ELSEVIER

Thermochimica Acta 302 (1997) 69–75

thermochimica acta

Thermal behaviour of Moroccan phosphogypsum

Saloua Sebbahi[a], Mohamed Lemine Ould Chameikh[a], Fatima Sahban[c], Jilali Aride[a,*], Larbi Benarafa[b], Larbi Belkbir[c]

[a] *Laboratoire de physico-chimie des matériaux, Laboratoire associé à l' AUPELF-UREF (LAF,502) ENS Takaddoum, B.P. 5118, Rabat, Maroc*
[b] *Laboratoire de spectroscopie infrarouge, Département de chimie, Faculté des Sciences, Rabat, Maroc*
[c] *Laboratoire de Réactivité des Systèmes Solide/Gas, Département de chimie, Faculté des Sciences, Rabat, Maroc*

Received 19 July 1996; received in revised form 9 January 1997; accepted 4 April 1997

Abstract

In this article, we have examined the thermal behaviour of Moroccan phosphogypsum in the absence of additives. We have used very diversified techniques: thermogravimetric analysis (TGA), differential thermal analysis (DTA), infrared spectroscopy and X-ray diffraction. DTA has allowed us to point out several transformations. Moreover, TGA has shown that the dehydration can occur in one step, which confirms that the sample is not bihydrated. The infrared spectroscopy has allowed us to characterize the water molecules of crystallization and the sulphate grouping of phosphogypsum. © 1997 Elsevier Science B.V.

Keywords: Anhydrite; DTA; Gypsum; Phosphogypsum; TGA; Thermal decomposition

1. Introduction

With three quarters of the world reserves of phosphates, Morocco is the third producer and the first exporter of this substance. Phosphates are important because they are used in producing phosphoric acid, which is an important derivative for the elaboration of most of the phosphorus components (fertilizers, detergents, food,...). There are several processes for the fabrication of this acid. The sulphuric process is most commonly adopted in industry because the reaction products can be easily separated through filtering. This process is the only one used in Moroccan industry. Despite its relatively easy usage, it entails a certain amount of economic problems given the fact that Morocco does not have the necessary conventional sulphur resources for the production of sulphuric acid. Hence, we have to import 100% of our sulphur needs. As for the diversification of sulphur resources, Morocco can simultaneously foreshadow several solutions such as the salvage of sulphur from gypsum and phosphogypsum [1–3]. This operation aims at making the cycle of phosphoric acid fabrication a closed one: recycling of sulphur. Even if the solution to the problem of gypsum seems to be costly as far as energy is concerned, Morocco finds it necessary to intensify research in this domain.

The purpose of this paper is to contribute to the study of possible production of sulphuric acid from

*Corresponding author. Tel.: 00 212 775 0025; fax: 00 212 775 0047.

0040-6031/97/$17.00 © 1997 Elsevier Science B.V. All rights reserved
PII S0040-6031(97)00159-7

Table 1
Chemical analysis of phosphogypsum

Compouds	H_2O	SO_3	CaO	SiO_2	CO_2	Fe_2O_3	Al_2O_3	P_2O_5	F	MgO
% in mass	3.5	42.9	30.5	9.5	4.5	0.9	2.8	0.5	0.15	0.3

Moroccan phosphogypsum prior to the study with additives. Besides, using phosphogypsum has become a crucial operation because it causes a very serious problem when eliminated, especially when we consider its over production and the damage it causes to the environment [4].

2. Experimental

The phosphogypsum used comes from JorfLasfar factories situated 30 km from Eljadida. Its chemical analysis is presented in Table 1. Its granulometry lies in the (0.063–0.250) mm range. We have chosen the JorfLasfar phosphogypsum because it has two advantages: first, it has never been studied before; and second, its percentages are < 1 for P_2O_5 and < 0.25 for phosphor (fluor).

The study through TGA was carried out in air under non-isothermal system, with a heating rate of 350°C/h. The apparatus used is SETARAM type. This thermobalance is constituted of a measure box, a heating furnace and a recording device. The furnace used is equipped with a programmer which permits variation of temperatures up to a maximum of 1000°C.

As for the study through the coupled TGA–DTA, we have used the thermobalance Stanton Redcroft STA, 781 model which can reach 1500°C. This thermobalance is constituted of: a balance, furnace and a registering device. The registration gives the simultaneous tracing of thermogravimetric signal (TGA), the differential thermal analysis (DTA) and the temperature provided by the thermocouple placed close to the sample. DTA permits the determination of the temperature and the nature of the different transformations (dehydration and allotropic transformation) that the sample presents in the course of its treatment. In the course of our test, we have used argon as a vector gas. The heating rate was of 360°C/h.

3. Results and discussion

3.1. Thermogravimetric analysis:

The obtained TG curve is represented in Fig. 1. We notice two fields of loss. The first one is between ambient temperature and 280°C. It represents 3.42% of the initial mass (387.7 mg). This loss corresponds to the elimination of the hydration water. The heating up of phosphogypsum at atmospheric pressure up to 280°C leads to an anhydrous form: the anhydrite III. This anhydrite is interpreted on the gravimetric curve by a change in the slope and on the derived curve by an accentuated peak. After these losses of water, the curve increases slightly according to temperature. This second loss is probably due to the decomposition of impurities contained in the phosphogypsum. Therefore, we notice a total loss at 980°C of 4.71% of the initial mass.

Thus, Baraka [5] having obtained the TGA on the natural gypsum of Safi between 20–1400°C, obtains a curve on which we can identify our first phase, corresponding to the total loss of water of crystal-

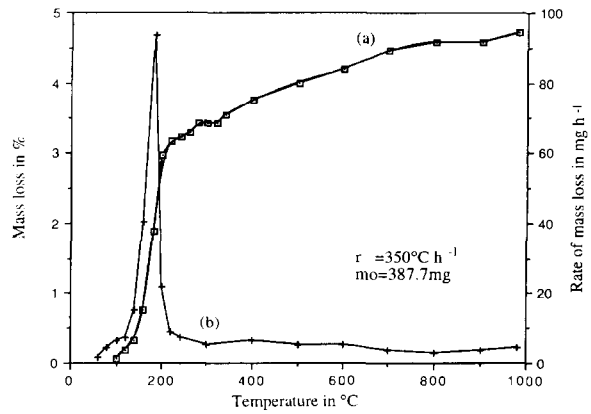

Fig. 1. TGA of JorfLasfar phosphogypsum: (a) – TG curve; and (b) – derived curve.

lization and presenting a mass loss of 20%. The second phase, starting at 1200° C and becoming more and more important as the temperature rises, corresponds to the beginning of the decomposition of $CaSO_4$ to CaO and SO_2 and presents a mass loss of 9%.

Ould Chameikh [6], studying the dehydration of Mauritanian gypsum, obtains a curve which reveals a total decrease of the sample mass at 20% showing the total elimination of the water of crystallization, that is to say the two water molecules of $CaSO_4 \cdot 2H_2O$.

However, the mass loss obtained by these authors in the first phase, is higher than ours. This difference could be due to the fact that our sample, having been previously dried up, could no longer be bihydrated. In fact, the water of crystallization contained in a bihydrated gypsum $CaSO_4 \cdot 2H_2O$, corresponds to 20.9% in mass.

The TG curves obtained by thermogravimetric analysis are influenced by different factors relative to the sample and experimental conditions. Thus, we have tested the influence of the environmental nature, of the sample form and of the heating rate, on the kinetics of the phosphogypsum thermal treatment. For future tests, we will keep the same initial mass (m_0 = 387.7 mg) in order to make our comparisons in the right way.

In order to examine the environmental effect, we have carried out the same study as before but in an open system, then under nitrogen atmosphere (Fig. 2). In the open system, we have noticed that the anhydrite

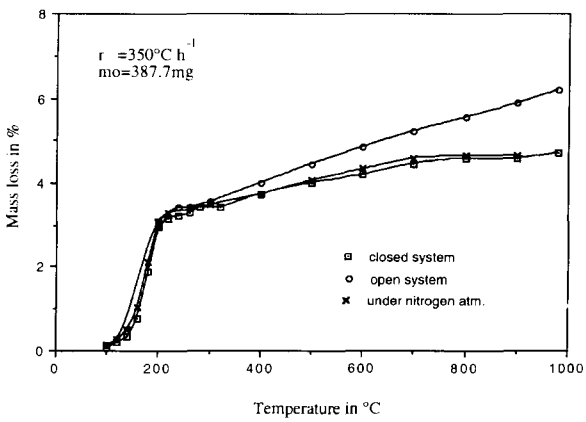

Fig. 2. Phosphogypsum TGA with variation in environment.

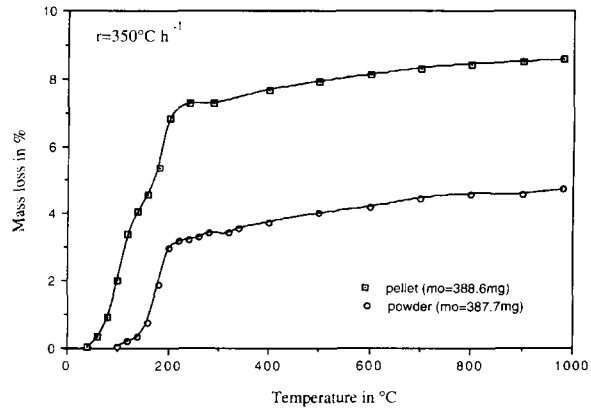

Fig. 3. Phosphogypsum TG for the two different forms.

has been obtained with the same yield as in the case of closed system, but at a temperature of 240°C. However, at higher temperatures, the mass loss was more accentuated for the open system, and at 980°C, the difference of mass was 1.5%. Regarding the thermal treatment under nitrogen atmosphere, the curve keeps the same state as it does in the closed system. We can conclude then that the gas has no effect on this thermal treatment.

To determine the influence of the sample form on the phosphogypsum thermal behaviour, we have used two samples: one in the powdery form, the other as pellets. The latter has been realized in the following conditions: a mass of 388.6 mg, with a granulometry similar to that of the first sample, has been placed in the pellet machine and then subjected to a mechanical pressure of 3 ton. The TG curves relative to both samples are represented in Fig. 3. The examination of these curves shows that, at 280°C, the loss of water is 7.27% for the sample in pellets, whereas it is 3.42% for the powdery sample. This difference is explained by the absorption water of humidity during the preparation of the pellets. The second loss is independent of sample form.

In order to obtain additional information concerning possible modifications, which could interfere in the course of physico-chemical transformations, we found it very interesting to study the effect of the heating rate while keeping the other parameters stable. To this effect, we have achieved a series of experiments at three different heating rates (250°C/h, 350°C/h and 500°C/h). The results of the study are

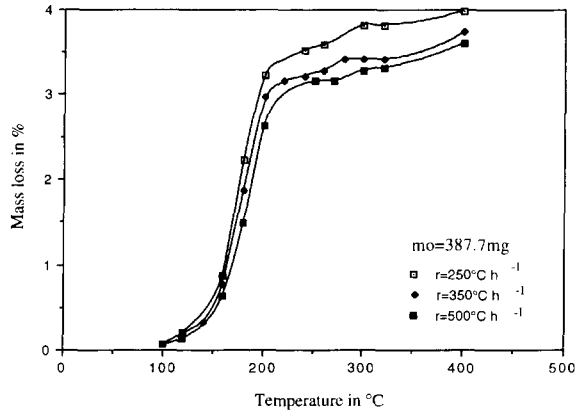

Fig. 4. Variation of phosphogypsum mass loss as a function of temperature, at different heating rates.

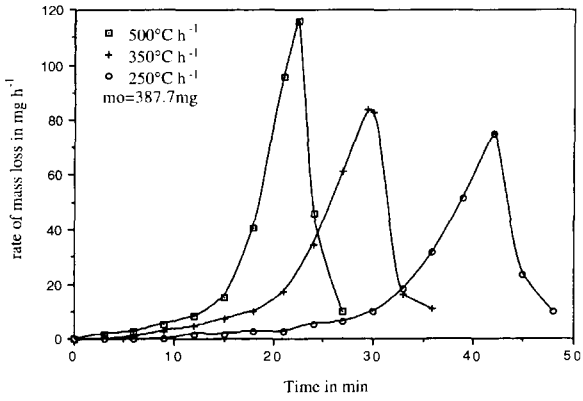

Fig. 5. Mass-loss rate variation as a function of time for different heating rates.

represented in Fig. 4, wherein we notice that the general state of dehydration does not change, although at a given temperature, the mass loss is inversely proportional to the heating rate. On the other hand, the increase in the heating rate displaces the reaction towards high temperature. The representation of the derived mass in terms of time (Fig. 5) allows us to determine, for each heating rate, the maximum dehydration rate and its corresponding timing. See Table 2 for a summary. We notice that the rise in the heating rate entails the decrease of time at the end of which the maximum rate is reached. These results correspond to the Arrhenius law.

Table 2
Values of maximal rates and corresponding temperatures and times

Heating rate/°C/h	250	350	500
r_{max}/mg/h	74.7	83.7	116.1
Time/min	42	29′24″	22′30″
$T_{(r\ max)}$/°C	170	175	190

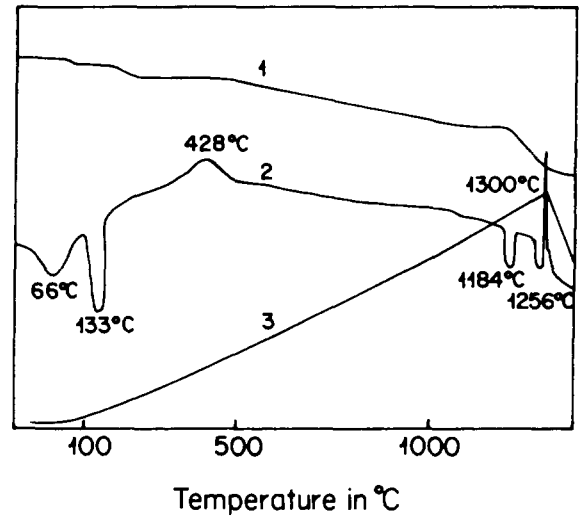

Fig. 6. Thermal analysis of phosphogypsum alone: Curve 1 – TGA; Curve 2 – DTA; and Curve 3 – Temperature (T) in °C.

3.2. Study through coupled TGA–DTA

The thermogravimetric and the differential thermal curves are represented in Fig. 6. The DTA curve shows several peaks:

The first two peaks are endothermic and are to be found at 66 and 133°C. They are attributed to the phosphogypsum dehydration to anhydrite III. In fact, the transformation of gypsum into semi-hydrate, then into anhydrite III, is completed after the following two endothermic reactions [7]:

$$CaSO_4 \cdot \frac{1}{2} H_2O \Leftrightarrow CaSO_4 \frac{1}{2} H_2O + \frac{3}{2} H_2O \quad (66°C)$$

$$CaSO_4 \frac{1}{2} H_2O \Leftrightarrow CaSO_4 III + \frac{1}{2} H_2O \quad (133°C)$$

These peaks can be interpreted as modifications of the crystalline structure. Moreover, these modifications are characterized by mass losses illustrated by

the TGA curve. In general, all of the studies of the $CaSO_4 \cdot 2H_2O$ dehydration through DTA, show the presence of the two endothermic peaks. However, the corresponding temperatures have been quite varied [8,9]. Some authors, such as Grin and Rowland [10] have obtained the double peak at 130 and 180°C, respectively, while for West and Suiton [11], the two endothermic peaks appear, respectively, at 180 and 215°C. These results seem to be emphasized by Holdrich and Walker [12] for the natural gypsum as well as for the synthetic one. Other authors [13,14] point out the existence of the two peaks within 100 and 250°C. Likewise, Ould Chameikh [6] obtained double peaks at 149 and 169°C with the Mauritanian gypsum. All these authors, having worked in air and under atmospheric pressure, have obtained these peaks at temperatures which are different from ours. This difference might be explained by the influence of nature and the surrounding area, as well as by the different origins of the samples. However, in our case, the experiment was carried out in the presence of argon. The next peak is exothermic and observed at 428°C. It is the result of the transition of soluble anhydrite III to insoluble anhydrite II[7]:

$$CaSO_4III \rightarrow CaSO_4II \quad 428°C$$

On the TG curve, no loss has been noticed at this temperature.

Another endothermic peak emerges by 1184°C and corresponds to the transition of anhydrite II to anhydrite I. This was seen just before the beginning of phosphogypsum decomposition.
Around 1250°C, the last peak is endothermic and carries a mass loss corresponding to the decomposition of the first molecules from $CaSO_4$ to CaO and SO_2 according to the following reaction:

$$CaSO_4 \rightarrow CaO + SO_2 + \tfrac{1}{2}O_2$$

Baraka's results [5] show some similarity to ours; he has been able to emphasize the last three peaks just as we have identified them on our curve, but the temperatures which correspond to these peaks are a little different from ours.

On TGA curve, we notice a mass loss which goes through several stages:

The first loss starts at 66°C and is due to the elimination of water of humidity.
The second loss starts at 133°C and ends at ca. 400°C. It corresponds to the elimination of the entire water of crystallization.
The third loss which starts at 500°C and ends at 1100°C corresponds to the loss of CO_2.
The fourth loss starts slowly at 1184°C and increases beyond 1300°C, which shows the decomposition of $CaSO_4$ into CaO, SO_2 and O_2.

The total loss obtained at 1300°C is of 25.4% of the initial mass. We have presented on Table 3, the temperature values and the nature of each studied phosphogypsum transformation.

The difference of mass loss obtained through TGA and coupled TGA–DTA is due to the nature of environment area and to the maximum temperature achieved.

3.3. Radiocrystallographic analysis:

The two diffractograms relative to phosphogypsum before, and after thermal treatment are represented in Fig. 7. The reticular distances calculated while examining the spectrums are to be found in Table 4. The analysis of both powder diagrams obtained, show a strong resemblance between the first and the $CaSO_4 \cdot 2H_2O$ one crystallizes in the monoclinic system with spacing group $C_{2/c}$ [15], whereas the second one is rather similar to the anhydrite one which crystallizes in the orthorhombic system of the spacing

Table 3
Temperature and nature of each thermal transformation of studied phosphogypsum

Peak	Temperature/°C	Reaction	Nature
1	66	$CaSO_4 \cdot 2H_2O \Leftrightarrow CaSO_4 \cdot 1/2H_2O + 3/2H_2O$	Endothermic
2	133	$CaSO_4 \cdot 1/2H_2O \Leftrightarrow CaSO_4III + 1/2H_2O$	Endothermic
3	428	$CaSO_4III \rightarrow CaSO_4II$	Exothermic
4	1184	$CaSO_4II \rightarrow CaSO_4I$	Endothermic

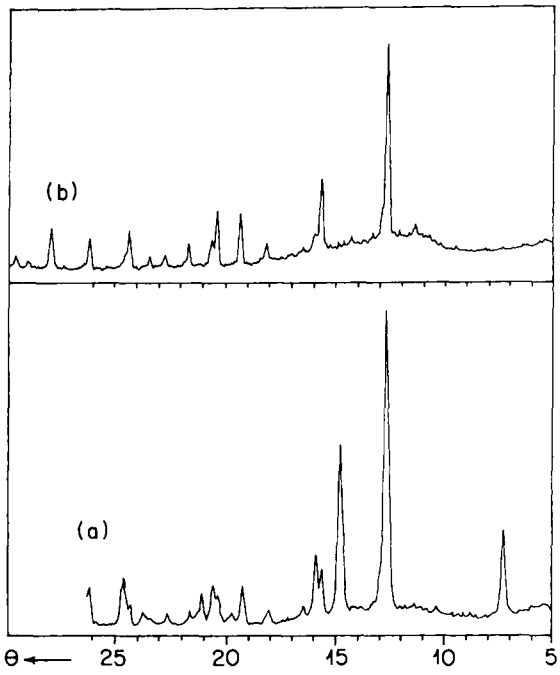

Fig. 7. Powder diagram of samples: (a) – raw phosphogypsum; and (b) – phosphogypsum having undergone a TGA (T_{max} = 980°C).

Table 4
Examination of phosphogypsum X-ray diffraction spectra before, and after thermal treatment

Phosphogypsum before thermal treatment		Phosphogypsum after thermal treatment	
I/I_0	d/Å	I/I_0	d/Å
31.76	6.021	—	—
—	—	23.66	3.897
100	3.504	100	3.517
—	—	20.97	3.348
—	—	19.35	3.129
58.43	3.0054	—	—
19.61	2.855	43.01	2.855
24.90	2.794	20.97	2.811
9.02	2.720	14.52	2.720
7.84	2.479	17.2	2.479
14.90	2.336	29.57	2.336
7.06	2.274	—	—
12.55	2.210	30.64	2.215
15.29	2.189	17.74	2.189
12.16	2.135	—	—
7.06	2.088	16.13	2.088
6.67	1.996	11.83	1.996
—	—	11.29	1.939
7.45	1.909	—	—
9.80	1.868	21.5	1.868
18.04	1.847	—	—
14.51	1.748	18.28	1.748

group C_{mcm} [16]. This stresses the elimination of water of crystallization during the thermal treatment.

3.4. Infrared spectroscopy study

We have recorded the phosphogypsum infrared spectra before, and after thermal treatment (in the same conditions) using the pellet technique in KBr; the obtained spectra are represented in Fig. 8. We have interpreted them by referring to the results available in the literature [17,18]. Spectrum (a) presents three absorption areas of different intensities: area I – (4000–1600) cm^{-1}; area II – (1400–900) cm^{-1}; and area III – (800–400) cm^{-1}.

The observed bands in area I of spectrum (a) attest the presence of water of crystallization. The absorption taken from area II corresponds to vibration of valence O–S. Area III corresponds to defect vibrations of the angle OSO. The disappearance of the bands relative to water in spectrum (b) asserts the elimination of water of crystallization. The comparison of the two spectra in areas II and III attests the difference of structure indicated during the radiocrystallographic study. In Table 5, we present the frequencies in cm^{-1} and the attributions relative to raw phosphogypsum (spectrum a) and to phosphogypsum having undergone TGA (spectrum b).

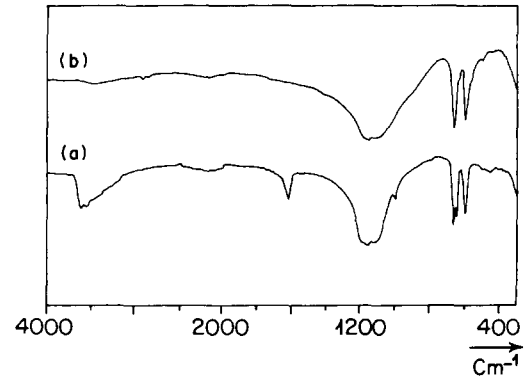

Fig. 8. Infrared spectrum of: (a) – raw phosphogypsum, and (b) – phosphogypsum having undergone a TGA (T_{max} = 980°C)

Table 5
Attribution of phosphogypsum infrared spectra (a) – before, and (b) – after thermal treatment

$CaSO_4 \cdot 2H_2O$ (a)		$CaSO_4$ (b)		Attribution
1170	(S) [a]	1190	(S) [a]	ν_3(S–O)
1150	(S) [a]	1150	(S) [a]	—
—	—	—	—	—
1115	(S) [a]	1100	(S) [a]	—
—	—	—	—	ν_1(S–O)
1010	(vf) [b]	—	—	—
—	—	—	—	ν_4(O–S–O)
670	(S) [a]	675	(S) [a]	—
655	(S) [a]	610	(S) [a]	—
610	(S) [a]	—	—	—
—	—	—	—	ν_2(O–S–O)
465	(vf) [b]	515	(vf) [b]	—

[a] S: strong.
[b] Vf: very feeble.

4. Conclusion

The main point of this paper has been to study the thermal behaviour of the JorfLasfar phosphogypsum without additives.

The differential thermal analysis has allowed us to clarify several transformations. The first two (66 and 133°C) are endothermic and correspond to the two stages of the phosphogypsum dehydration. The third transformation (428°C) is exothermic and shows the move from anhydrite III (hexagonal) to anhydrite II (orthorhombic). The fourth modification (1184°C) is endothermic and displays a transformation from anhydrite II to anhydrite I. The last one corresponds to the phosphogypsum decomposition.

Besides, thermogravimetric analysis has revealed that powdery phosphogypsum dehydration in a linear rise of temperature is located in the following temperature interval: ambient–280°C, and occurs in only one stage. Otherwise, this dehydration is influenced by temperature programming: the reaction moves towards high temperatures from (170–190)°C and its rate also rises when we increase the heating rate from (350–500)°C/h. The mass loss (3.42 %) has allowed us to prove that our sample is not bihydrated.

Finally, the infrared spectroscopy made it possible for us to characterize the water of crystallization as well as the sulphate grouping of the phosphogypsum dealt with.

References

[1] M. Ragin, R. Brooks, Donalds, Bur. Mines Rep. Invest. RI (1990) 9323.
[2] El.A. Trikk, L. Turn and R. Kÿsik, Estinsvtead, akademie. toim, Keem., 38(3) (1989) 150–158.
[3] D.A. Rice and May A. Swanton, Trans. Soc. Min. Eng., 284 (1988) 1848–1853.
[4] M. Wimmer, Chimie Linz AG. P.O.B. 296, A-4021 Linz Austria (1980).
[5] A. El Hadj Baraka, D.E.S. de troisième cycle, Rabat (1988).
[6] M. Ould Chameikh, Thèse de troisième cycle, E.N.S. de Takaddoum Rabat (1990).
[7] Bulletin de la sociètè chimique de France, No.12, (1967).
[8] R. Piece-Helv, Chem. Acta, 34(5) (1956) 1427.
[9] P. Barriac, Thèse de Doctorat d'ètat, Lyon (1968).
[10] R.E. Grin and R.A. Rowland, J. Amer, Soc., 27(65) (1944).
[11] R.R.West and W.J. Suiton, J. Amer Ceram. Soc., 27(221) (1954).
[12] D.A. Holdrige and E.C. Walker, Trans. Brit. Ceram. Soc., 66(10) (1967) 485.
[13] T. Wiedmann, Zement, Kalk, gyps otsch, 17 (1960) 293–302.
[14] M. Sekiya and K. Setoyoma, Koyokaga KU, Zasski, 69(9) (1966) 1933–1935.
[15] Joint Committee on Powder Diffraction Standards, Technisch Physische Dienst, Delft-Holland, 1971.
[16] Swanson and Al., NBS Circular 539 IV (1953) 65–67.
[17] H. Takahashi and Ikumi Maehara, Spectrochimica Acta., 39A(5) (1983) 449–455.
[18] M. Aslam and A.K. Minocha, Research and Industry, 37 (1992) 121–123.