A Study of the Hydration of Calcium Orthoplumbate. III. The Behavior of Dehydration

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The following facts have been observed regarding the process and products of the hydration of calcium orthoplumbate at various temperatures in an atmosphere of nitrogen-water vapor:[1] i) In the hydration process, the mole ratio of CaO/PbO_2 in calcium orthoplumbate decreased linearly, while that of H_2O/CaO decreased step-by-step, with the increase in temperature. ii) The powder which appeared in the hydration process changed color parallel with the inversion rate of the anhydrous compound. iii) The composition and nature of completely-hydrated products at various temperatures were examined by X-ray diffraction analysis, thermobalance analysis, chemical analysis, differential thermal analysis, infrared absorption spectrum and electron microscopy. The results of all the methods showed good agreement.

In this paper, the dehydration of calcium orthoplumbate hydrates will be examined by a differential thermal analysis pattern, and the information thus obtained will be used for analyzing the dehydration behavior of the crystalline water and negative catalytic effects of calcium hydroxide. The results of present experiment will support the conclusion of the previous paper. The reaction order (n) and the frequency factor (A) of the dehydration stage will also be discussed.

Theoretical

The Determination of the Activation Energy (E) and the Frequency Factor (A). — The activation energy (E) was obtained from the variation in the peak temperature with the rate of heating.[2] Kissinger derived the following equation from the theoretical consideration:

$$\frac{d(\ln \phi/T_m{}^2)}{d(1/T_m)}=-\frac{E}{\boldsymbol{R}} \qquad (1)$$

where ϕ(°C/min.) denotes the rate of heating; T_m (°K), the temperature of maximum deflection; $\boldsymbol{R}$, the gas constant, and E, the activation energy. The variation in the peak temperature with the rate of heating is governed only by the activation energy. The plot of $-\boldsymbol{R}\cdot\ln \phi/T_m{}^2$ vs. $1/T_m$ should give a straight line; the slope of this line will be E according to Eq. 1.

The reaction order (n) and the frequency factor (A) are calculated from Eqs. 2 and 3:

$$n(1-x)_m{}^{n-1}=1+(n-1)\cdot 2\boldsymbol{R}T_m/E \qquad (2)$$

$$E\phi/\boldsymbol{R}T_m{}^2=A\cdot n(1-x)_m{}^{n-1}\cdot e^{-E/\boldsymbol{R}T_m} \qquad (3)$$

where $(1-x)_m$ denotes the amount of material left unreacted and n, the empirical order of reaction.

The Estimation of the Reaction Order from the Peak Shape.—Kissinger proposed a "shape index (S)" to obtain the reaction order. When S is plotted against n^2, the points fall roughly on a straight line defined by

$$S=0.63\cdot n^2 \qquad (4)$$

This expression was used to estimate the reaction order of the dehydration reaction from the differential thermal analysis data.

Experimental Procedure

Material.—*Calcium Orthoplumbate Hydrate-Calcium Hydroxide Mixtures.*—The mixture applied in this experiment was prepared by hydrating calcium orthoplumbate. The process of hydration was carried out at 30, 50, 80 and 100°C in an atmosphere of nitrogen-water vapor. The ratio of H_2O/Ca_2PbO_4 was 10 in the process. Hydration finished after 390 min. Hydrated mixtures were identified by X-ray diffraction patterns, differential thermal analysis curves, thermobalance, and chemical measurements.

Calcium Orthoplumbate Hydrate. — The Franke method[3] was applied in order to remove calcium hydroxide from hydrated mixtures. The Franke method (or the acetoacetic ester method) for the extraction of free calcium hydroxide in calcium orthoplumbate hydrate-calcium hydroxide mixtures gave good results.

The general formula $(2-N)CaO\cdot PbO_2\cdot mH_2O+N\cdot Ca(OH)_2$ was assigned to the completely-hydrated mixture in the preceding paper.[1]

The samples employed for thermal analysis are

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[1] This paper was presented at the Autumn Meeting of the Japan Society of Color Material, Tokyo, 1960; *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kogyo Kagaku Zasshi*), **67**, (1964), in press.

[2] H. E. Kissinger, *J. Research Natl. Bur. Standards*, **57**, 217 (1956); *Anal. Chem.*, **29**, 1702 (1957).

[3] E. E. Pressler, S. Brunauer and D. L. Kantro, *Anal. Chem.*, **28**, 897 (1956).

TABLE I. MATERIALS USED FOR DIFFERENTIAL THERMAL ANALYSIS

Material	Composition			Condition of reaction	
	Hydrate		Free $Ca(OH)_2$		
	$(2-N)$	m	N	Temp. °C	Time min.
A	1.5	3.0	0.5	50	390
B	1.2	1.8	0.8	80	390
C	1.0	1.0	1.0	100	390
D	1.5	3.0	—	50	390
E	1.2	1.8	—	80	390
F	1.0	1.0	—	100	390
G	$Ca(OH)_2$: Extra pure reagent				
H	$Mg(OH)_2$: Extra pure reagent				

Formula: $(2-N)CaO \cdot PbO_2 \cdot mH_2O + NCa(OH)_2$

listed in Table I. Samples A, B and C were calcium orthoplumbate hydrate - calcium hydroxide mixtures. D, E and F were calcium orthoplumbate hydrate. Two chemical reagents, calcium hydroxide, and magnesium hydroxide, were employed as reference samples.

Apparatus and Procedure. — The apparatus of differential thermal analysis employed in this work consists of an analytical furnace, a transformer, and recording equipment. Specimen holders made of pure nickel have a diameter of 1/4 inch and a length of 1/2 inch.

A chromel-alumel thermocouple was used. The reference material was α-aluminum oxide. Each of the eight samples was run in differential thermal analysis at the rate of 3, 4, 5, 7, 9, 10 and 13°C per min. to determine the variation in the peak temperature with the rate of heating. The samples were ground to pass through a 250-mesh sieve. Specimen holders were filled loosely with 500 mg. of the sample, and a gentle tapping was carried out. The standard deviation of a single measurement was within 2.5°C. The thermobalance apparatus employed in this work was the same as that described in the preceding paper.1) The loss in weight was recorded continuously as the furnace temperature increased. About 1 g. of the sample was used for each determination.

Results and Discussion

The loss in weight accompanying the heat treatment of calcium orthoplumbate hydrate and calcium orthoplumbate hydrate - calcium hydroxide mixtures in the thermobalance measurement is given in Figs. 1 and 2 respectively.

It is apparent from Figs. 1 and 2 that the dehydration of samples D, E and F proceeds in one stage, and that of A, B and C, in three

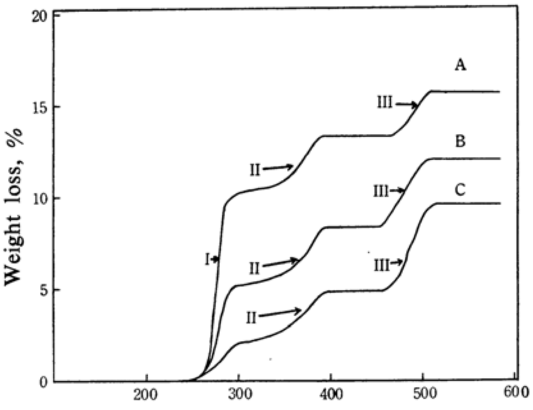

Fig. 1. Thermobalance results for calcium orthoplumbate hydrate - calcium hydroxide mixtures.

TABLE II. DATA OF DIFFERENTIAL THERMAL ANALYSIS MEASUREMENTS

Heating rate ϕ	Peak temp. (T_m, °C)														
	A			B			C			D	E	F	G	H	Ia
	I	II	III	I	II	III	I	II	III						
3	322	—	534	316	402	—	318	405	—	303	306	306	540	411	461
4	333	—	—	324	—	543	—	410	—	317	320	—	553	—	469
5	—	—	—	336	414	—	337	416	552	—	—	332	—	431	484
7	353	—	565	—	421	—	346	422	—	348	350	352	578	443	494
9	365	—	—	—	447	578	—	427	—	361	363	362	587	454	505
10	368	—	—	360	429	—	359	—	580	—	370	370	—	—	—
13	—	—	—	370	—	—	370	—	590	382	—	—	602	465	—
ϕ	Shape index (S)														
3	0.73	—	0.27	0.71	0.59	—	0.80	0.54	—	0.48	0.58	0.67	0.28	0.67	0.12
4	0.76	—	—	0.80	—	0.28	—	0.59	—	0.49	0.57	—	0.22	—	0.11
5	—	—	—	0.74	0.51	—	0.73	0.53	0.26	—	—	0.66	—	0.61	0.13
7	0.76	—	0.28	—	0.54	—	0.75	0.50	—	0.49	0.60	0.74	0.28	0.65	0.16
9	0.71	—	—	—	0.50	0.28	—	0.54	—	0.58	0.58	0.75	0.29	0.63	0.19
10	0.81	—	—	0.77	0.54	—	0.76	—	0.27	—	0.60	0.71	—	—	—
13	—	—	—	0.76	—	—	0.74	—	0.28	0.48	—	—	0.28	0.63	—

Ia ; $\phi = 3, 4, 5, 6, 10, 12.5$

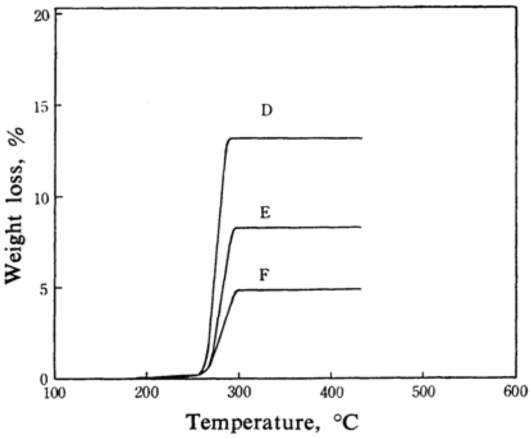

Fig. 2. Thermobalance results for calcium orthoplumbate hydrate.

stages. Stages I and II in Fig. 1 seem to show the first and second stage of the dehydration respectively; III may show the decomposition of calcium hydroxide.

The results of the differential thermal analysis experiments with samples A—H are listed in Table II. In the case of samples A, B and C the dehydration proceeded in two steps in the range of 316～370°C and 402～430°C when the rate of heating was varied from 3°C per min. to 13°C per min. On the other hand, in the case of the extracted hydrate (D, E and F), the dehydration proceeded in one step. The dehydration temperature was 303～382°C.

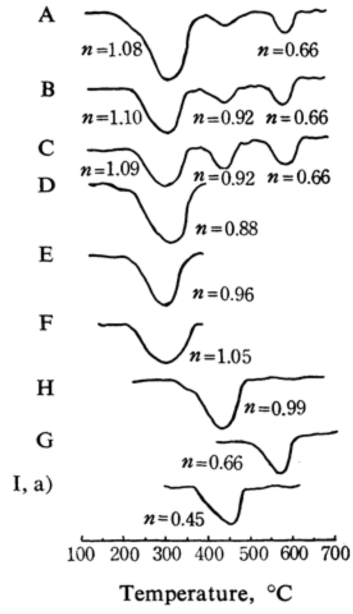

Fig. 3. Typical differential thermal analysis curves for the samples used in the present study.

It may be concluded from the comparison of the results of the thermobalance with those of the differential thermal analysis that the dehydration of the two-stage mechanism starts at a slightly higher temperature and proceeds over a wider range than does the one-stage dehydration.

This conclusion seems to show that the dehydration of the hydrated mixture is partially retarded by the presence of liberated calcium hydroxide. This negative catalytic

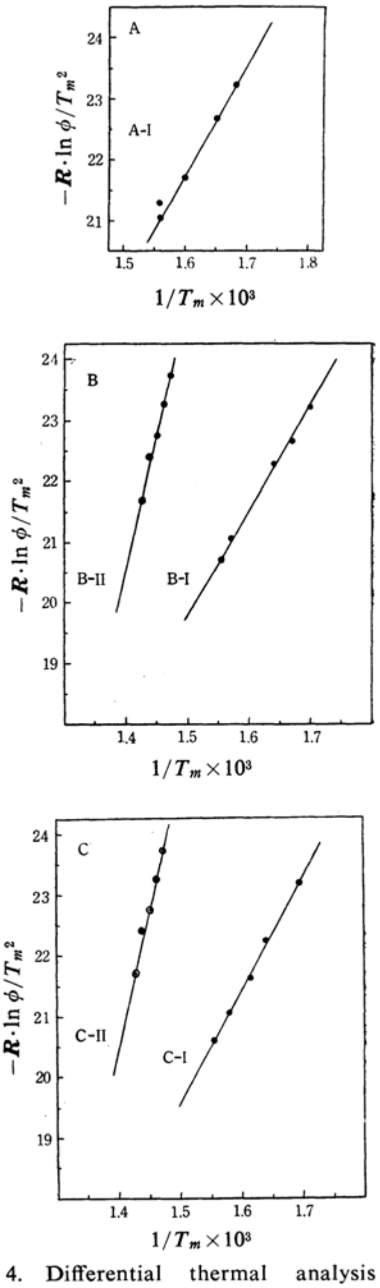

Fig. 4. Differential thermal analysis data obtained for samples A, B and C.

action of calcium hydroxide can reasonably be explained by the results of the reaction order (*n*) and the activation energy (*E*).

The shape of the endothermic peak associated with the thermal decomposition of these samples is depicted in Fig. 3. The corresponding values of *n* obtained from Eq. 4 are also given there. Each differential thermal analysis datum in Table II gives a straight line of $-\boldsymbol{R}\cdot\ln\phi/T_m{}^2$ vs. $1/T_m$, thus enabling us to calculate the activation energy (*E*). The case of A is shown in Fig. 4 as an example. The values of *n*, *A* and *E* obtained are given in Table III.

TABLE III. KINETIC RESULTS BY DIFFERENTIAL THERMAL ANALYSIS METHODS

Material		*n*	ln *A*	*E*, kcal./mol.
A	I*	1.08	12.85	18.2
	II**	—	—	—
	III***	0.66	18.05	33.0
B	I	1.10	12.86	18.0
	II	0.92	27.62	41.0
	III	0.66	18.05	33.0
C	I	1.09	12.82	18.0
	II	0.92	29.94	43.0
	III	0.66	18.05	33.0
D		0.88	7.15	11.5
E		0.96	7.11	11.5
F		1.05	7.57	12.1
G		0.66	16.02	30.7
H		0.99	15.84	25.0
I	a)	0.55 to 0.44	15.18	31.4
	b)	0.69	13.26	27.2

* First dehydration step.
** Second dehydration step.
*** Liberated calcium hydroxide.
a) Kissinger's data by DTA method for Brucite.
b) Kissinger's data by isothermal weight-loss measurements for Brucite.

Gregg and Razouk reported that the reaction order of Brucite $Mg(OH)_2$ was 0.66 and the activation energy, 27.6 kcal. per mole. Kissinger②) obtained the reaction order of 0.55∼0.44 and the activation energy of 31.4 kcal. per mole from his differential thermal analysis, and the reaction order of 0.69 and the activation energy of 27.2 kcal. per mole, from the results of the isothermal reaction rate for the same compound. The value of the reaction order of magnesium hydroxide (0.99) reported in this paper (Table III) differs from those reported by Kissinger and by Gregg and Razouk, but the activation energy of 25.0 kcal. per mole is similar to their values in order of magnitude.

The values of the reaction order derived from the differential thermal analysis are nearly equal to unity in the cases of samples A, B and C. While the activation energies of the first dehydration were found to be 18.2, 18.0, and 18.0 kcal. per mole, those of the second dehydration were from 41.0 to 43 kcal. per mole. The second dehydration of sample A was not obtained exactly. The activation energies for D, E and F were

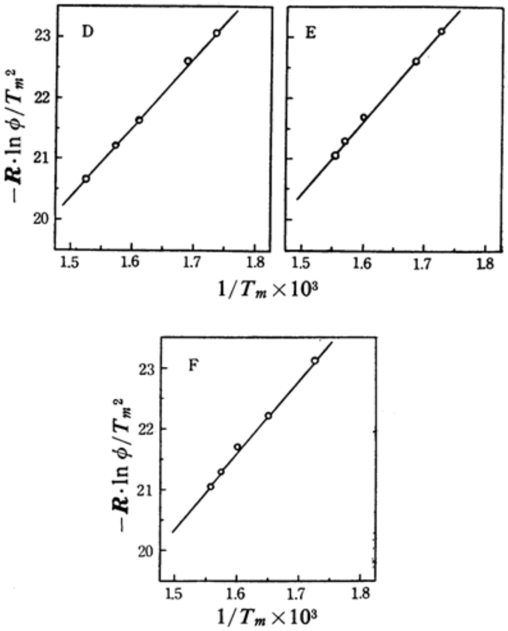

Fig. 5. Differential thermal analysis data obtained for samples D, E and F.

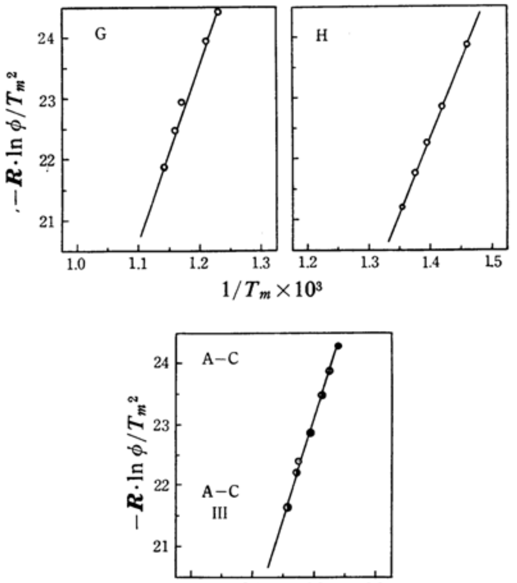

Fig. 6. Differential thermal analysis data obtained for samples A, B and C.
● 50°C; ○, 80°C; ◑, 100°C (temperature of hydration)

found to be 11.5, 11.5 and 12.1 kcal. per mole; the reaction orders of E and F were nearly equal to unity, while that of D was apart from unity, that is, 0.88. The lack of agreement in the case of the dehydration of sample D can not be explained. The difference in activation energy between the first and second dehydration processes indicates that the dehydration is influenced by the inhibitive action of the calcium hydroxide liberated; that is, the elevation of the activation energy of the second dehydration seems to arise from the fact that small particles of calcium hydroxide liberated in hydrate mixtures are firmly bound to the hydrate.

The behavior of the binding of calcium hydroxide to hydrate is considered to be as follows: a comparison of the electron micrograph reported in the preceding paper[1] with the above-mentioned results suggests that the crystals of calcium hydroxide produced by the hydration link together to form a three-dimensional network and that hydrated calcium orthoplumbate fills up the space existing in the calcium hydroxide network. The three-dimensional network of calcium hydroxide may be a linkage consisting of crystals of a spherical form, as suggested by the results of Sato,[4] because the values of the reaction order in this study agree with those of Sato.

Summary

The behavior of the dehydration of a hydrate mixture of calcium orthoplumbate and calcium hydroxide and of the hydrate of calcium orthoplumbate has been studied with a thermobalance and by differential thermal analysis.

It has been shown that the dehydration of crystalline water in the hydrate mixture was retarded by the presence of the calcium hydroxide liberated; this conclusion has been based on both the activation energy of the hydrate and its loss of weight.

It seems that calcium orthoplumbate fills the space in a network consisting of calcium hydroxide particles.

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[4] N. Sato, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zassi*), **76**, 862 (1955).