

ACTIVATION ENERGIES OF THE THERMAL DECOMPOSITIONS OF C_3AH_6 AND C_3AD_6 BY THE ISOTHERMAL TG METHOD

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Dehydroxylation of C_3AH_6 and C_3AD_6 minerals was studied by means of the isothermal TG method in ambient air and in a constant stream of nitrogen. It was found that the mechanism of dehydroxylation changed during the reaction in ambient air. In a dynamic inert atmosphere the experimental data conform very closely to a first order kinetics model. The activation energy values $85.4 \text{ kJ} \cdot \text{mole}^{-1}$ and $103.4 \text{ kJ} \cdot \text{mole}^{-1}$ were obtained for C_3AH_6 and for C_3AD_6 samples, respectively.

C_3AH_6 , one of the chief hydration products of aluminous clinker, the end member of the hydrogrossular series exhibits the garnet structure. The bisphenoids $(OH)_4^{4-}$ with an atomic arrangement similar to that of the tetrahedra $(SiO_4)^{4-}$ are situated in its elementary unit cell [1]. The presence of $(OH)^-$ groups in the structure of C_3AH_6 has been proved by Majmudar and Roy [2]. Proks and Nerád [3] described the mechanisms of thermal decomposition of C_3AH_6 and C_3AD_6 up to 900° . The present paper is devoted to research into the kinetics of dehydroxylation of C_3AH_6 and C_3AD_6 .

Experimental

C_3AH_6 and C_3AD_6 samples were prepared under hydrothermal conditions. D_2O of 99.74% purity was used for the synthesis of C_3AD_6 . The results of IR spectroscopy confirmed the presence of $(OH)^-$ and $(OD)^-$ groups in the samples (Fig. 1). A Perkin-Elmer 221 spectrophotometer was used. The difference in the

Table 1
Total weight losses

Sample	Temperature range $^\circ\text{C}$	Weight loss, %
C_3AH_6	260–400	22.53
C_3AD_6	250–425	25.48

frequencies of the vibrations of OH^- and OD^- groups is evident. The total weight losses for the first stage of the thermal decomposition are shown in Table 1. Thermogravimetric experiments were performed in a Du Pont 990 thermobalance module in an ambient air environment at a heating rate of $5^\circ/\text{min}$.

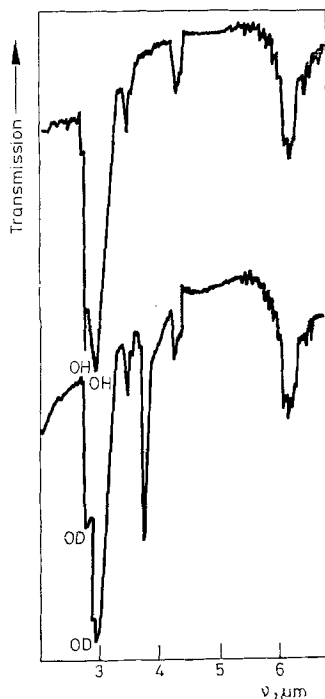


Fig. 1. IR spectra of C_3AH_6 and C_3AD_6 samples

The rate of the dehydroxylation process was studied by measuring the weight change upon heating as a function of time at constant temperature in the range $280-310^\circ$. Isothermal weight loss curves were obtained from 11–15 mg powder samples which were heated in ambient air and in a constant stream of N_2 (100 ml/min) in a Du Pont TGA assembly.

Kinetics studies

The isothermal weight loss data for C_3AH_6 in a flow of N_2 are shown in Fig. 2. α stands for the fraction decomposed, defined by the relation

$$\alpha = \frac{W}{W_f}$$

where W and W_f are the actual and final weight of the sample, respectively.

When plotted on a reduced time scale of $t/t_{0.5}$, where $t_{0.5}$ is the time corresponding to $\alpha = 0.5$, the curves of $\alpha = f(t/t_{0.5})$ are obtained; these can be compared with model curves derived from the following kinetic equations [4]:

$$F_1: -\ln(1 - \alpha) = kt$$

$$R_2: 1 - (1 - \alpha)^{0.5} = kt$$

$$A_2: -\ln(1 - \alpha)^{0.5} = kt$$

$$D_1: \alpha^2 = kt$$

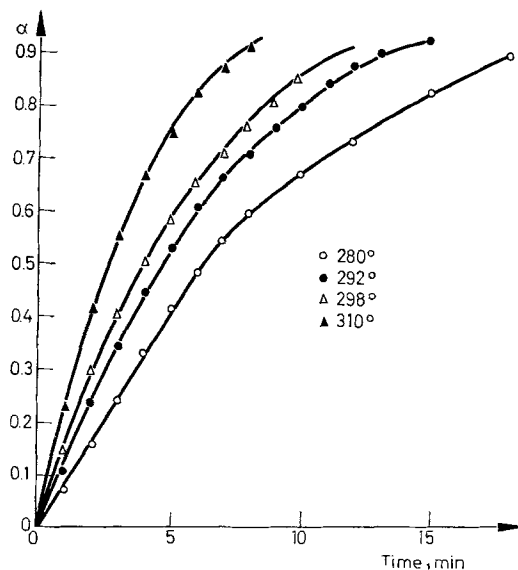


Fig. 2. Fraction reacted vs. time for dehydroxylation of C_3AH_6 in a flow of N_2

These equations represent the variation of α with t according to the following mechanisms:

(F_1) – first-order kinetics;

(R_2) – uniform movement of a reaction interface in two dimensions;

(A_2) – Avrami–Erofeyev equation;

(D_1) – diffusion-controlled process.

From the rate constants of the most suitable model the plots $\ln k$ vs. $1/T$ give the activation energies.

The rate constants, half-times and activation energies are collected in Table 2.

The mechanisms of dehydroxylation of the C_3AH_6 and C_3AD_6 samples in an ambient static air atmosphere change during the reaction. The plots of $\alpha = f(t/t_{0.5})$ conform rather to the model curve A_2 up to about $\alpha = 0.5$; with proceeding of the reaction its rate is changed and the plots better fit the F_1 or R_2 models, respectively (see Fig. 3). It appears [3] that in the first stage of the reaction the

Table 2
Results of isothermal measurements

Sample	T_i , °C	Weight of sample, mg	$t_{0.5}$, min	Rate constant, min^{-1}	Energy of activation
C_3AH_6 (in air)	279	15.89	28		
	285	17.72	22.6		
	290	15.07	12.8		
	300	12.61	9.4		
C_3AD_6 (in air)	279	14.76	31.8		
	291	11.48	12.3		
	302	11.21	8.6		
	311	11.13	6.7		
C_3AH_6 (in nitrogen)	280	11.27	6.2	0.1169	85.4 kJ. mole^{-1} $0 < \alpha < 0.8$
	292	17.83	4.5	0.1622	
	298	14.74	4.0	0.1790	
	310	12.42	2.6	0.2837	
C_3AD_6 (in nitrogen)	283	12.84	6.7	0.1131	103.4 kJ. mole^{-1} $0 < \alpha < 0.8$
	296	12.08	4.6	0.1774	
	304	12.18	2.8	0.2593	

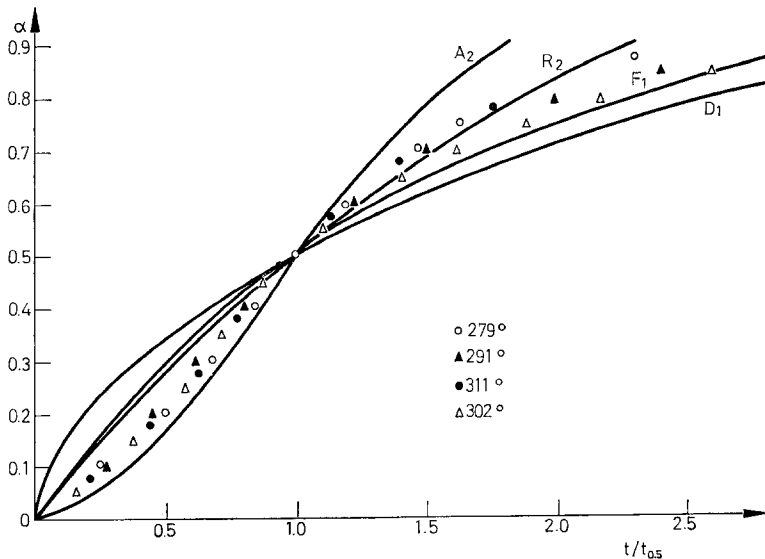


Fig. 3. Fraction reacted vs. $t/t_{0.5}$ for dehydroxylation of C_3AH_6 in ambient air, compared with model curves

sorption of $H_2O(g)$ by the decomposed phase takes place. Desorption of this water influences the second step of the reaction.

In a dynamic atmosphere the acceleratory effect of the flowing N_2 can be ob-

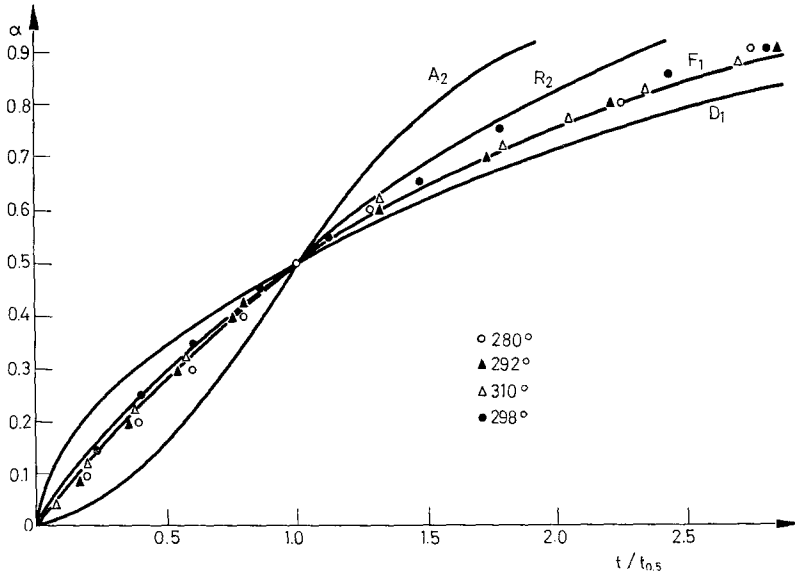


Fig. 4. Fraction reacted vs. $t/t_{0.5}$ for dehydroxylation of C_3AH_6 in a flow of N_2 , compared with model curves

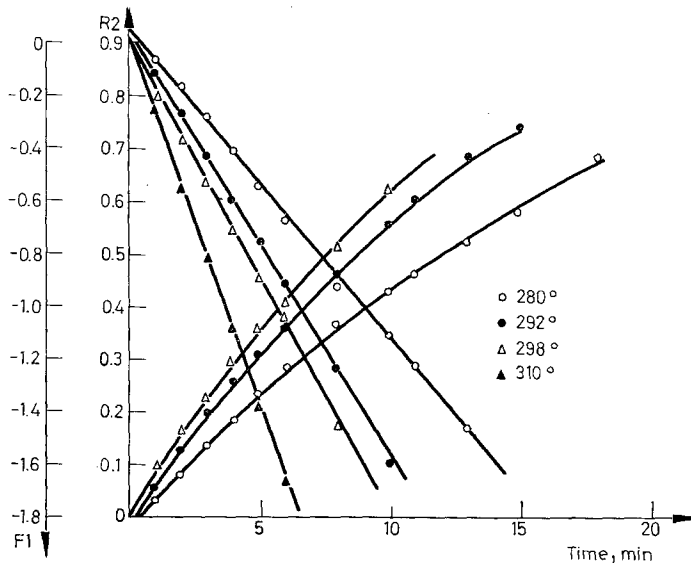


Fig. 5. Linearity test of F_1 and R_2 models for the C_3AH_6 sample in a flow of N_2

served. The half-times are about 5 times smaller than those determined in static air. This is probably caused by the action of the flowing nitrogen on the transport of the water released from the reaction interface.

Similar differences were observed with respect to the reaction mechanism. The presence of the flowing nitrogen leads to a change of the function $\alpha = f(t/t_{0.5})$ just from the beginning of the reaction. The results conform very closely to model curves F_1 or R_2 (see Fig. 4). Plots of the F_1 and R_2 function vs. t tend to become straight lines for the F_1 model (Fig. 5).

Conclusions

The dehydroxylations of C_3AH_6 and C_3AD_6 in the temperature range 280–310° under a dynamic atmosphere of N_2 follow first-order kinetics. With the exception of the activation energies, no differences have been found between the thermal decompositions of C_3AH_6 and C_3AD_6 . The activation energies determined are nearly the same as those obtained by Sharp and Brindley [5] for brucite, or by Giovanoli and Brüttsch [6] for γ -FeOOH dehydroxylation. On the other hand, the activation energies of dehydroxylation of the natural hydrosilicates (kaolinite, montmorillonite) are approximately twice those determined for the C_3AH_6 and C_3AD_6 samples.

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RÉSUMÉ — On a étudié la déshydroxylation des minéraux C_3AH_6 et C_3AD_6 par TG isotherme, dans l'air et dans un courant constant d'azote. Dans l'air ambiant, on trouve que le mécanisme de la déshydroxylation se modifie pendant la réaction. En travaillant dans une atmosphère inerte dynamique, les données d'expérience sont en bon accord avec un modèle cinétique du premier ordre. On a obtenu les énergies d'activation suivantes: 85.4 kJ · mol⁻¹ pour C_3AH_6 et 103.4 kJ · mol⁻¹ pour C_3AD_6 .

ZUSAMMENFASSUNG — Die Dehydroxylierung der Mineralien C_3AH_6 und C_3AD_6 wurde mittels isothermer TG-Methode in Luft und in einem konstanten Stickstoffstrom untersucht. Hierbei zeigte sich, daß sich der Mechanismus der Dehydroxylierung während der Reaktion in Luft ändert. Wenn in einer dynamischen inerten Atmosphäre gearbeitet wird, sind die Daten in guter Übereinstimmung mit einem kinetischen Modell erster Ordnung. Aktivierungsenergien von 85.4 kJ · mol⁻¹ für C_3AH_6 und 103.4 kJ · mol⁻¹ für C_3AD_6 wurden erhalten.

Резюме — Изучено дегидроксилирование C_3AH_6 и C_3AD_6 минералов с помощью изотермического ТГ метода в атмосфере воздуха и в постоянном токе азота. Найдено, что механизм дегидроксилирования в атмосфере воздуха изменяется в процессе реакции. При работе в динамической инертной атмосфере, экспериментальные данные очень близко соответствуют кинетической модели первого порядка. Полученные значения энергии активации для C_3AH_6 и C_3AD_6 , соответственно равны 85.4 кДж·моль⁻¹ и 103.4 кДж·моль⁻¹.