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SOME ASPECTS OF THE HYDROTHERMAL CALCINATION OF GYPSUM

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ABSTRACT

Lump-size and powdered gypsum samples were calcined at 135, 150 and 180°C The products were thoroughly investigated by differential thermal analysis and X-ray diffraction, and their chemically-combined water was determined thermogravimetrically. Results indicated that almost all the treated samples contained gypsum, hemihydrate and anhydrite in varying proportions Gypsum and anhydrite increased, and the hemihydrate decreased as the heating temperature was increased and the grain size decreased. Such a variation in the phase constitution of the treated samples is discussed

The relative intensity of the main gypsum X-ray diffraction characteristic lines changes upon treatment. In the atmospheric calcination the relative intensities of the lines at 3 059, 2 867, 2 679, 2 59, 2 495, 2 45 and 2.40 Å show a pronounced decrease Autoclaving, on the other hand, causes a detected decrease in the relative intensity of the line at 7.56 Å and an increase in the 4.27, 3 059, 2 59, 2 495 and 2.45 Å lines These findings postulate that X-ray diffraction data could hardly be used for the quantitative assessment of the gypsum phase in the dehydration products of any calcined material

INTRODUCTION

The so-called plaster of Paris is conventionally produced in two forms recognized as the β- and α-hemihydrates. The β-form can be prepared by atmospheric calcination of the fine-grained gypsum in kettles or rotary kilns. The α-modification, however, can be manufactured either by autoclaving gypsum lumps in saturated steam or treating the finally pulverized gypsum in saturated salt solutions. Combe and Smith [1] mentioned that α-hemihydrate could also be produced by autoclaving powdered gypsum in the presence of a mineralizer and they used sodium succinate in this respect. Various investigators studied the effect of variation in grain size of the original gypsum raw material on the phase constitution of the calcination products [1–4]. However, no one tried to follow the characteristic changes taking place in the original gypsum, prior to any phase change, upon scanning by X-ray diffraction.

The present work aims at a comparative study of the hydrothermal dehydration of the lump-size and fine-grained gypsum samples treated under atmospheric pressure and autoclaving. The calcined materials were assessed for their phase constitution by differential thermal analysis. Actual amounts of the characteristic phases were quantitatively determined using differential thermal endotherms, chemically combined water, and previously published formula [5]. The treated samples were subjected to X-ray diffraction and the most distinguished features were followed.

EXPERIMENTAL

Egyptian gypsum raw material, from the Sinai locality [6], containing 98% $CaSO_4 \cdot 2H_2O$, was used in this study. Table 1 summarizes the experimental conditions used in treating the raw material either in the atmospheric calcination or autoclaving. All the previously published precautions were practised in both methods [7]. Accurately weighed samples were used in the X-ray diffraction (1 g) and differential thermal analysis (0.7 g) for the sake of comparison and the correlation of results.

Quantitative determination of phases

Gypsum was determined in the treated samples using DTA curves following the previously mentioned method of Holdridge [8]. The peak area arising from extrapolation of the first endotherm at 150°C was measured in the tested samples and correlated with that of the starting material, the sample weight being the same (0.70 g), and all the experimental conditions remaining constant. Hemihydrate, on the other hand, was calculated using the empirical formula

$$0.2093X + 0.0621\,Y = W_n$$

where X = gypsum %, as determined in the fore-mentioned step; W_n = water of crystallization as determined in accordance with $C_{471} -_{76}$ of the ASTM; and Y = hemihydrate %. Accordingly, anhydrite $= 100 - (X + Y)$.

TABLE 1

Conditions used in the atmospheric calcination and autoclaving

No	Grain Size [a]	Treatment process	Temp (°C)	Time (h)	Symbol
1	Lump	Autoclaving	135	8	LA
2	Lump	Dry calcination	135	8	LD
3	Powder	Dry calcination	135	8	PD
4	Lump	Autoclaving	150	4	LA
5	Lump	Dry calcination	150	4	LD
6	Powder	Dry calcination	150	4	PD
7	Lump	Autoclaving	180	2	LA
8	Lump	Dry calcination	180	2	LD
9	Powder	Dry calcination	180	2	PD

[a] Lump = 20 mm, powder = <0.086 mm

RESULTS AND DISCUSSION

DTA curves of the treated samples are shown in Fig. 1 while their X-ray diffraction patterns are illustrated in Figs. 2–4. Almost all the investigated samples show two endothermic peaks occurring successively at about 150 and 190°C, followed by a small exotherm. The relative amounts of these two endotherms indicate the coexistence of gypsum and hemihydrate phases [2–4,7]. Their amounts varied, however, according to the conditions used; gypsum increased in the order PD > LA > LD with temperature increase. Hemihydrate, on the other hand, decreased as gypsum was increased. Careful investigation of these endothermic peaks suggests the presence of detectable amounts of anhydrite. X-Ray diffraction data confirmed these findings but unfortunately the great similarity in the *d* spacings of the hemihydrate and γ-anhydrite made the interpretation of the latter difficult. The calcination conditions used in the present work are, however, beyond that leading to the formation of β-anhydrite [2,9]; therefore its identification is unexpected.

It could be noted that in the differential thermograms of the treated samples the peak temperature of the exotherm varies; it occurred around 220°C in the autoclaved samples while the dry-calcined samples revealed 360°C. Such an exotherm, which characterizes the phase change of γ- to β-anhydrite takes place at a lower temperature in the autoclaved samples than the dry-calcined ones. This indicates that α-hemihydrate results from autoclaving while β-hemihydrate is the result of atmospheric calcination of gypsum. The present results are in agreement with the conclusions of various investigators [4,6,10].

The results of phase calculations are tabulated in Table 2 from which it is clear that the gypsum content ranges between 9.1 and 32.4%; it increased as the heating temperature was increased which confirms the previous results deduced in the differential thermal analysis and X-ray diffraction experiments. All the samples except No. 2 contain anhydrite, most probably the soluble γ-form. The content of

TABLE 2

Calculated phases in the treated samples

Sample		W_n (%)	Calculated phases (%)		
			G	H	A[a]
1 AL	135/8	7 12	10 2	80 3	9 5
2 DL	135/8	6 28		100 0	
3 DP	135/8	7.43	18 3	57 97	23 73
4 AL	150/4	7 02	9 1	82 37	8 53
5 DL	150/4	6 91	9 2	80 26	10 54
6 DP	150/4	7 59	20 4	53.47	26 13
7 AL	180/2	7 31	13 9	70 87	16.23
8 DL	180/2	7.15	12 3	73 68	24 02
9 DP	180/2	8 14	32 4	21 88	45 72

[a] G=Gypsum, H=hemihydrate, A=anhydrite

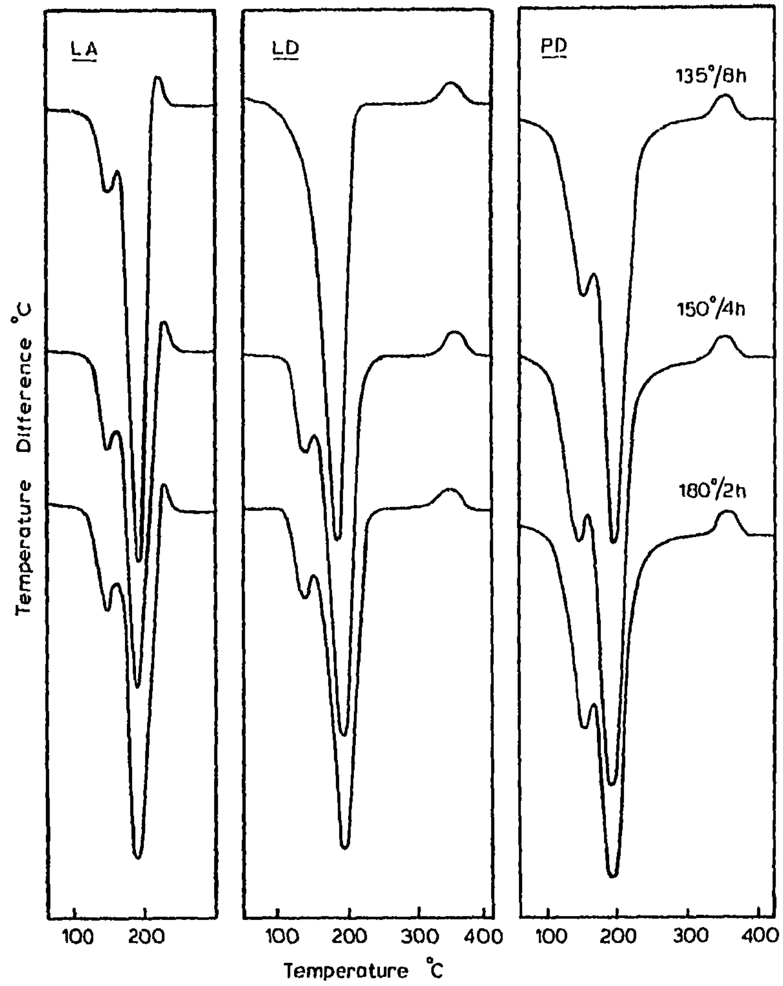

Fig 1. Differential thermograms of the treated gypsum samples

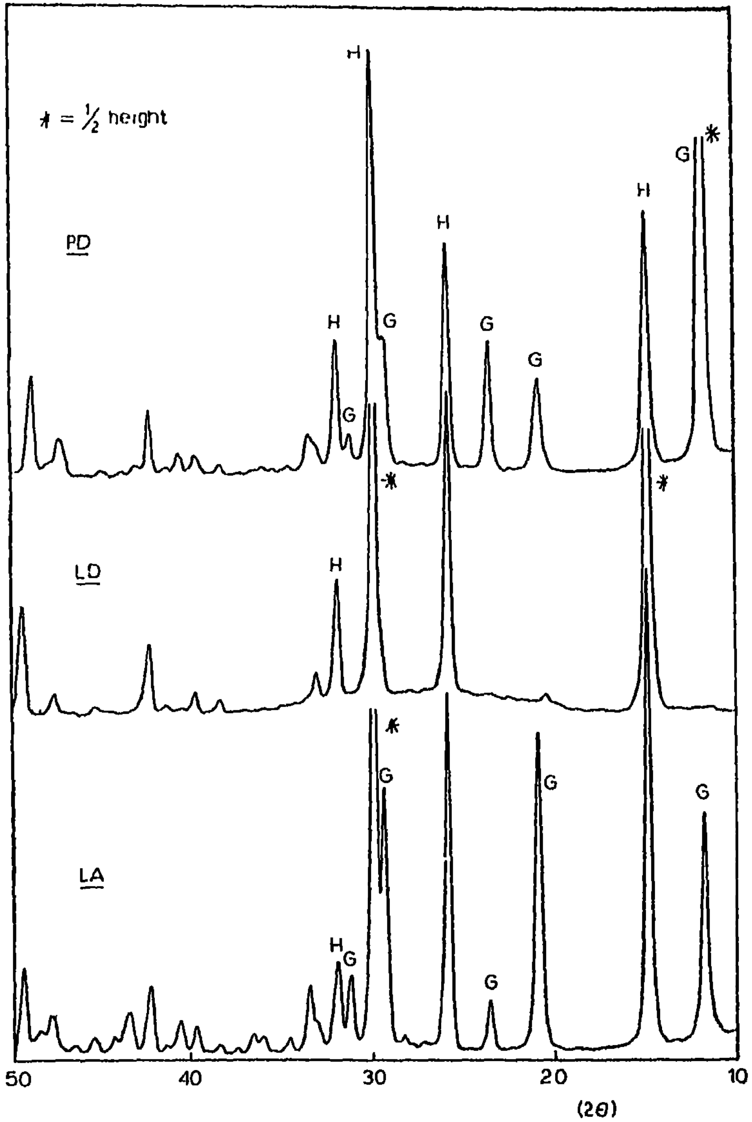

Fig 2 X-Ray diffraction patterns of the gypsum samples (135°C/8h)

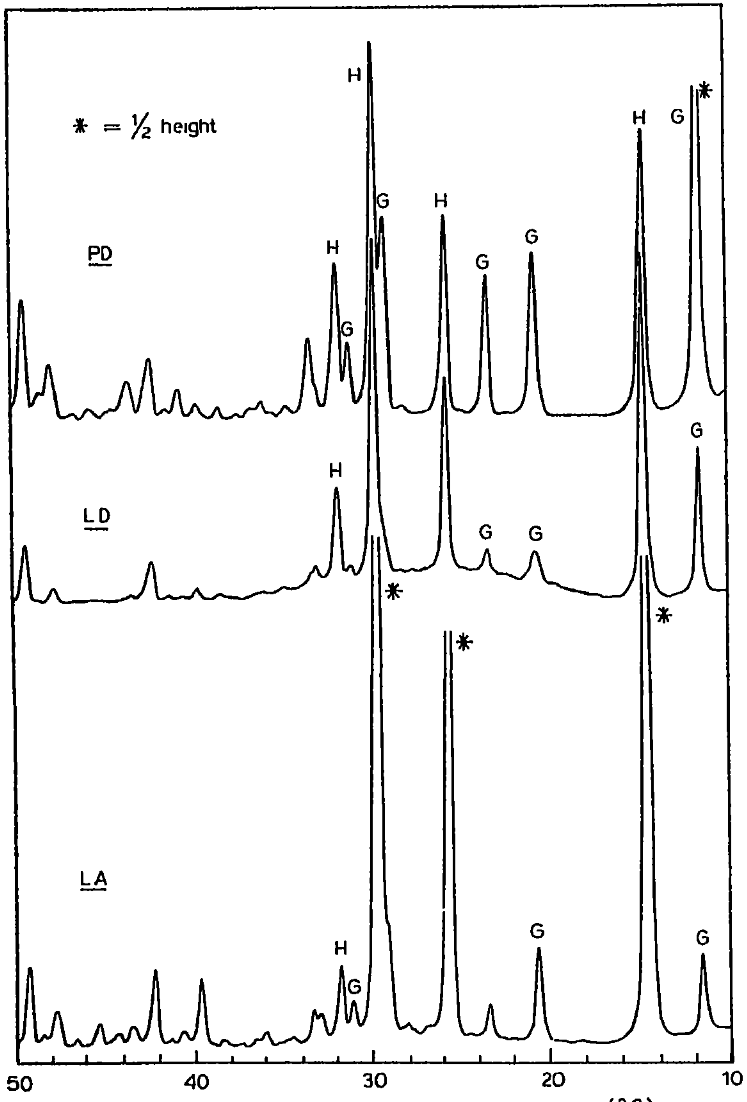

Fig. 3 X-Ray diffraction patterns of the gypsum samples (150°C/4 h)

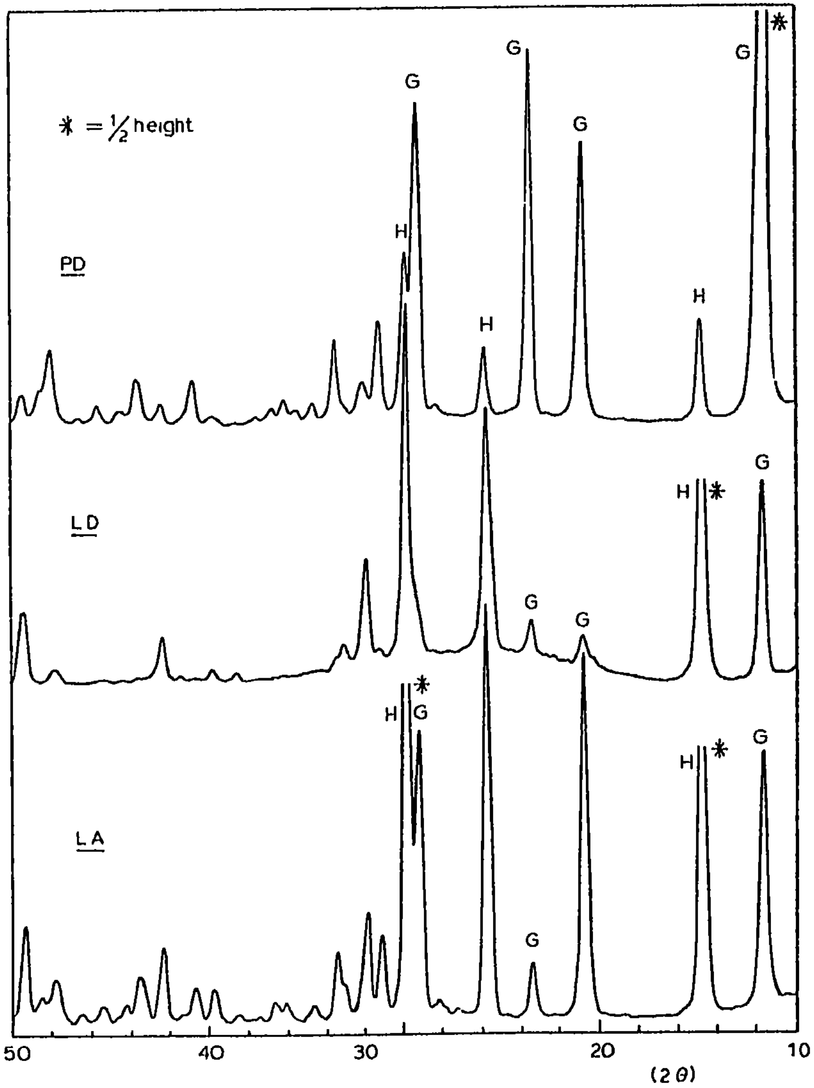

Fig 4 X-Ray diffraction patterns of the gypsum samples (180°C/2 h)

TABLE 3

Changes in relative intensity of the treated samples compared with those of the starting material and ASTM data

hkl	*d* (A)	ASTM	Raw	1	2	3	4	5	6	7	8	9
020	7 56	100	100	70	100	100	82	100	100	80	100	100
121	4 27	51	31	100	28	15	82	27	31	100	21	30
031 040	3 79	21	70	15	21	20	27	23	33	21	31	40
$1\bar{1}\bar{2}$	3 16	3	1	2	2	1	18	2	1	2	2	2
$14\bar{1}$	3 059	57	46	76	30	23	100	31	27	90	28	34
002	2 867	27	11	20	10	5	36	11	21	23	17	10
022 053	2 679	28	13	20	20	6	27	13	19	27	19	9
150 207	2 591	4	3	4	2	1	9	2	12	5	1	2
200	2 495	6	3	4	3	1	18	3	8	6	1	3
$22\bar{2}$	2 45	4	1	2	2	1	7	1	6	3	2	2
141	2 40	4	1	2	2	1	8	1	6	4	1	1

the latter increased as gypsum content increased and, accordingly, the hemihydrate decreased. The best hemihydrate formation was exhibited by sample 2.

The fluctuation in the phase constitution of the treated samples could be visualized in the light of the following. It was previously mentioned that autoclaving offers a good chance for the production of α-hemihydrate by the recrystallization process where the presence of undecomposed gypsum is at a minimum [10]. In the present work, the autoclaved samples, exhibit the minimum amounts of gypsum in comparison with the dry-calcined ones. The present result revealed, however, that the dry-calcined lumps contain smaller amounts of gypsum than the autoclaved lumps. This lower gypsum content of the samples treated under atmospheric pressure could be related to the lower degree of equilibrium in addition to the fact that atmospheric dehydration of gypsum is a continuous process; whenever the calcination temperature is above 90°C there are almost always three successive layers of gypsum, hemihydrate and anhydrite coexisting in each grain of the treated material [2]. Moreover, it was mentioned that the thickness of such layers varies according to the calcination temperature, rate of heating, grain size and the possibility of rehydration of the resultants [3]. The author believes that the difference in the thermal conductivity between the dehydrated products plays another role in this respect ($\lambda = 0.0031$ and 0.0007 for gypsum and hemihydrate, respectively). Thus, when the calcined products are taken from the oven they retain some residual heat energy due to the poor conductivity of the bodies and the poorer conductivity of the hemihydrate. Such a residual energy acts to accelerate the transformation process of the undecomposed gypsum to the hemihydrate. The liberated water (1.5 moles/mole gypsum) is used to rehydrate the available γ-anhydrite to the hemihydrate. The content of the latter increases with the simultaneous decrease of both gypsum and anhydrite. Fine-grained gypsum, on the other hand, reveals the mutual transformation of gypsum and anhydrite to the hemihydrate to a slight degree; a case which could be related to the smaller particle size and minute layer thickness of the three successive layers and, accordingly, the least amount of residual trapped heat energy. The gypsum content of the fine-grained samples is higher than that of the lump size. Moreover, the possibility of rehydration of the fine part is an additional parameter in increasing the gypsum in the treated fine samples, where some of the already formed fine hemihydrate passes into gypsum.

It should be noted that some changes take place in the original lattice of gypsum on calcination, prior to the transformation to the hemihydrate. It could be said that treatment of gypsum causes a lattice ordering in the original material; the monoclinic lattice of the naturally-occuring gypsum converts to another variety before the dehydration process starts. Such a lattice ordering is demonstrated in the steam-treated samples as an increase in the relative intensity of the 4.27, 3.059, 2.59, 2.495 and 2.45 Å lines and a decrease in that of the line at 7.56 Å. Dry-calcination, on the other hand, causes a decrease in the relative intensity of the lines at 3.059, 2.867, 2.679, 2.59, 2.495, 2.45 and 2.40 Å. Table 3 summarizes the most striking changes in the relative intensity of the 11 major lines of the gypsum pattern which occurred because of heating. The relative intensity of some lines, on the other hand, reveals a slight change indicating that this change took place across some axial planes only and not affecting the whole crystal. The newly formed crystal mostly belongs to the monoclinic system but the change most probably occurs in decreasing the β-angle value, being closer to the right angle, i.e. moving in the direction where the monoclinic lattice is gradually changing to the orthorhombic system. The newly formed crystal is considered as a case of lattice ordering; i.e. the progressive transformation of the monoclinic originally present to another variety of higher symmetry, or as a phase change of the stable into metastable monoclinic crystal. In both cases the crystal lattice belongs to the monoclinic system and still contains two molecules of water of crystallization. It could be concluded that the first effect of heat on gypsum is to increase its crystal symmetry within the same system. The role of steam pressure in altering the relative intensity of certain planes, and its relation to the distribution of water and sulphate groups in the lattice of gypsum, however, needs further experimental support for elucidation; this may be undertaken in another paper.

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