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Dehydration kinetics of hydrated calcium dialuminate

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Abstract

Synthetically prepared calcium dialuminate samples were subjected to the hydration process at room temperature for different periods of time. Hydrated products have been identified by DTGA techniques. The thermogravimetric method has been applied to obtain dehydration rate curves in the 100–400°C range and formal first-order kinetics have been followed. The activation energy values of the dehydration reactions have been determined by studying the thermal stability of the hydrated calcium dialuminate. © 1997 Elsevier Science B.V.

1. Introduction

Calcium aluminate cements continue to be the most important hydraulically setting cements used for bonding refractory castable. The major hydraulic phase in all the commercially available calcium aluminate cement is monocalcium aluminate (CA; C=CaO, A=Al_2O_3). Calcium dialuminate (CA_2), although considered to be only a minor constituent, may constitute an important proportion, up to 54%, in more recently developed refractory cement [1,2]. Like CA, CA_2 also hydrates to form metastable CAH_{10} (H=H_2O) which slowly converts, first to C_2AH_8 and alumina gel and, finally, to stable cubic C_3AH_6 and monoclinic AH_3 [3,4]. Both the hydration and strength development take place at a slower rate in case of CA_2 [5,6]. It has been already shown [2], that CA is considered to be the hydraulic optimum, but perhaps requirements for a more refractory material will lead to a greater use of the hydraulic properties of CA_2. The hydration rate and strength development of CA_2 can be accelerated by autoclaving or using reactive additives which does not affect its high-temperature properties. It has been suggested [7] that the activation energy values of the hydration of the hydrated calcium aluminates may be utilized in explaining the stability of hydrated compounds. In the present investigation, dehydration characteristics have been studied by thermogravimetry and the activation energy values determined by using the Arrhenius equation to obtain some understanding about the thermal stability of hydrated CA_2.

2. Experimental

Reagent grade $Ca(OH)_2$ and $Al(OH)_3$ were dry mixed in a pot mill after required proportioning. The mixture was then shaped in the form of small balls using water as binder. The ball were dried and fired in an electric furnace at 1500°C for 2 h. The heating was done at an average rate of 5 °C min^{-1}.

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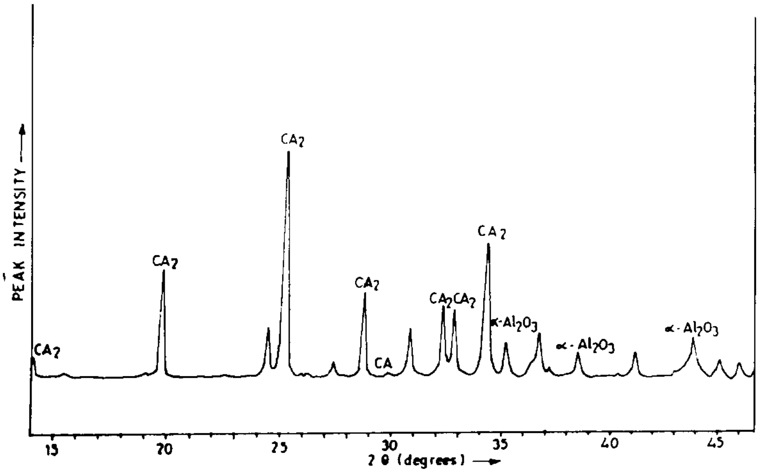

Fig. 1. XRD pattern of synthetically prepared anhydrous CA_2.

The material after heating was crushed and ground in a steel pot mill to a fineness of ~0.32 $m^2\,g^{-1}$. X-ray diffraction results (Fig. 1) confirmed the presence of CA_2 as the main constituent, although traces of CA and α-Al_2O_3 were also detected.

Synthetically prepared CA_2 samples were allowed for hydration at room temperature for a different period of time. 1 g of hydrated material was subjected to thermogravimetric analysis to study the dehydration characteristics of hydrated calcium dialuminate. The temperature during dehydration was accurately maintained within ±0.5°C.

3. Results and discussion

Differential thermogravimetric analysis curves for the hydrated calcium dialuminate in relation to curing time are shown in Fig. 2. The corresponding degrees of hydration are also shown in parentheses. It may be necessary to mention here that due to a very slow rate of hydration and strength development of CA_2, the one-day hydrated sample was not considered in this study. The curves of Fig. 2 indicate the formation of hydrated calcium aluminates (CAH_{10}, C_2AH_8 and C_3AH_6) and alumina gel during hydration of calcium dialuminate. Weight loss vs. time plot (Fig. 3) for three-day hydrated calcium dialuminate exhibits exponential behaviour, indicating the possibility of first-order kinetics. At a fixed temperature, if L_t is the weight loss at any time t, and L_α is the total weight loss at infinite time, $L_\alpha - L_t$ is the concentration of water remaining in the sample at any time t and, according to first-order kinetics, the rate of dehydration will be as follows:

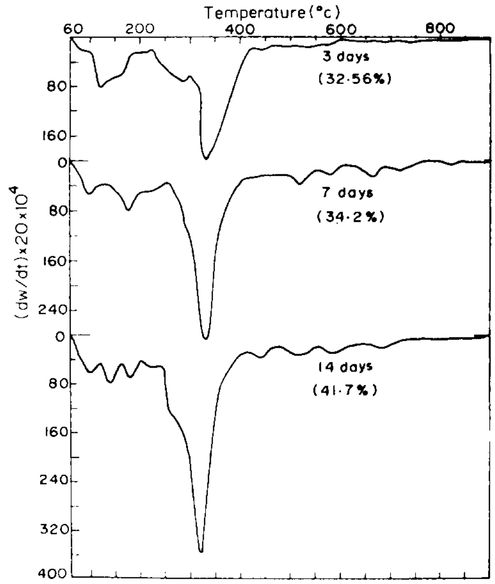

Fig. 2. DTGA curves for hydrated CA_2 in relation to curing time.

$$\frac{dL_t}{dt} = k(L_\alpha - L_t) \qquad (1)$$

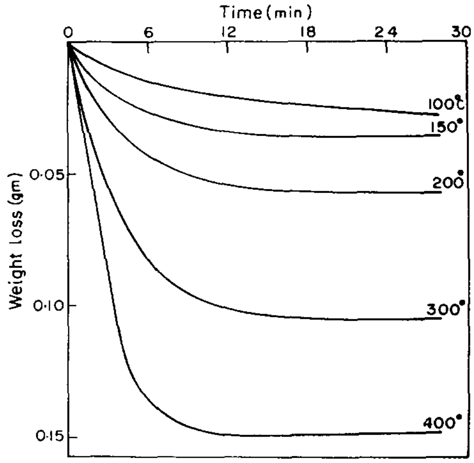

Fig. 3. Weight loss vs time curves at different fixed temperatures for CA_2 hydrated for three days.

The rate constant k can be determined from a plot of $\log(L_\alpha - L_t)/L_\alpha$ vs time.

The method originally suggested by Guggenhein and followed by Murray and White [8] may also be adopted. This method involves the use of the following equation:

$$\log\Delta L = \frac{kt}{2.303} + \log[L_\alpha\{l_\alpha - \exp(-k\Delta t)\}] \tag{2}$$

where ΔL is the difference between the weight loss at time $t + \Delta t$ and that at time t. The time interval Δt between the two sets of readings being kept fixed at a value greater than twice the time for 50% dehydration. The values of L_α, calculated by this method, do not differ substantially from the direct experimental determination using Eq. (1).

In the present investigation, L_α values were taken from direct experimental determination, while hydration at a particular temperature has been assumed to be complete when the weight loss becomes 0.0002 g in 5 min time or even lower. Plots of $\log[(L_\alpha - L_t)/L_\alpha]$ vs time at different temperatures for hydrated CA_2 samples are shown in Fig. 4. The rate constants of dehydration (k) at different temperatures were calculated from the slopes and the values presented in Table 1. The limits of applicability of the first-order law, as determined from the linearity of plots of $\log[(L_\alpha - L_t)/L_\alpha]$ vs time, varied from 90 to 95%.

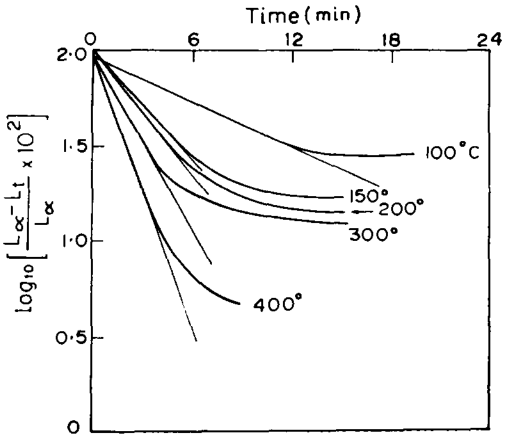

Fig. 4. Isothermal dehydration rate curves for hydrated CA_2.

Table 1
Rate constants of dehydration of hydrated calcium dialuminate in relation to temperature

k values (min^{-1}) at different temperatures				
100°C	150°C	200°C	300°C	400°C
0.087	0.222	0.252	0.340	0.545

Arrhenius plots for the samples using rate constants from the Table 1 are shown in Fig. 5. The activation energy of the dehydration reaction calculated from the

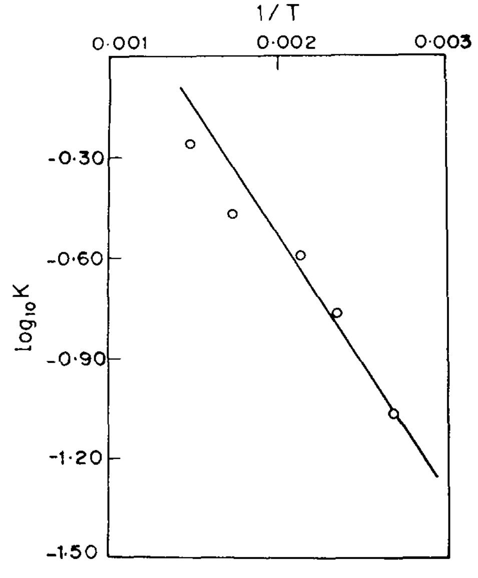

Fig. 5. Arrhenius plot for hydrated CA_2.

Table 2
Activation energy for dehydration of hydrated calcium aluminates

Sample	Activation energy/(cal/g mol)
CA_2	3558
CA	5152

Arrhenius equation is shown in Table 2 along with that of activation energy of hydrated monocalcium aluminate determined earlier [9].

The values indicate that the thermal stability of hydrated calcium dialuminate is less than hydrated monocalcium aluminate. This study has significance in that high alumina cement containing calcium dialuminate is often used in the preparation of refractory castables [10] where dehydration is accompanied by reduction in mechanical strength up to sintering temperature, beyond which ceramic bonding starts and strength gradually improves [5,11].

4. Summary

Hydrated calcium aluminates, such as CAH_{10}, C_2AH_8, C_3AH_6 and alumina gel, are formed during hydration of calcium dialuminates. The activation energy value for dehydration of hydrated calcium dialuminate indicates lower thermal stability of hydrated calcium dialuminate.

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