

KINETICS OF GYPSUM DEHYDRATION

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ABSTRACT

A systematic study was conducted to investigate the correlation between the dehydration of gypsum and the time and temperature of calcination as well as the grain size of the starting material. It was found that the proposed formula

$$t = \exp\left(\frac{KT\alpha^{1/2}}{r^{1/2}}\right) \text{ or } \ln t = \frac{KT\alpha^{1/2}}{r^{1/2}}$$

may be considered as a real expression of the dehydration reaction throughout the major part of α . However, the initial and final stages of dehydration revealed a slight shift due to the induction period and the residual amount of water retained by the soluble anhydrite crystal lattice, respectively. The dehydration reaction at 160°C is nearly double that at 100°C and four times that at 70°C, using one particle size. Generally, as the grain size of gypsum becomes less than about 0.13 mm an abrupt increase in the dehydration process occurs with any slight decrease in diameter. A moderate change occurs, however, as the grain size changes over 0.13 mm.

INTRODUCTION

The dehydration of gypsum is a complex operation involving chemical, physical and geometrical aspects. On heating gypsum the geometry of the calcined material suffers successive changes from the monoclinic form of gypsum via the rhombohedral shape of the bassanite to the orthorhombic lattice of the stable insoluble anhydrite. In due time the water of crystallization is liberated and most of the physical properties of the calcined material simultaneously alter.

Extensive work has been done on the dehydration of gypsum—starting as early as the time of the building of ancient Egyptian pyramids [1]. Numerous publications have appeared on the subject but the majority of these deal with the temperature of phase transformations and the characterization of the hemihydrate, commercially known as plaster of Paris [2]; few have tried to discuss this dissociation reaction in terms of mathematical formulae [3]. In a previous work Khalil et al. [2b] studied the dehydration of gypsum which was confined only to the phases developed in one fine-sized gypsum sample.

TABLE 1

Grain size data of the investigated gypsum samples

No.	Mesh range ^a	Diameter (mm)	Mean diameter (r) (mm)
1	6- 10	2.812-1.405	2.109
2	10- 16	1.405-1.003	1.204
3	16- 52	1.003-0.295	0.649
4	52-100	0.295-0.149	0.222
5	100-150	0.149-0.105	0.127
6	150-170	0.105-0.088	0.0965
7	<170	<0.088	0.088

^a Mesh range was selected in accordance with the B.S. 410 (1969) comprising the number of meshes per linear inch.

The lack of an equation capable of describing the dehydration of gypsum precisely has prompted the author to test various equations and to suggest a selected formula which may be considered as a real expression of the case. The proposed formula correlates, in a systematic manner, the process of

TABLE 2

Fraction decomposed (α) % of coarse gypsum samples calcined at various temperatures

Diameter (mm)	temp. (°C)	Time (h)					
		0.25	0.5	1	2	5	10
2.109	100	0.59	1.08	7.79	24.07	62.77	82.68
	120	11.84	37.18	67.17	95.50	96.48	97.85
	140	38.16	69.47	93.44	96.87	98.68	98.97
	160	48.09	88.16	94.18	98.83	98.97	99.07
	180	90.07	96.72	98.83	99.51	99.51	99.71
1.204	100	0.78	1.86	9.51	35.62	64.97	85.13
	120	14.04	41.59	73.97	95.60	97.06	97.85
	140	45.30	72.80	93.69	98.34	98.78	98.97
	160	57.44	93.05	96.53	98.83	98.97	99.07
	180	91.88	97.85	98.83	99.51	99.51	99.71
0.649	100	0.98	2.45	17.22	38.41	68.05	89.29
	120	14.33	43.20	74.95	95.40	97.06	98.78
	140	50.68	72.99	94.18	98.83	98.83	99.07
	160	65.95	93.49	96.62	98.92	99.02	99.07
	180	92.25	97.85	98.83	99.51	99.51	99.71
0.222	100	1.22	3.52	21.53	46.53	73.09	90.85
	120	14.82	44.03	85.86	95.99	97.11	98.83
	140	53.47	74.07	94.91	98.83	98.92	99.07
	160	69.08	95.40	97.16	99.02	99.07	99.07
	180	92.56	98.83	99.07	99.70	99.71	99.71

TABLE 3

Fraction decomposed (α) % of fine gypsum samples calcined at various temperatures

Diameter (mm)	Temp. (°C)	Time (h)					
		0.25	0.5	1	2	5	10
0.127	100	1.57	5.48	27.45	46.87	76.42	93.69
	120	17.12	47.06	86.40	96.97	97.11	98.83
	140	56.41	75.24	96.38	98.83	98.97	99.07
	160	73.92	95.79	98.29	99.07	99.07	99.07
	180	95.80	99.07	99.07	99.61	99.71	99.71
0.0965	100	2.05	7.14	36.74	56.36	81.95	94.77
	120	19.67	49.22	87.67	96.97	97.60	98.83
	140	59.30	78.96	96.92	99.07	99.07	99.07
	160	79.26	98.58	98.97	99.07	99.12	99.12
	180	96.33	99.07	99.22	99.71	99.80	99.80
0.088	100	2.50	7.83	40.46	57.78	89.63	98.34
	120	23.58	51.66	90.12	97.46	97.60	98.83
	140	62.67	80.04	97.85	99.07	99.07	99.07
	160	84.39	99.12	99.12	99.12	99.12	99.12
	180	98.87	99.07	99.22	99.71	99.80	99.80

dehydration with both the time and temperature of calcination as well as the grain size of the starting gypsum raw materials.

EXPERIMENTAL

Seven gypsum (different sizes) samples were subjected to isothermal thermogravimetry (1 g each) at 70–180°C for various time periods. The grain size was carefully selected to lie within a narrow range of two successive diameters, mesh numbers; their mean value, however, was considered in the calculations (Table 1). The conditions of TG were as previously described [2b]. The fraction of gypsum which dehydrates (α) at time t was calculated as

$$\alpha = \frac{W_i - W_t}{W_i - W_f}$$

where W_i = initial gypsum sample weight; W_t = sample weight after heating for time t ; and W_f = sample weight corresponding to complete water loss.

Representative α % values of the investigated gypsum materials calcined at different temperatures are shown in Tables 2–4 as a function of time.

TABLE 4

Fraction decomposed (α) % of sample 7 calcined at lower temperatures

Time (days)	Temperature (°C)		
	70	80	90
0.25		1.47	37.33
0.5	0.78	5.23	75.54
1	0.78	18.40	75.83
2	1.02	75.49	
4	1.23	75.73	
6	9.25	75.83	75.83
8	14.53		
10	33.32		
15	73.78	75.83	75.83
20	75.24	75.83	75.83

RESULTS AND DISCUSSION

Tables 2-4 reveal that the dehydration of gypsum increases with time and temperature increase as well as with a decrease in grain size. Various mathematical expressions have been tested to describe this; the one which may be considered as a real representation of the dehydration of gypsum is as follows: at constant temperature, isothermal dehydration

$$\ln t = A\alpha^{1/2} \text{ or } t = \exp(A\alpha^{1/2}) \quad (1)$$

where t = heating time (used in the calculation in min); A = reaction (dehy-

TABLE 5

Correlation coefficient (f) of the samples calcined at various temperatures

Sample No.	Diameter (mm)	Calcination temp. (°C)				
		100	120	140	160	180
1	2.109	0.986	0.902	0.826	0.726	0.623
2	1.204	0.987	0.818	0.649	0.706	0.663
3	0.649	0.991	0.886	0.829	0.729	0.561
4	0.222	0.987	0.840	0.964	0.658	0.477
5	0.127	0.988	0.827	0.832	0.732	0.371
6	0.0965	0.974	0.793	0.805	0.746	0.369
7	<0.088	0.969	0.812	0.808	0.551	0.332

TABLE 6

Correlation coefficient (f) of sample 7 calcined at relatively low temperatures

Temp. (°C)	100	90	80	70
f	0.9692	0.885	1.05	0.8994

dration) constant; and α = fraction of gypsum decomposed after heating for time t .

Equation (1) was suggested by the author and was found to be a real expression for the dehydration reaction throughout the major part of α . This conclusion was confirmed by calculating the correlation coefficient (f) for each grain size calcined at various temperatures, which was done through the use of the basic equation for a straight line

$$f = \frac{n\sum_{XY} - \sum_X \sum_Y}{\sqrt{\{n\sum X^2 - (\sum X)^2\} \{n\sum Y^2 - (\sum Y)^2\}}}$$

where X and Y are the two variables ($\ln t$ and $\alpha^{1/2}$) and n is the number of trials. Tables 5 and 6 show the calculated data from which it is clear that each approaches unity in the case of the samples calcined at comparatively low temperatures for all the investigated sizes. This indicates that the proposed formula discusses the case of gypsum dehydration and the semilog function gives a straight-line relation. As the heating temperature was increased and/or the grain size decreased, a pronounced negative deviation in the calculated data from unity was detected. This is related to the fact that in both cases the dehydration process accelerates and in a comparatively short time the major part of the water is suddenly expelled off. A pronounced improvement in such a calculation is expected when the chosen time intervals are less than those practised here to allow a gradual rather than an abrupt dehydration. Moreover, it was concluded by various investigators that a residual amount of water is retained by the γ -anhydrite crystal

TABLE 7

Correlation coefficient data of sample 6

Calcination temp. (°C)	First calculation ^a	Recalculation ^b
100	0.9737	0.981
120	0.7933	0.938
140	0.8053	0.9541

^a All values of α are considered

^b Values up to 99% of α are considered.

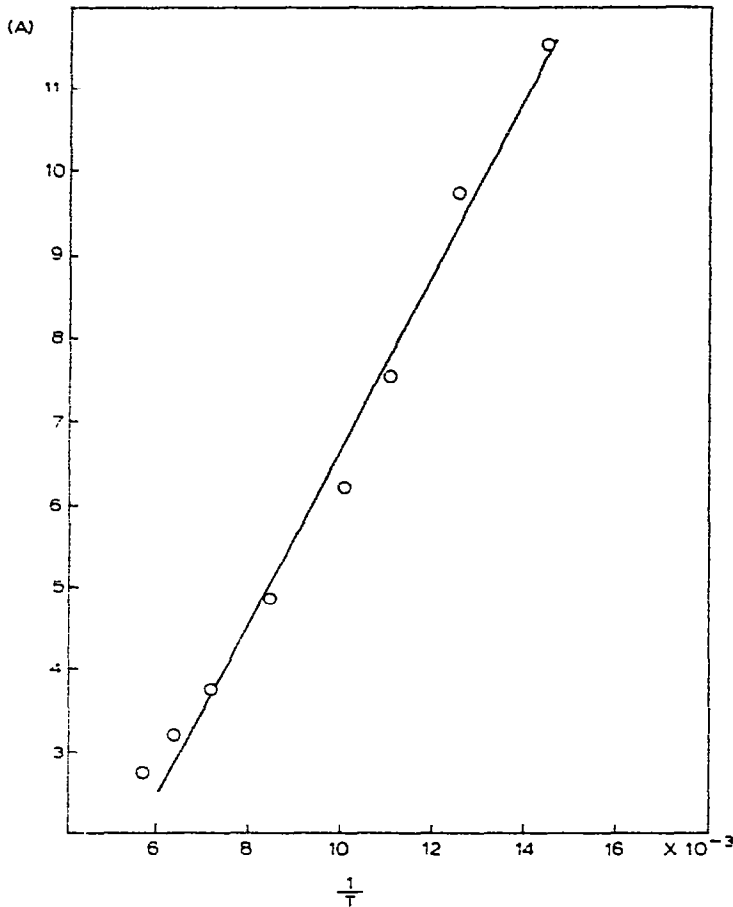


Fig. 1. The relationship between the dehydration reaction constant and the calcination temperature for sample 7.

lattice [2b]. For this reason the reaction constant A was recalculated taking into consideration all the α values up to a maximum of about 99% to neglect the period spent because of this residual water. Table 7 shows representative data of recalculation for sample 6 calcined at 100, 120 and 140°C in comparison with the initial calculated data. From Table 7 it is evident that the recalculated coefficient (f) values are much closer to unity in comparison with the previously calculated data. This again confirms the straight-line relation and the validity of the formula for discussing the dehydration reaction when the residual water is considered.

The relation between the reaction constant A and temperature was studied for the fine size (sample 7) only. When $1/T$ was plotted against A , a straight line was obtained (Fig. 1). It should be noted that on plotting fig. 1 the calculated data of A corresponding to the initial and final stages of dehydration were excluded in order to avoid any confusion due to the induction period or the delayed time for the retained residual water. Only least values of A were considered in constructing Fig. 1, which indicates that the reaction

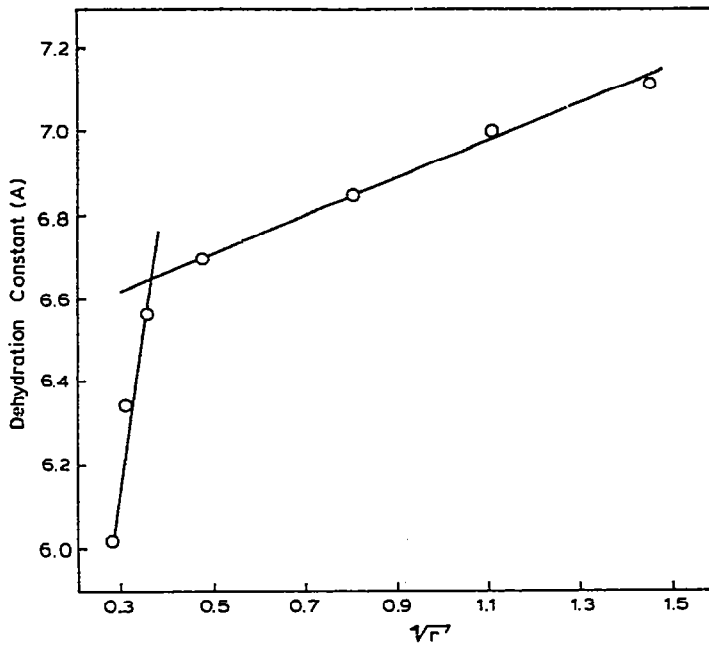


Fig. 2. The relationship between the dehydration reaction constant and the diameter of gypsum grains calcined at 100°C.

constant A is inversely proportional to T . Equation (1) could accordingly be changed to

$$\ln t = BT\alpha^{1/2} \text{ or } t = \exp(BT\alpha^{1/2}) \quad (2)$$

where B is another reaction constant.

It should be noted that the reaction constant A varies with the calcination temperature in a way that we can deduce that its rate at 70°C is nearly double that at 100°C and four times at about 160°C. This may lead to the conclusion that the dissociation reaction of gypsum at 160°C is four times greater than at 70°C and double that at 100°C.

The relation between the reaction constant A and the mean diameter r of the calcined gypsum grains was also investigated. Different equations were attempted in this connection and the one which seems to be most fit is that which results from plotting A vs. $r^{1/2}$ where we get the relation presented in Fig. 2. This diagram could be considered as an intersection of two straight lines with different slope values. It could be said that when the grain size (diameter) of the original gypsum particles is coarser than about 0.13 mm (the point of intersection of the two straight lines) there is a moderate change in the dehydration of one sample and the other. Finer sizes (below 0.13 mm diameter) reveal an abrupt behaviour as the grain size is being changed. This indicates the higher reactivity of the fine grains of gypsum which confirms the straight-line relation results from plotting $1/A$ vs. $r^{1/2}$ with two rates.

Equation (2) could be finally put in the form of the general formula

$$\ln t = KT \frac{\alpha^{1/2}}{r^{1/2}} \text{ or } t = \exp\left(\frac{KT\alpha^{1/2}}{r^{1/2}}\right) \quad (3)$$

which we believe serves as a real expression of the dehydration reaction of gypsum in terms of the fore-mentioned parameters of time, temperature and grain size.

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