



## Thermal Study of Tunisian Phosphogypsum for Use in Reinforced Plaster

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### Authors' contributions

*This work was carried out in collaboration between all authors. Author NM designed the study, performed the statistical analysis, wrote the protocol, wrote the first draft of the manuscript and managed literature searches. Authors MA, ML and EE managed the analyses of the study and literature searches. All authors read and approved the final manuscript.*

### Article Information

DOI: 10.9734/BJAST/2016/25728

#### Editor(s):

(1) Yoshitaka Okitsu, Automobile R&D Center, Honda R&D Co., Ltd., Japan.

#### Reviewers:

(1) Hisham M. Khater, Housing and Building National Research Center, Egypt.

(2) Khadija Nabih, University Mohammed V, Rabat, Morocco.

(3) Adriana Estokova, Technical University of Kosice, Slovakia.

(4) Lia Rimondini, University of Piemonte, Italy.

Complete Peer review History: <http://sciencedomain.org/review-history/14753>

Original Research Article

Received 17<sup>th</sup> March 2016  
Accepted 7<sup>th</sup> May 2016  
Published 23<sup>rd</sup> May 2016

### ABSTRACT

This work presents a promising way to investigate the valorization of natural residual from Tunisian industrial wastes. In fact, large quantities of phosphogypsum which are obtained from Tunisian Chemical Group "TCG" are accumulated every year in Tunisia. The rational valorization of these available renewable resources fits very well with the recent sustainable approach, established nowadays. This work aims at ascertaining the chemical composition of this inorganic residue and structural characterization for use as a reinforced plaster.

Several thermal treatments from 100°C to 800°C were established to prepare from phosphogypsum various qualities of this material to be characterized by numerous techniques such as the FTIR, XRD, SEM, DSC, DTG and TGA in order to apply in potential application. Calcination temperature that gave the best value for the beginning and the end of setting was 200°C. The experimental tests showed height values of flexural strength for the calcined PG at 200°C (0.45 MPa).

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*Keywords: Phosphogypsum; thermal treatments; thermo gravimetric analysis; setting time.*

## 1. INTRODUCTION

Phosphogypsum (PG) is an acidic by product of the phosphate fertilizer industry, formed during the production of phosphoric acid from phosphate rock. It is composed mainly of gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) but contains various harmful impurities which depend on the type of the attacked phosphate rock (magmatic or sedimentary), the used process (dihydrate, hemihydrate and recrystallization) and the storage duration (which affects the amount of soluble impurities in water). Up to now, large amounts of PG have been produced world – wide. If the historic trends continue the production will increase to several hundred million metric tons annually. In Tunisia, the production rate exceeds 10 million tons per year. The problems of pollution generated by this product have been discussed by many authors in the world [1,2]. For many years, the Tunisian Chemical Group "TCG" and the Tunisian Environmental Ministry were dealing with the problems of its management and valorization [2]. However, because of economic restraints (e.g. land price) and pressing environmental issues, the development of a safe disposal procedure is necessary. Although, the best option for dealing with the PG problem appears to be the commercial use of this material in the agriculture (e.g. amelioration of acid soils) and construction industry (building/ road construction), only a relative small portion of the PG produced (14%) is reprocessed, a significant part was dumped into water bodies (28%) and the largest amount of the material was accumulated in large sludge ponds and retaining stockpiles [3,4].

In light of the above, the aim of the present study is the characterization of raw phosphogypsum to produce composite plaster.

## 2. RAW MATERIALS

Phosphogypsum (PG) was obtained from Tunisian Chemical Group "TCG" (15 km south of Gafsa, the capital of Gafsa M'Dhilla TCG). The sample (raw PG) was collected from 20 meters deep, as far as possible. The homogenized sample was then washed, dried and weighted. The pH value of the material was 2.32 when tested with mass ratio of solid-liquid (dry PG-distilled water) of 1:10.

## 3. MATERIALS AND METHODS

### 3.1 Calcination of PG

Calcined PG was produced by heating raw PG at different temperatures from 100°C to 800°C in the furnace during 3 h, cooled and ground to pass 100  $\mu\text{m}$  IS sieve [5].

### 3.2 Characterization of PG

Crystalline phases of the samples were identified by X-ray diffraction (XRD) in a diffractometer (Philips X'Pert) with Cu K $\alpha$  radiation, from 5.00° to 70.00° with a step of 0.05° and counting time of 80 s [6,7]. FTIR spectra of the different samples were collected on a FTIR spectrophotometer (Bruker) by preparing KBr pellets using a PG concentration of 1% (w/w). Spectra were recorded between 600 and 4000  $\text{cm}^{-1}$  at a resolution of 4  $\text{cm}^{-1}$  and co-adding forty sixteen scans [8]. X-Ray Fluorescence (XRF) Philips model PW-1404 sequential wavelength dispersion unit were used to determine the elemental composition of PG. For thermal gravimetric analysis (TGA; Perkin-Elmer Pyris 1 TGA-7), about 12 mg of PG was put into a platinum sample pan and heated from 50 to 900°C at a heating rate of 10°C/min under a nitrogen atmosphere with a flow rate of 20 mL/min. Curves of weight loss and derivative weight loss (DTG) were plotted. The microstructure of PG is identified with the help of scanning electron microscopy (SEM) [9] and Differential scanning calorimetric (DSC). The principle of differential calorimetric techniques quantification is based on variations in the heat energy supplied to the test sample relative to that provided to control called an inert body in a controlled temperature variation.

PG plaster samples were elaborated with addition of water, the water/PG ratio was 1. Setting time is the time taken by the sample to be completely cured, after that, samples were unmolded. Then they were kept for 6 days in laboratory atmosphere and later stored for 24 h in a stove (CENTERM 150 model), at 40 $\pm$ 2°C, to reach a constant mass. The following day, the samples were cooled in desiccators to achieve the room temperature and being subsequently mechanically tested.

## 4. RESULTS AND DISCUSSION

### 4.1 Chemical Composition

The composition of raw PG, as determined by X-ray fluorescence analysis, is shown in Table 1, the PG is made up of CaO (32%) and SO<sub>3</sub> (46%). The remaining components are present at low percentage.

The mineralogical phases were identified by X-ray diffraction (XRD), The result of this characterization is presented in Table 2. It shows a predominant presence of bassanite (Ca(SO<sub>4</sub>)<sub>1/2</sub>(H<sub>2</sub>O) 90% for raw PG sample and Anhydrite Ca(SO<sub>4</sub>) 97% for calcined PG [10,11]. The presence of gypsum in calcined PG at 200°C should have caused setting time decreases and an enhancement of mechanical strength during the plaster synthesis. The calcined PG at 200°C contains the highest yield of gypsum which decreases the setting time and enhances the mechanical properties. Miloš and Dragan, explained that PG presents a more complex composition than natural gypsum (characterized by a poorly expressed crystalline structure), which may influence its chemical behavior [12]. In phosphogypsum, P<sub>2</sub>O<sub>5</sub> generally exists as H<sub>3</sub>PO<sub>4</sub>, Ca(H<sub>2</sub>PO<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O, CaHPO<sub>4</sub>·2H<sub>2</sub>O and Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>. P<sub>2</sub>O<sub>5</sub> found adhered to the surface of gypsum crystals is water leachable, whereas P<sub>2</sub>O<sub>5</sub> present in the crystal lattice is difficult to be removed by simple water washing [13].

### 4.2 Degree of Whiteness

The whiteness is an important factor of characterization of PG that is why we conducted this test with different temperature of calcinations. Table 3 shows the whiteness of the phosphogypsum, as shown before and after calcinations at different temperatures. These results shown that the variation in the value of brightness depends on the calcinations temperature. The increasing the calcination temperature increases the whiteness gradually until it reaches a maximum at 800°C.

### 4.3 Morphological Analysis SEM

Examination with scanning electron microscopy showed that the studied PG samples have a tubular shapes (platelets) or hexagonal well known Fig. 1a, with over a certain district of form that is clearer for the calcined PG at 800°C and at 200°C Figs. 1b, c.

The formations of such type of tubular shapes (Fig. 1a) confirm adverse effect of impurities present in phosphogypsum [14].

The sample of raw PG (Fig. 1a) has rectangular platelet morphology such that the particles have lengths of between 0.2 and 180 μm in length and about 50 μm median. The photograph of calcined PG at 800°C Fig. 1b, highlights several types of particles. This explains the presence of other compounds formed after calcinations.

**Table 1. Chemical composition of raw PG in mass %**

CaO	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	MgO	SO <sub>3</sub>	Na <sub>2</sub> O	P <sub>2</sub> O <sub>5</sub>	F	H <sub>2</sub> O
32	1	0.1	0.1	0.4	46	0.3	1.2	1.2	17.7

**Table 2. Chemical composition of PG before and after calcination**

Minéral composition	Raw PG	Calcined PG at 200°C	Calcined PG at 800°C
Bassanite Ca(SO <sub>4</sub> ) <sub>1/2</sub> (H <sub>2</sub> O)	90%	7 %	-
Gypsum Ca(SO <sub>4</sub> ) <sub>2</sub> (H <sub>2</sub> O)	9%	92%	-
Brucite HP Mg(OH) <sub>2</sub>	1%	-	-
Anhydrite Ca(SO <sub>4</sub> )	-	-	97%
Calcite CaCO <sub>3</sub>	-	-	3%

**Table 3. Whiteness of PG at different temperature of calcinations**

Samples	Dried sample	Calcined at 200°C	Calcined at 400°C	Calcined at 600°C	Calcined at 800°C
Degree of whiteness (%)	48.7	51.2	57.6	86.3	92.4

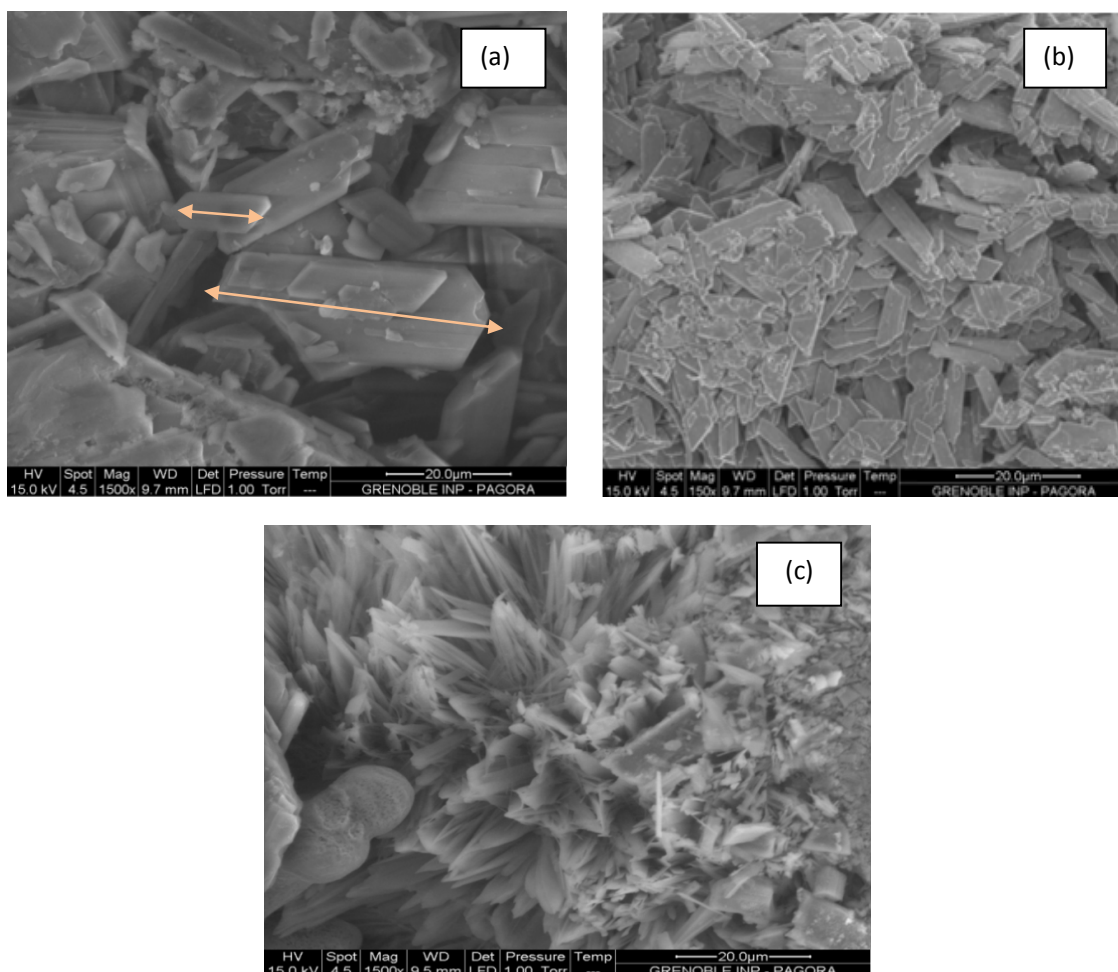


Fig. 1. SEM photo of the studied PG pure (a), PG 800°C (b) and PG 200° (c) (scale 20 µm)

#### 4.4 X-ray Powder Diffraction (XRD)

The samples of PG were dried at 105°C for 48 hours before performed tests of X-ray diffraction [15].

The diffractograms obtained (Fig. 3) show the presence of hydrated calcium sulfate  $\text{CaSO}_4 \cdot 1/2 \text{H}_2\text{O}$  and anhydrite  $\text{CaSO}_4$ ,  $\text{SiO}_2$  quartz and gypsum  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ , with different proportion. The peak at 15°, 30°, 32°, 49° shows the presence of hydrated calcium sulfate  $\text{CaSO}_4 \cdot 1/2 \text{H}_2\text{O}$ . The peak at 12° indicates the presence of the Gypsum  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  and the peak at 26.5° as attributed to anhydrite  $\text{CaSO}_4$ .

It should be noted that there are three degrees of hydration as possible for gypsum 0, 2 and  $1/2 \text{H}_2\text{O}$ . The comparison of chemical composition of

the raw PG and calcined PG demonstrated significant increases in anhydrite content (peak at 26.5°).

#### 4.5 EDX – Ray Analysis

Following the morphological analysis (SEM) of phosphogypsum samples, we studied the X-ray analysis using the apparatus of SEM coupled with EDX (Fig. 2).

From these spectra, we can deduce the key chemical elements of phosphogypsum. The elements that are present in all samples are carbon, oxygen, calcium, sulfur, silica and phosphorus.

Indeed, the dominant elements after calcination at 800°C are calcium and oxygen [11].

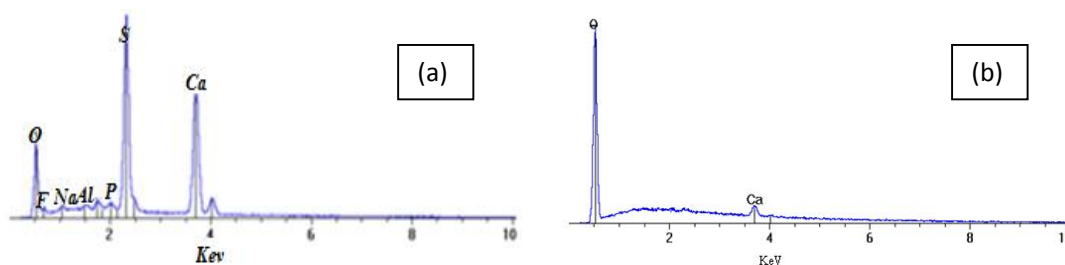


Fig. 2. EDS of raw PG (a) calcined PG at 800°C (b)

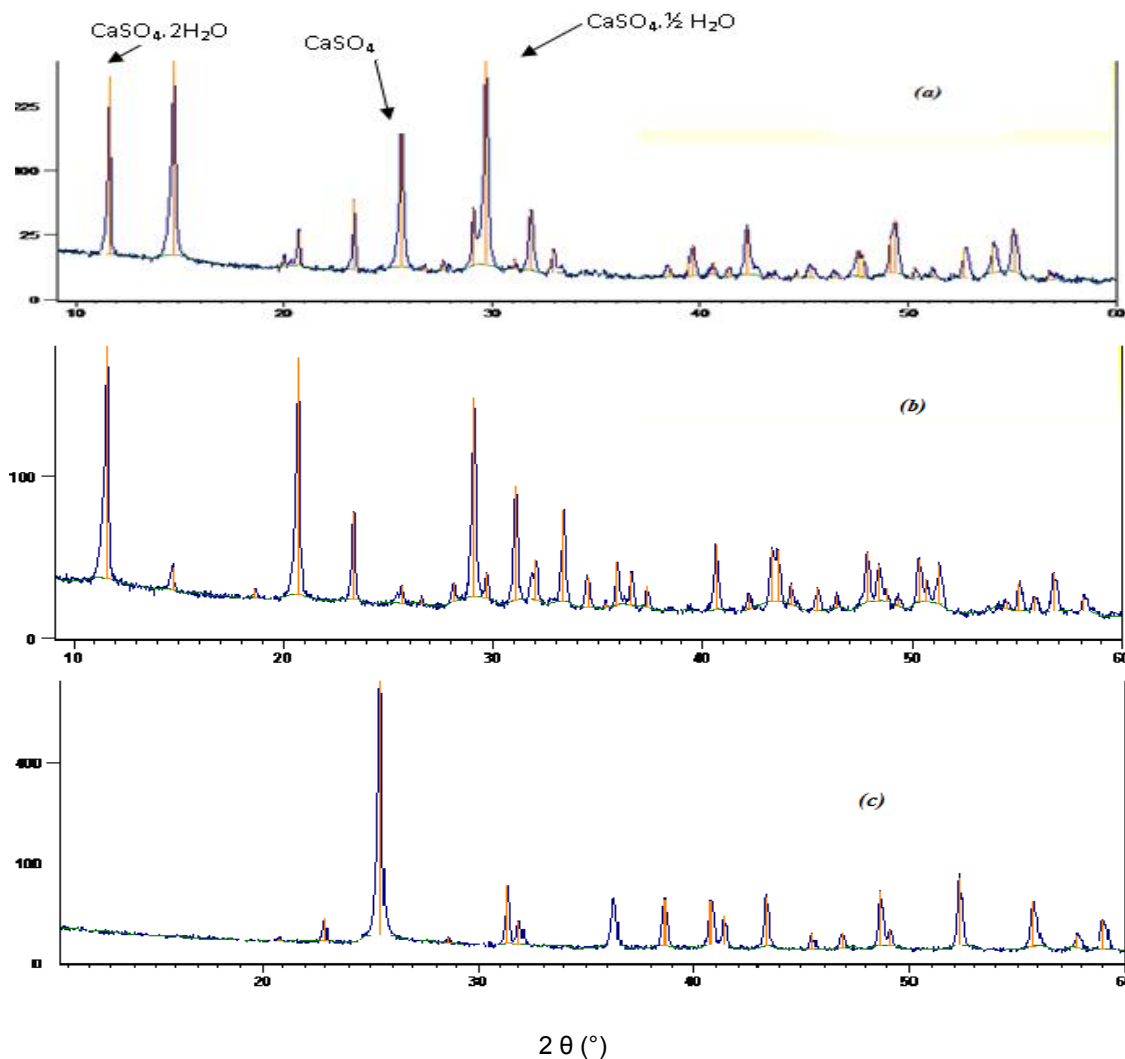


Fig. 3. XRD spectra of raw PG (a), PG calcined at 200° (b) and PG calcined at 800°C (c). As the calcination temperature increased from 200 to 800°C, several peaks become more distinct and narrow which suggested an increase in the degree of crystallinity

#### 4.6 FTIR Spectra

The IR spectrogram of a solid provides various information about PG structure. The sample was

analyzed by phospho-IR spectrometer in the Fourier transformed.

The IR spectrum of raw PG (Fig. 4) shows a main peak at  $1099\text{ cm}^{-1}$  corresponds to the

elongation of the sulfate ion ( $\text{SO}_4^{2-}$ ) gypsum in the network and another less intense peak at  $594 \text{ cm}^{-1}$  which corresponds to the deformation of  $\text{SO}_4^{2-}$ . The presence of water is characterized by two peaks around  $1620 \text{ cm}^{-1}$  and  $3590 \text{ cm}^{-1}$  correspond to the two states of water can be: water for hydration and free water  $\text{CaSO}_4$ . These bands (crystallization and absorbed water) become weaker by calcination process.

Figs. 4a and b show the infrared spectrum of the raw PG and calcined PG at  $800^\circ\text{C}$ . The presence of water molecules vibrations  $\nu_{\text{O-H}}$  and  $\delta_{\text{O-H}}$  was observed at  $1684 - 1622 \text{ cm}^{-1}$  as well as the presence of those of sulfate groups, this peak disappeared for the calcined PG.

The vibration located at the  $1152\text{-}1099 \text{ cm}^{-1}$  range is attributed to the stretching of sulfate groups, this peak is more intense for PG 800 than raw PG which indicates the dehydration of gypsum to anhydrite during calcinations; this

result is confirmed by the bands observed at  $658$  and  $601 \text{ cm}^{-1}$  which correspond to the bending modes vibrations  $\delta_{\text{O-S-O}}$  [16].

#### 4.7 Differential Scanning Calorimetric (DSC)

Differential Scanning Calorimetric DSC is a technique for accessing the amounts of heat put into play during physical transformations (recrystallization, phase change ...) or chemical (oxidation-reduction, dehydration, decomposition ...). It allows studying the thermal transitions of the sample that is to say, the changes occurring in the sample when heated. As it measures the enthalpy difference between a sample and a reference material with temperature (Fig. 5).

The shape of the thermogram indicates the existence of a main endothermic peak around  $220^\circ\text{C}$ . This peak corresponds to the dehydration of PG.

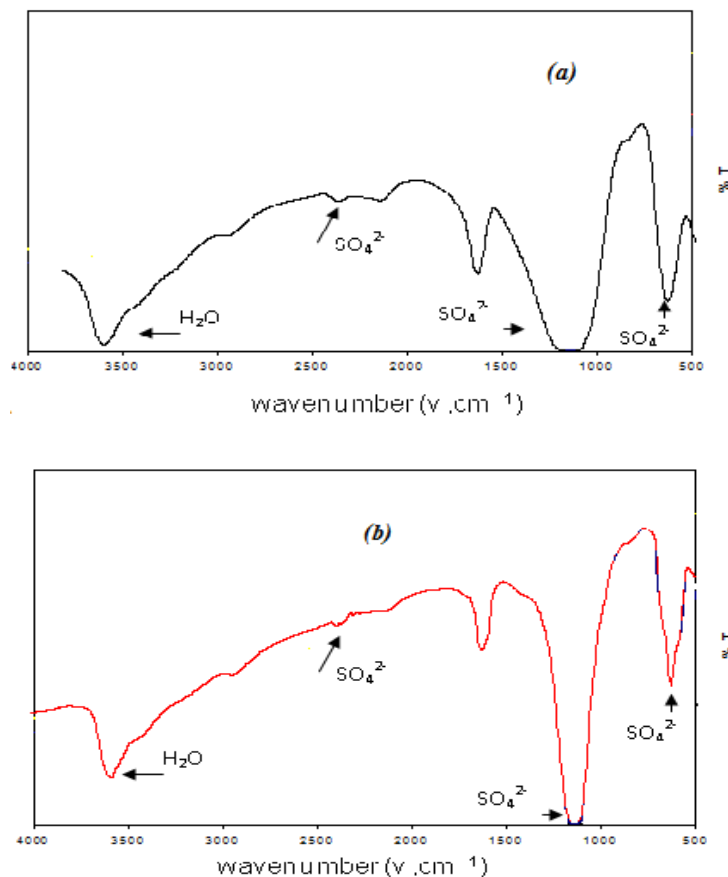


Fig. 4. IR spectrometer in the Fourier transformed of raw PG (a) and calcined PG at  $800^\circ\text{C}$  (b)

We notice after calcinations of PG at 800°C there is disappearance of the endothermic peak around 220°C, which confirm the dehydration.

The peak at 180°C corresponds to the condensation of organic compounds; this peak disappears in the calcined PG which confirms the elimination of this impurities.

#### 4.8 Thermogravimetric Analysis (TGA)

Differential thermal analysis is usually associated with a thermogravimetric analysis to measure the change of mass (or vapor emission gas uptake) of a sample as a function of heat treatment temperature that can reach 1700°C and under a controlled atmosphere.

Fig. 6 shows the TGA and DTG curves of raw PG and calcined PG at 200 and 800°C. The calcined PG has better heat resistance than that of raw PG and less weight loss during the period of heating. The thermal-degradation of three samples can be divided into two temperature regions, lower than 300°C and higher than 600°C. For temperatures below 300°C, the weight loss includes the evaporation of water related to the residual moisture; this result is observed only in the raw PG spectra. For temperatures higher than 300°C, the weight loss might be due to the dehydration of PG which confirms the increase of the anhydrite content. This latter confirms the XRD and FTIR observation. Thus, the calcined PG has less acid

impurity than raw PG which is explained by the weight-loss at the end of heat [17-19].

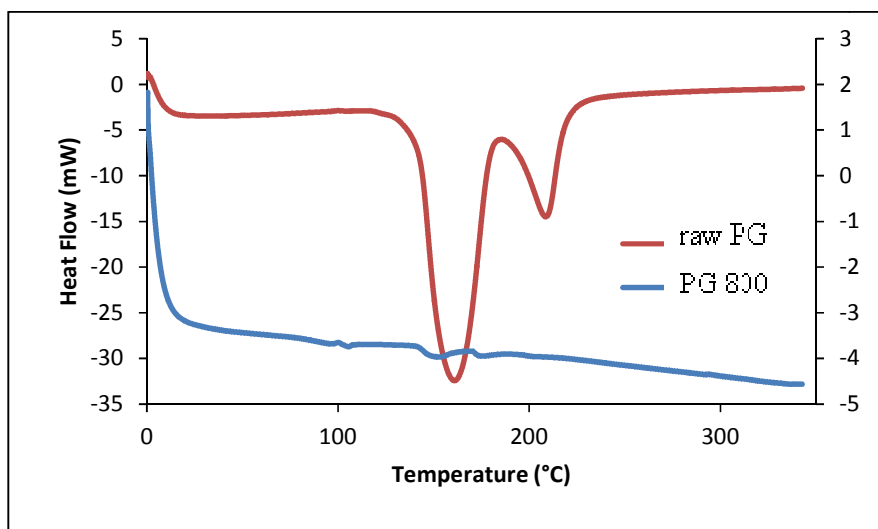
#### 4.9 Flexural Characterization

Fig. 7 shows the evolution of setting time as a function of temperature. The setting time increases when the temperature rises. Thus, temperature of calcination does effect the setting time by retardation increasing. There was clear indication that the differences in the calcium and sulfate content can alter the rate of reaction and thus the setting time.

Calcination temperature that gives us the best value for the beginning and the end of setting is 200°C (Initial Setting 6.2 min and the end of Setting 15 min). Table 4 shows average values of flexural strength for PG plaster calcined at 200°C, 600°C and 800°C. The experimental tests show height values flexural strength for calcined PG at 200°C (0.45 MPa). This can be explained because the mechanical properties depend on the ratio of anhydrite, which confirm the low value obtained for calcined PG at 800°C (0.22 MPa) [20,21].

**Table 4. Mechanical strength (MPa) of PG plaster at different temperature of calcinations**

Temperatures of calcinations	Raw PG	200	600	800
Mechanical strength (MPa)	0.39	0.45	0.25	0.22



**Fig. 5. DSC spectra of raw PG and calcined PG at 800°C**

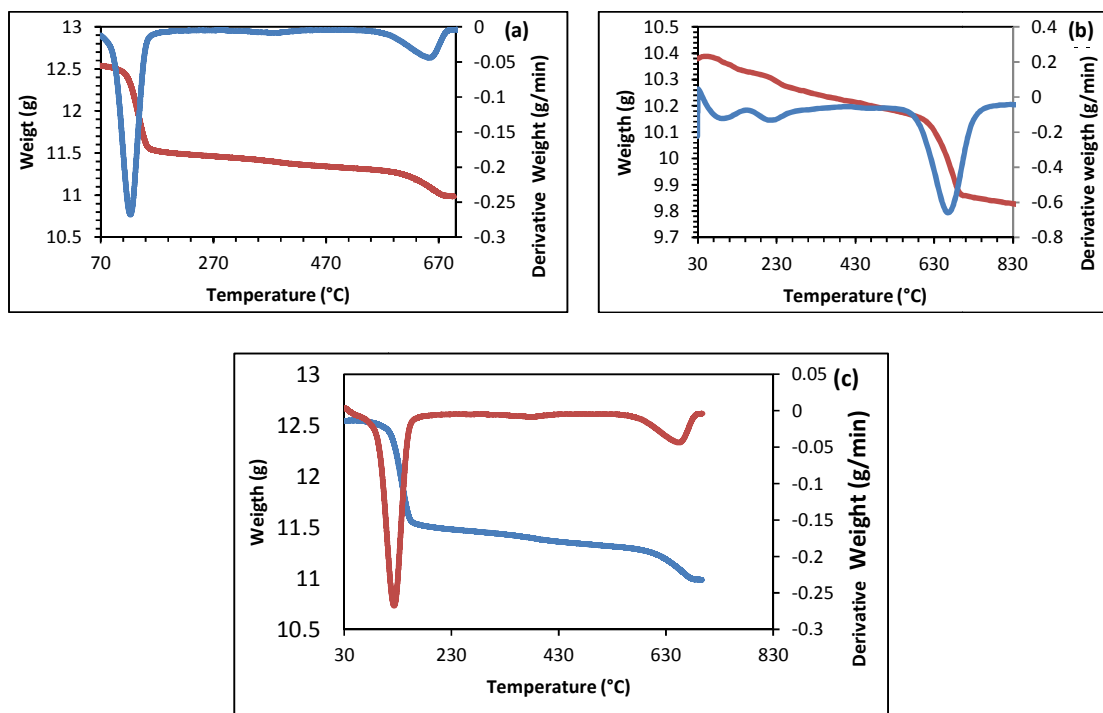


Fig. 6. TGA and DTG curves of raw PG (a), calcined PG at 800°C (b) and calcined PG at 200°C (c)

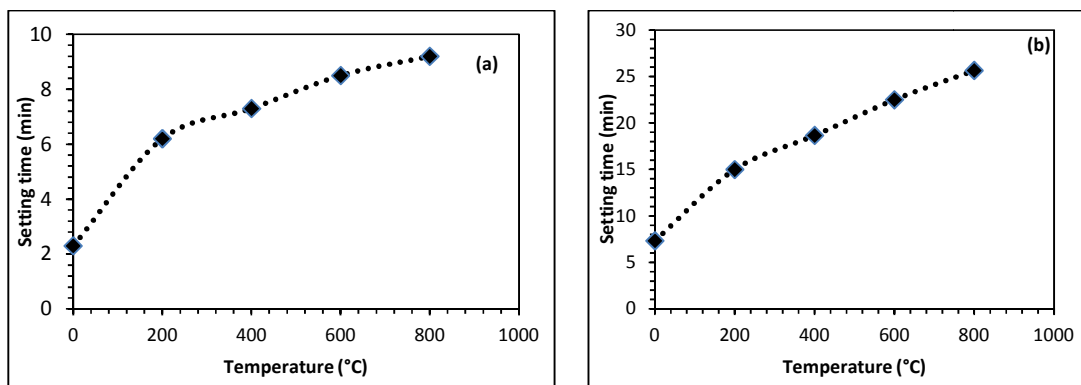


Fig. 7. Setting time as a function of temperature (initial setting (a), end of setting (b))

## 5. CONCLUSION

- The high strength anhydrite plaster can be produced by heating the waste phosphogypsum at 200°C.
- The calcined PG is thermally most stable than raw PG.
- The use of PG in plaster industry does not require grinding, as is the case for natural

gypsum, but against, it is necessary to remove the soluble impurities therein (fluorine, organic material ...). Indeed, a small amount of these impurities affects the setting time and mechanical strength.

- The phosphogypsum was calcined at 800°C to reach a good brightness value enough to integrate the powders produced for example in the paper-making.



## ACKNOWLEDGEMENTS

The authors would like to express their sincere thanks to Professor Mohamed Naceur Belgacem, Director of PAGORA, and all researchers of LGP2 for here valuable advice and assistance.

## COMPETING INTERESTS

Authors have declared that no competing interests exist.

## REFERENCES

1. Hammas K, Horchani-Naifer FM. Solubility study and valorization of phosphogypsum salt solution. *International Journal of Mineral Processing*. 2013;123:87–93.
2. Lina Nafeh K, Talal D, Amin S, Bruno L, Naim O. Mobility of selected trace elements in Mediterranean red soil amended with phosphogypsum: Experimental study. *International Journal of Environmental Monitoring and Assessment*. 2012;184:4397–4412.
3. Xiaohong R, Baoguo M, Jian H, Yun H. Phosphogypsum transition to  $\alpha$ -calcium sulfate hemihydrate in the presence of omongwaite in NaCl solutions under atmospheric pressure. *Journal of the American Ceramic Society*. 2012;95:3478–3482.
4. Li J, Yu S, Ma L. Feasibility analysis for decomposition of phosphogypsum in cement precalciner. *Environmental Progress & Sustainable Energy*. 2011;30:44–49.
5. Antanas K, Maryte B. Accumulation of alkalis in the recycling filtrate of the phosphogypsum pulps *Ceramics – Silikáty*. 2011;55(4):390–393.
6. Basak M, Nurdan Gamze T, Okan O. Investigation of the Possibility of Copper Removal from Industrial Leachate by Raw and Calcined Phosphogypsum: D-optimal and Taguchi designs. *Clean – Soil, Air, Water*. 2012;40(8):850–855.
7. El-Didamony H, Ali MM, Awwad NS, Fawzy MM, Attallah MF. Treatment of phosphogypsum waste using suitable organic extractants. *Journal of Radioanalytical and Nuclear Chemistry*. 2012;291: 907–914.
8. Ines H, Karima HN, Mokhtar F. Solubility study and valorization of phosphogypsum salt solution. *International Journal of Mineral Processing*. 2013;123:87–93.
9. Shweikani R, Kousa M, Mizban F. The use of phosphogypsum in Syrian cement industry: Radiation dose to public. *Annals of Nuclear Energy*. 2013;54:197–201.
10. Sorina Z, Iuliana L, Brice Ulrich S F, Traian V, Gabriel L. Cluster analysis based of geochemical properties of phosphogypsum dump located near Bacau City in Romania. *APCBEE Procedia*. 2013;5:317–322.
11. El Samad O, Aoun M, Nsouli B, Khalaf G, Hamze M. Investigation of the radiological impact on the coastal environment surrounding a fertilizer plant. *Journal of Environmental Radioactivity*. 2014;133:69–74.
12. Miloš BR, Dragan VT, Phosphogypsum surface characterisation using scanning electron microscopy. *BIBLID*. 2003;34:61–70.
13. Manjit S, Role of phosphogypsum impurities on strength and microstructure of selenite plaster. *Construction and Building Materials*. 2005;19:480–486.
14. Semra C, Osman NE. Use of fly ash, phosphogypsum and red mud as a liner material for the disposal of hazardous zinc leach residue waste. *Journal of Hazardous Materials*. 2010;173:468–473.
15. Kurandt HF. Emploi de gypse de l'acide phosphorique dans l'industrie du bâtiment; *Congrès technique de l'IFA*; 10-13 Septembre; 1968.
16. El-Didamony H, Gado HS, Awwad NS, Fawzy MM, Attallah MF. Treatment of phosphogypsum waste produced from phosphate ore processing. *Journal of Hazardous Materials*. 2013;245:596–602.
17. Tranchida G, Oliveri E, Angelone M, Bellanca A, Censi P, D'Elia M, Neri R, Placenti F, Sprovieri M, Mazzola S. Distribution of rare earth elements in marine sediments from the Strait of Sicily (western Mediterranean Sea): Evidence of phosphogypsum waste contamination. *Marine Pollution Bulletin*. 2011;62:182–191.
18. Xiushan Y, Zhiye Z, Xinlong W, Lin Y, Benhe Z, Jingfeng L. Thermodynamic study of phosphogypsum decomposition by sulfur. *The Journal of Chemical Thermodynamics*. 2013;57:39–45.
19. Lin Y, Yun Y, Zhihua H. Utilization of phosphogypsum for the preparation of non-autoclaved aerated concrete.

- Construction and Building Materials. 2013; 44:600-606.
20. Jun Z, Hui G, Zhu S, Yanxin W, Chunjie Y, Utilization of waste phosphogypsum to prepare non-fired bricks by a novel Hydration–Recrystallization process. Construction and Building Materials. 2012;34:114–119.
21. Antanas K, Maryte B. Accumulation of alkalis in the recycling filtrate of the phosphogypsum pulps Ceramics. Silikáty. 2011;55(4):390-393.

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