

THE DEHYDROXYLATION OF TRICALCIUM ALUMINATE 6-HYDRATE

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(Received 17 February 1976)

ABSTRACT

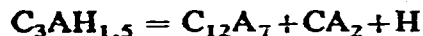
The thermal decomposition of tricalcium aluminate 6-hydrate* has been studied and kinetic parameters determined for each of the two stages in the reaction. The first stage was studied in the temperature range 505–610 K and the second between 950 and 1025 K at partial pressures of water vapour between 0.1 mN m⁻² and 3.2 kN m⁻². For the first stage below 555 K the rate-controlling process is one of nucleation and growth of product phase, which changes at higher temperatures to a diffusion-controlled process. The Arrhenius parameters for each of these processes vary with external water vapour pressure. The second stage of the reaction is controlled by a phase boundary reaction for which Arrhenius parameters are given.

INTRODUCTION

The calcium aluminate hydrates are of importance by virtue of their occurrence in various hydrated cements. Tricalcium aluminate 6-hydrate (Ca₃Al₂(OH)₁₂, 3CaO·Al₂O₃·6H₂O, C₃AH₆) is of particular importance due to its formation in the conversion of high alumina cements according to the following equation:



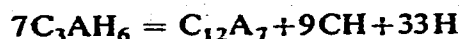
The formation and properties of C₃AH₆ have been studied by Thorvaldson and his coworkers^{1,2} who suggested that the thermal decomposition followed the equations:



This interpretation was challenged by Majumdar and Roy³ who suggested that the normal thermal decomposition was a non-equilibrium decomposition which only occurred at low vapour pressures of water. In addition to outlining the reactions taking place at high pressures, they suggested that the atmospheric pressure de-

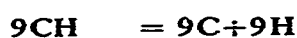
*Cement nomenclature will be used throughout, C = CaO, A = Al₂O₃, H = H₂O, therefore Al(OH)₃ = AH₃, Ca(OH)₂ = CH, CaO·Al₂O₃·10H₂O = CAH₁₀.

composition should be formulated as:



and that the second stage in the reaction is the dehydroxylation of the calcium hydroxide produced by the first stage.

It has recently been suggested⁴, on the basis of infrared and weight-loss data, that the slight discrepancy between experimental and calculated weight losses in the decomposition can be explained by the formation of the monohydrate of C_{12}A_7 , and that the best formulation for the reaction is as follows:



EXPERIMENTAL

Starting material

The hydrate was prepared by heating stoichiometric quantities of CaO and Al_2O_3 in water in a glass pressure vessel at 423 K for two weeks. X-ray diffraction (CuK_α radiation) gave a pattern in excellent agreement with that published³. S.E.M. examination showed well-crystallised material and a particle size analysis indicated that 80% of the crystals had diameters between 1.5 and 3 μm .

Dehydration techniques

Isothermal dehydrations were carried out using a recording electrobalance and sample weights of 9.0 ± 0.3 mg were used throughout. Constant temperatures ($\pm 1^\circ\text{C}$) were maintained using an electric furnace and controller. Partial pressures of water vapour were maintained by passing nitrogen through water or salt solutions, or over drying agents and then over the sample. Thermogravimetric runs were carried out in a similar fashion except that the controller was used to programme the furnace. Heating rates between 2 and 100 K min^{-1} were used.

Enthalpic measurements

A DuPont 950 thermal analyser with a calorimeter module was used for enthalpy of decomposition measurements. Sapphire was used as the calibration standard⁵.

RESULTS

Weight losses

The maximum apparent weight loss varied with heating rate, as did the apparent number of stages in the decomposition. These effects are shown in Fig. 1, from which it can be seen that the lowest heating rates produced two obvious stages in the overall reaction.

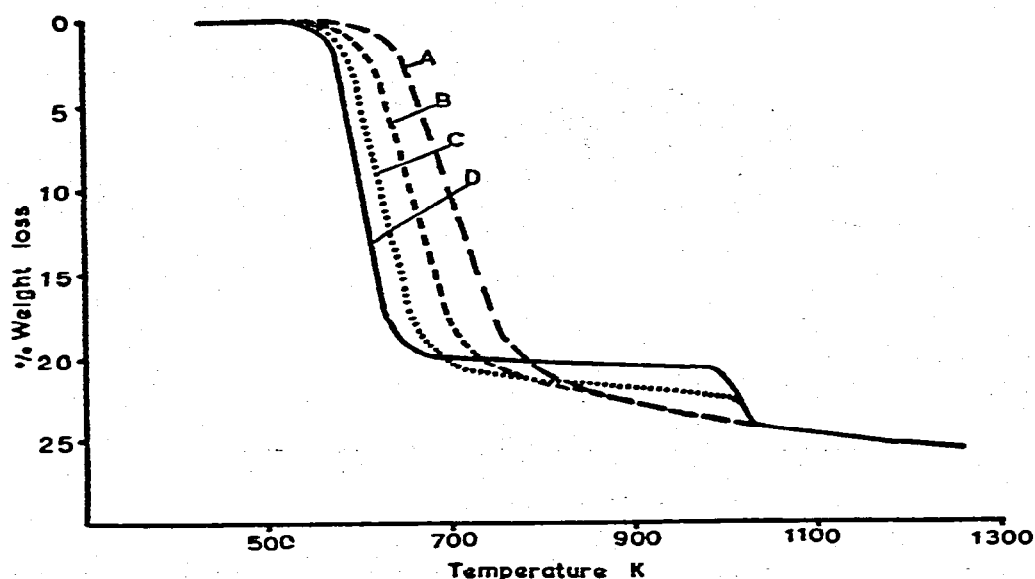


Fig. 1. Effect of heating rate on decomposition of C_3AH_6 . Curve A, 100 K min^{-1} ; Curve B, 50 K min^{-1} ; Curve C, 10 K min^{-1} ; Curve D, 3 K min^{-1} .

Reducing the heating rate also increased the temperature separation between the two stages of the reaction by raising the decomposition temperature of the calcium hydroxide. This meant that attempts to study this stage isothermally were difficult using the present apparatus, since this meant operating the furnace at or near its maximum temperature for long periods of time. The next section therefore refers to the first stage of the reaction only.

Isothermal heating

The results for all runs (39 in all) were tested by comparison of experimental reduced time plots, based on the time for 50% reaction (α vs. $t/t_{0.5}$, where α = proportion decomposed) with those for various model systems based on nucleation and growth control, phase boundary control, or diffusion control of the dehydration reaction⁶. In all cases a correction was made to the starting time to allow for the heating-up of the sample.

For temperatures above 550 K and for all partial pressures of water vapour studied, the curves were deceleratory and some of the experimental curves are shown in Fig. 2, together with curves calculated for various reaction models. It can be seen that the 'best fit' between experiment and calculation varies slightly with temperature. However, many of the experimental data can be described fairly well by the parabolic law $\alpha^2 = kt$.

Figure 3 shows typical α^2 vs. t plots and Fig. 4 the derived Arrhenius plots for various partial pressures of water vapour. The values of activation energies and frequency factor are included in Table 1.

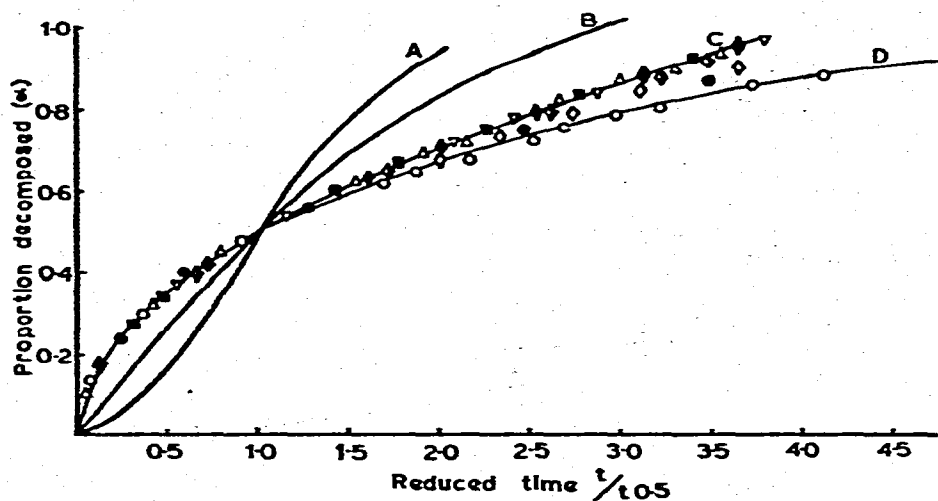


Fig. 2. Reduced time plot for high temperature dehydration of C_3AH_6 . Curve A, Avrami-Erofyev equation, $-\ln(1-\alpha)^2 = kt$; Curve B, contracting disc equation, $[1-(1-\alpha)^2] = kt$; Curve C, parabolic law, $\alpha^2 = kt$; Curve D, 2-dimensional diffusion, $(1-\alpha)\ln(1-\alpha) + \alpha = kt$; experimental points: \circ , 587K/0.6 kN m $^{-2}$; ∇ , 557K/3.2 kN m $^{-2}$; \bullet , 587K/0.13 mN m $^{-2}$; \blacksquare , 557K/2.3 kN m $^{-2}$; \diamond , 576K/2.3 kN m $^{-2}$; \blacklozenge , 576K/0.6 kN m $^{-2}$; \blacklozenge , 569K/3.2 kN m $^{-2}$; \triangle , 569K/0.6 kN m $^{-2}$.

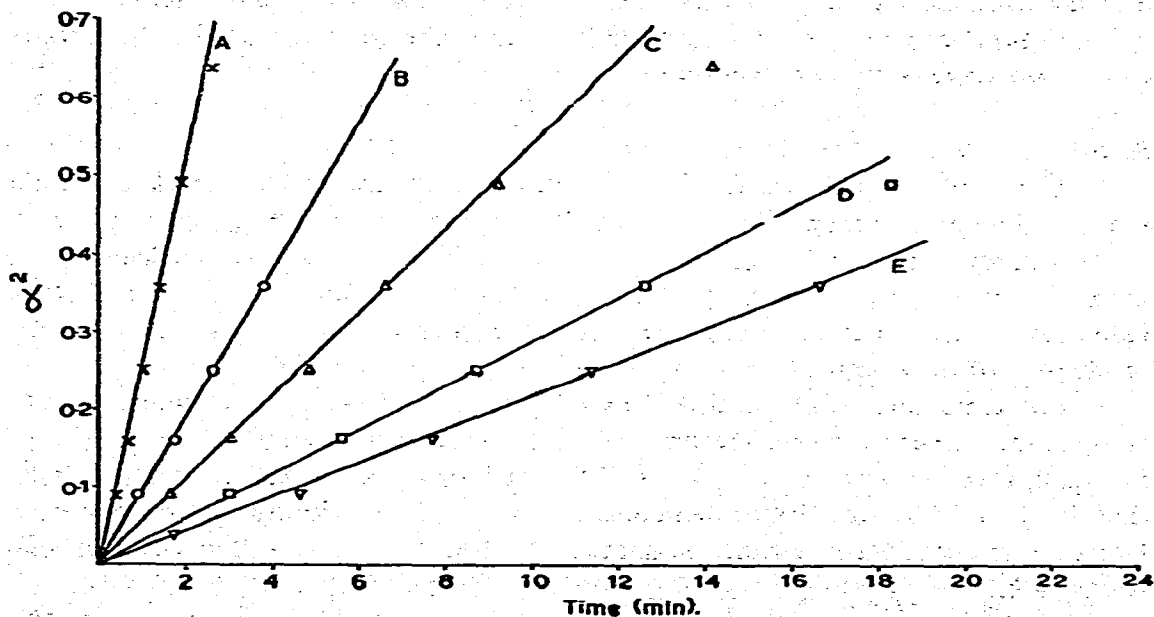


Fig. 3. Plot of parabolic law $\alpha^2 = kt$. Curve A, 567K, 0.6 kN m $^{-2}$; Curve B, 569K, 2.3 kN m $^{-2}$; Curve C, 569K, 0.13 mN m $^{-2}$; Curve D, 557K, 0.6 kN m $^{-2}$; Curve E, 557K, 3.2 kN m $^{-2}$.

TABLE I
 VARIATION OF ARRHENIUS PARAMETERS WITH WATER VAPOUR FOR THE FIRST STAGE IN
 THE DEHYDRATION OF C_3AH_6

Partial pressure of water	Isothermal diffusion		TG diffusion		TG nucleation and growth	
	Activation energy (kJ)	Log frequency factor (sec^{-1})	Activation energy (kJ)	Log frequency factor (sec^{-1})	Activation energy (kJ)	Log frequency factor (sec^{-1})
0.13 mN m^{-2}	84	6.43	88	7.0	185	6.9
0.6 kN m^{-2}	93	7.20	99	7.5	115	6.5
2.3 kN m^{-2}	114	8.98	112	9.8	109	6.2
3.2 kN m^{-2}	124	9.81	130	10.1	176	14.2

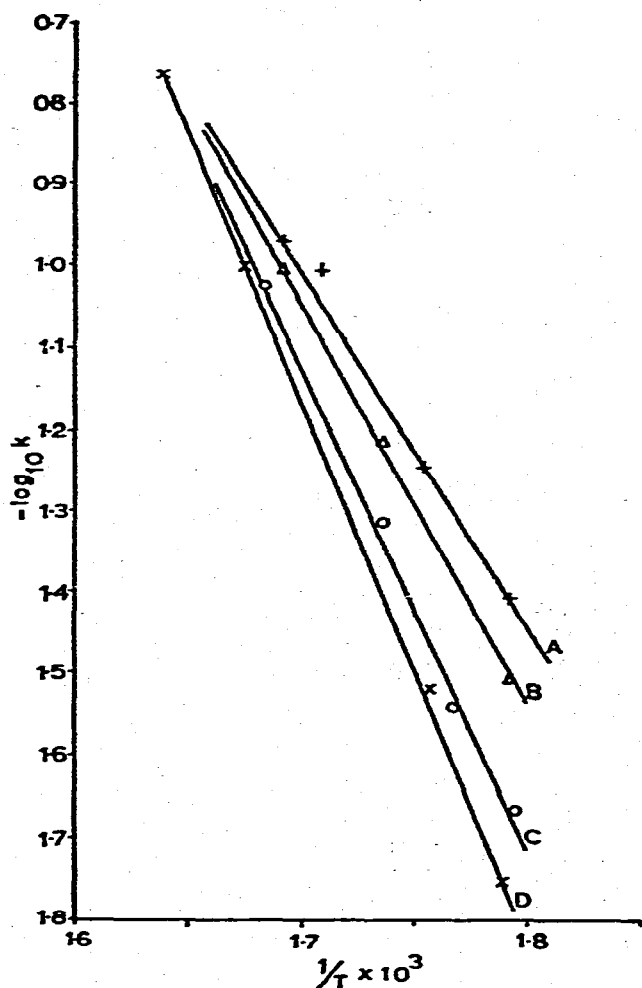


Fig. 4. Arrhenius plot for temperatures > 555 K. Curve A, 0.13 kN m^{-2} ; Curve B, 0.6 kN m^{-2} ; Curve C, 2.3 kN m^{-2} ; Curve D, 3.2 kN m^{-2} .

Runs carried out below 550 K showed different behaviour, in that the weight-loss curves showed increasing initiation periods as the temperature was lowered. At 507 K the best fit between experimental and calculated reduced time plots was in terms of the Avrami-Erofyev equation, with $n = 2$:

$$-\ln(1-\alpha)^{\frac{1}{2}} = kt$$

This equation implies that a nucleation and growth step is rate-controlling. The variation in reduced-time plot with temperature is shown in Fig. 5.

Temperature programmed heating

(a) *First stage.* The initiation periods for low temperature runs increased rapidly as the temperature was lowered and the time taken for a run became extremely long.

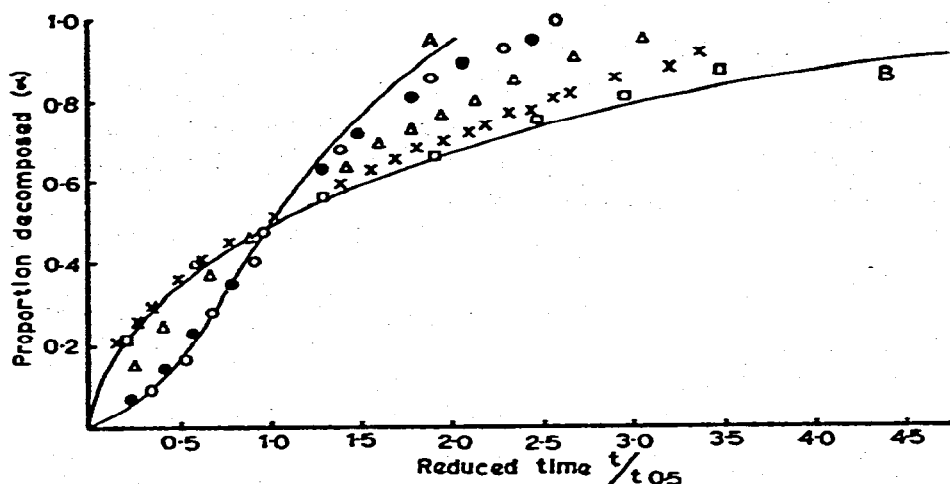


Fig. 5. Variation in mechanism with temperature at constant water vapour pressure. Curve A, Avrami-Erofyev plot ($n=2$), $-\ln(1-\alpha)^2 = kt$; Curve B, 2-dimensional diffusion, $(1-\alpha)\ln(1-\alpha) + \alpha = kt$. \circ 507K \times 569K; \bullet 520K; \square 577K; \triangle 537K. Pressure of water vapour = 0.13 mN m^{-2} .

The decomposition was therefore studied by TG and the curves interpreted by the method of Satava and Skvara⁷. This requires that a calculated curve, based on an assumed mechanism, be compared with another derived from the experimental TG curve, the variables involved being obviously the reaction mechanism and the Arrhenius parameters. It was assumed from the isothermal work that the first part of the reaction followed nucleation and growth kinetics and the latter part followed the parabolic law with the change at $\alpha = 0.4$. On this basis Arrhenius parameters were readily calculated from the TG curves and agreement between the isothermal and TG data for the diffusion process is very good (Table 1). This suggests that the method of data treatment is useful and lends support to the parameters calculated for the nucleation and growth process.

(b) *Second stage.* A few isothermal runs were carried out and reduced time plots suggested that the rate-controlling step was a phase boundary process occurring with spherical geometry. The best fit between experiment and theory was in terms of the

TABLE 2

VARIATION OF ARRHENIUS PARAMETERS FOR THE SECOND STAGE IN THE DEHYDRATION OF C_3AH_6

Partial pressure of water	Activation energy (kJ)	Log frequency factor (sec^{-1})
0.13 mN m^{-2}	63	8.2
0.6 kN m^{-2}	67	8.3
2.3 kN m^{-2}	60	7.9
3.2 kN m^{-2}	59	7.8

equation

$$[1 - (1 - \alpha)^3] = kt$$

The Satava-Skvara treatment was carried out on data from samples heated at 2, 3 and 5 K min⁻¹. Variation in water vapour pressure had little effect on the Arrhenius parameters calculated. These are included in Table 2.

Enthalpy of decomposition

The enthalpy of decomposition was calculated to be 260 kJ mol⁻¹, averaged over three runs.

DISCUSSION

Reaction mechanisms

If a chemical reaction occurs by two different mechanisms at different temperatures it would be expected that the process with the highest activation energy (i.e., temperature coefficient) should give way to a lower activation energy process at higher temperatures. From the results given in Table 1, it can be seen that the nucleation and growth step has a higher activation energy than the diffusion process at all water vapour pressures studied. It is satisfying that this expected change in mechanism has been observed in this case.

The nucleation and growth step

Both activation energies and frequency factors vary with external water vapour pressure, reaching a minimum at 2.3 kN m⁻². The activation energies are not particularly high for such a process and it seems likely that the rate is at least partly controlled by the variation in the frequency factor with water vapour pressure. Frequency factors in solid state reactions have been studied by Cordes⁸, who suggests that low values indicate a transition state with fewer degrees of freedom than a normal gaseous molecule ($A = 10^{13}$). This form of 'tight' complex can also be associated with a surface reaction, and this explanation best fits this case, since the increase in water vapour pressure parallels the increase in A to a value close to that for a gaseous molecule. Increases in external pressure are likely to affect the crystal surface by sorption more than the bulk of the material.

The value of $n = 2$ in the Avrami-Erofyev equation can be interpreted in two different ways: as two-dimensional nuclei growing from a constant number of nucleation sites or as one-dimensional nuclei growing from a linearly increasing number of sites. Attempts to determine how the number of nuclei changed with time were unsuccessful.

The diffusion-controlled regime

Again, both activation energy and frequency factors vary with water vapour pressure, but both increase linearly with the pressure. This suggests that the diffusion

process is a simple one and that the diffusing species is water. The frequency factors are again lower than 10^{13} suggesting a restricted transition complex.

It is considered that the low temperature nucleation and growth step, with its induction period, is the main reason for the rapid onset of decomposition. This rate-controlling step changes during the course of the reaction to one of diffusion, which, because it has a lower activation energy, gives a much slower rate of decomposition.

Dehydroxylation of calcium hydroxide

The results obtained in this work are very similar to those obtained by Mikhail et al.⁹, both in terms of mechanism and Arrhenius parameters. These authors have discussed the magnitude of the activation energy and decided that the phase boundary process was not single stage. Although they did not calculate frequency factors, values calculated from their paper are in agreement with the present work in being considerably less than 10^{13} sec^{-1} .

Enthalpy of decomposition

The measured enthalpy is $+260 \text{ kJ mol}^{-1}$ and the activation energy for decomposition should at least equal this value. An activation energy equal to the enthalpy would suggest a single-stage reaction; an activation energy less than the enthalpy indicates a multi-step process. The slowest of these steps is the true rate-determining step, and the activation energy, 185 kJ mol^{-1} , establishes the maximum enthalpy change which can occur in any step. The difference between the activation energy and the overall enthalpy establishes a minimum value for the enthalpy change in the individual steps, i.e., all the enthalpy changes must lie between 75 and 185 kJ mol^{-1} and total 260 kJ mol^{-1} .

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