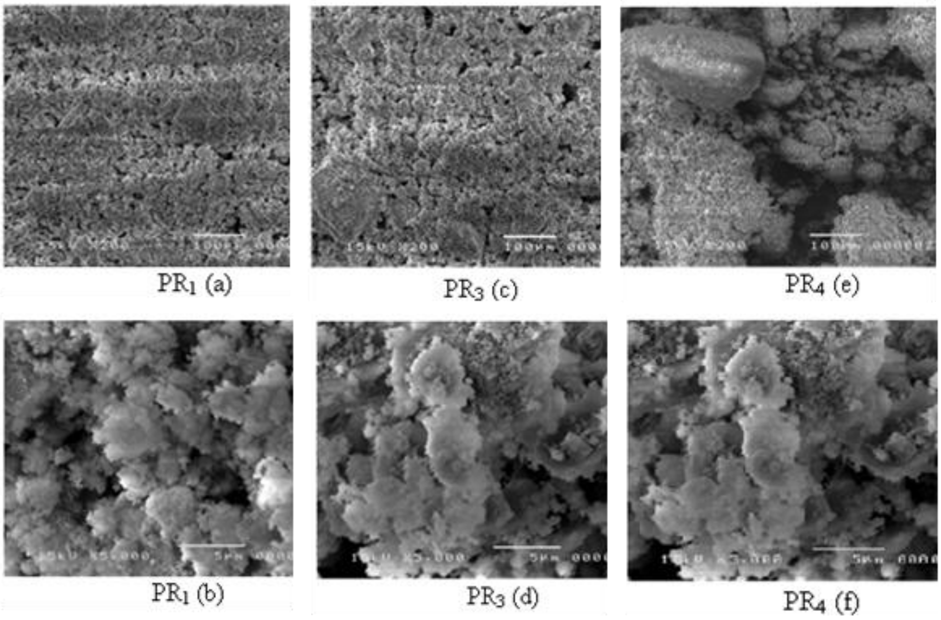


Fig. 8: SEM Micrographics of Phosphate Rock PR1 (a, b); RP3 (c, d) and RP4 (e, f) with Scale Bar 100υm and 5 υm Respectively.

4. Conclusion

Four samples of phosphate rock were collected from Hazm Al-Jalamid area of northern Saudi Arabia. These phosphate rocks were mainly composed of CaO, P_2O_5, SiO_2, Al_2O_3, MgO and Fe_2O_3 that reflect a good agreement with the literature. Quantitative and qualitative investigations showed that low chemical variability of the major elements, particularly the phosphate content, may present a good factor to producing a consistent commercial product. In addition, a good agreement between all techniques used concerning the determination of the major components (phases) of phosphate rock. The CaO/P_2O_5 ratio, significantly high (>1.6), is typical for carbonate apatites. Stoichiometric fluorapatite have a value of this ratio around 1.317 which increases with the substitution of PO_4^{3-} in the structure by CO_3^{2-}. This encouraged us to think about separating carbonate, organic and oxydable fractions using the fractional sequential method.

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