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Dehydration kinetics of calcium aluminate cement hydrate under non-isothermal conditions

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Abstract

Calcium aluminate cement (containing 75% Al_2O_3), which finds extensive high temperature applications, was synthesized by sintering a mixture of calcined alumina and synthetic calcium carbonate. The cement was hydrated and its kinetics of thermal dehydration was studied under non-isothermal conditions by thermo-gravimetry using the integral approximation model. It was observed that on heating the cement hydrate followed multistage dehydration with different reaction orders at different stages. The activation energies of dehydration for these different stages were compared.

Keywords: High alumina cement hydrate; Kinetics; Dehydration; Non-isothermal

1. Introduction

Various researchers have been working on the hydrates of calcium aluminate cement [1–6], which finds widespread uses in making castable refractories (containing refractory aggregates and cement) and also as a high temperature furnace liner. The development of initial strength in the castable refractories takes place by hydraulic bonding of the cement. At elevated temperature, the hydraulic bonds break due to the liberation of bonded water from the hydrate structures. At still higher temperature, ceramic bond formation takes place by the inter-diffusion of atoms and ions among the components to develop an energetically stable structure. In the interim period of hydraulic bond breaking and ceramic bond formation, the strength of the cement deteriorates as a natural consequence. Thus, this period is quite crucial for the initial heating of the furnace lined with castables or with the cement alone. A study on kinetics of dehydration of this cement hydrate would help in understanding the rate of the process.

In the present investigation, the kinetics of thermal dehydration of calcium aluminate cement hydrate was studied under non-isothermal conditions as the temperature inside the furnace continuously changes during the heating up of the furnace. This study will also help in determining the optimum heating up schedule of the furnace lined with calcium aluminate cement based castables for retention of critical strength of the refractory lining without any damage. Kinetic parameters such as order of the reaction and activation energy for the dehydration reaction were determined from this study.

2. Experimental

In the present investigation 75% alumina containing cement was synthesized by fusing technical alumina and limestone in the required mole proportion at 1550 °C for 3 h in an electrically heated muffle furnace followed by grinding of the fused mass. Chemical analysis of the cement sample was carried out by sodium carbonate fusion method. Surface area of the cement was measured by permeametry with Blain's apparatus. Bulk density of the cement was determined by measuring the weight of a fixed volume of

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Table 1
Chemical composition of calcium aluminate cement

Constituents	wt.%
Al_2O_3	74.48
CaO	24.21
SiO_2	0.48
Fe_2O_3	0.43
TiO_2	0.02
MgO	0.1
Na_2O	0.22
K_2O	0.05

the powder sample. Physico-chemical properties of the cement, thus measured, are given in Tables 1 and 2.

The hydration of the cement was carried out first by making paste of the cement, which was subsequently nodulized. The nodules were kept under saturated humidity in a humidity chamber for one week. After that the nodules are allowed to dry under ambient condition. The nodules were then crushed into powder in such a way that it passes through a 72 mesh sieve. FT-IR spectra of the cement hydrate were taken with a Perkin-Elmer instrument. Thermo-gravimetric analysis of the samples was carried out with a thermo-balance (model Okay, TG1200, India) in the form of a loose powder to ascertain the dehydration kinetic parameters.

3. Results and discussion

In the FTIR spectra of the hydrated cement sample (Fig. 1) seven peaks were observed. The peak at 3753.6 cm^{-1} was assigned to the surface moisture or free moisture of the hydrated sample. Presence of bonded water in the form of aluminium hydroxide gel and calcium aluminate hydrate ($CaOAl_2O_3 \cdot 10H_2O$) was indicated by the peak at 3461 cm^{-1}.These two peaks appeared due to the stretching vibration of the –OH groups. The peak at 1492 cm^{-1} was assigned to the bending vibration of the –OH group. The peaks at 1029 cm^{-1}, 777.3 cm^{-1} and 533 cm^{-1} were assigned to the stretching and bending vibrations of the Al–O bonds.

The cement hydrate on heating steadily looses water continuously.

Table 2
% Transmission and wave number of the FTIR spectral peaks for the hydrated samples

Transmission (%)	Wave number (cm^{-1})
42.40	3753.6
38.0	1029.0
38.04	3460.9
39.38	777.3
42.21	2368.8
39.04	533.0
37.90	1492.0

Physical properties of the cement: appearance = white; surface area = 4700 m^2/gm; bulk density = 2.08 gm/cc.

The rate for thermal dehydration of high alumina cement hydrate for the reaction,

CA cement hydrate → anhydrous phase + water, is given by:

$$-\frac{dW}{dt} = KW$$

By incorporating the Arrhenius equation:

$K = A\,e^{-E/RT}$ and the heating rate, $h = dT/dt$, and rearranging, we get:

$$\left[-\frac{1}{W}\frac{dW}{dT}\right] = \frac{A}{h}e^{-E/RT}$$

The rate equation may also be expressed in terms of fractional conversion X and the reaction order n as follows:

$$X = \frac{W_0 - W}{W_0 - W_\infty}$$

$$-\frac{dX}{dt} = K(1 - X)^n$$

By incorporating the expressions of heating rate h and the rate constant K in the above equation, and rearranging and integrating, the following equation can be written as:

$$\int_0^X \frac{dX}{(1 - X)} = \frac{A}{h}\int_0^T e^{-E/RT}\,dT$$

The equations given by Agarwal and Sivasubramanium model [7] are as follows:

$$\mathrm{Ln}\left[-\frac{\mathrm{Ln}(1 - X)}{T^2}\right] = \mathrm{Ln}\left[\frac{AR}{hE}\left(\frac{1 - 2RT/E}{1 - 5(RT/E)^2}\right)\right]\frac{E}{RT}$$

$$\mathrm{Ln}\left[\frac{-\mathrm{Ln}\{1 - (1 - X)^{1-n}\}}{(1 - n)T^2}\right] = \mathrm{Ln}\left[\frac{AR}{hE}\left(\frac{1 - 2RT/E}{1 - 5(RT/E)^2}\right)\right]\frac{E}{RT}$$

Therefore, a plot of $\mathrm{Ln}[-\mathrm{Ln}(1 - n)/T^2]$ versus $1/T$ for $n = 1$ and $\mathrm{Ln}[-\mathrm{Ln}\{1 - (1 - n)^{1-n}\}/(1 - n)T^2]$ versus $1/T$ for $n \neq 1$ gives the value of E.

In the DTGA diagram (Fig. 2) of the samples several peaks appeared at different temperatures. The different dehydration stages with the rise in temperature were attributed to the following phenomena:

(i) Removal of surface bonded water
(ii) Dehydration of aluminium hydroxide gel
(iii) Dehydration of CAH_{10} to C_2AH_8
(iv) Dehydration of C_2AH_8 to C_3AH_6
(v) Dehydration of C_3AH_6 to anhydrous CA

To determine the exact order of reaction at different stages (corresponding to different peaks at the DTGA diagram), the regression coefficient and standard error values of the linear plots for different n values (as described above)

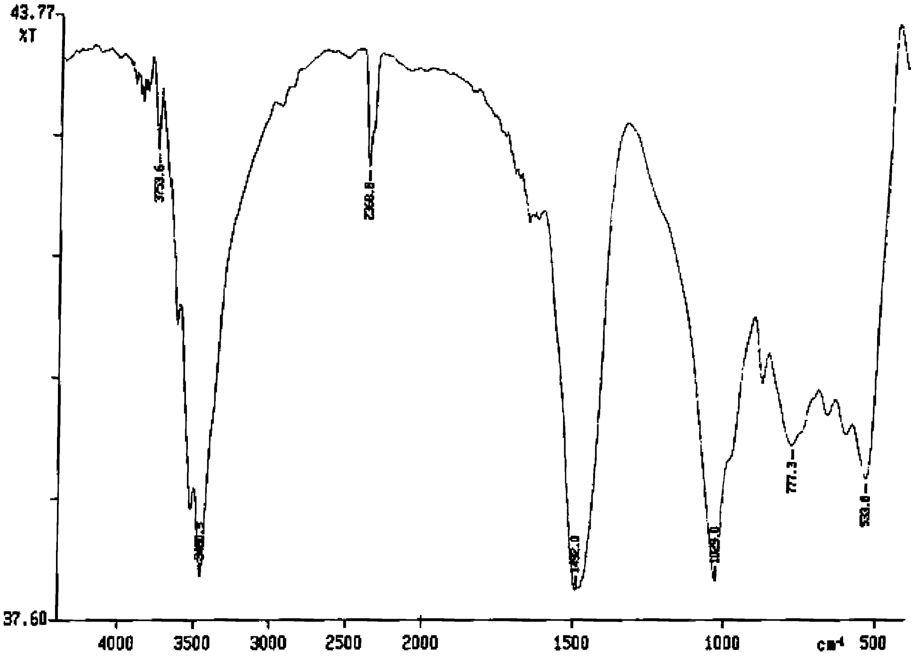

Fig. 1. FT-IR spectra of calcium aluminate cement hydrate.

were analyzed by trial and error method. The *n* value for which the maximum regression coefficient was obtained at each stage was taken as the order of the reaction (Table 3).

Activation energies for each stage of dehydration were calculated from the slope of the linear plots as explained above. It was observed that activation energies increased first up to 900 K and afterwards they gradually decreased with the increase in temperature. The increase in activation energy might be due to the collapsing of lattice of the calcium aluminate hydrates following dehydration and to the increase in cationic field of aluminium cation with the dehydration of the gel. After 900 K the decrease in activation energy might be due to the disintegration of compact structure, which facilitated the liberation of water molecules from the calcium, aluminate hydrates.

It has been further observed that up to 525 K, the order of the dehydration reaction at different stages was less than 1. The rate of dehydration probably depends on the concentration of physically bonded water molecules in the cement hydrate. Between the temperature range 525–675 K, the reaction followed 1st order reaction. Probably the concentration of both physically and chemically bonded surface

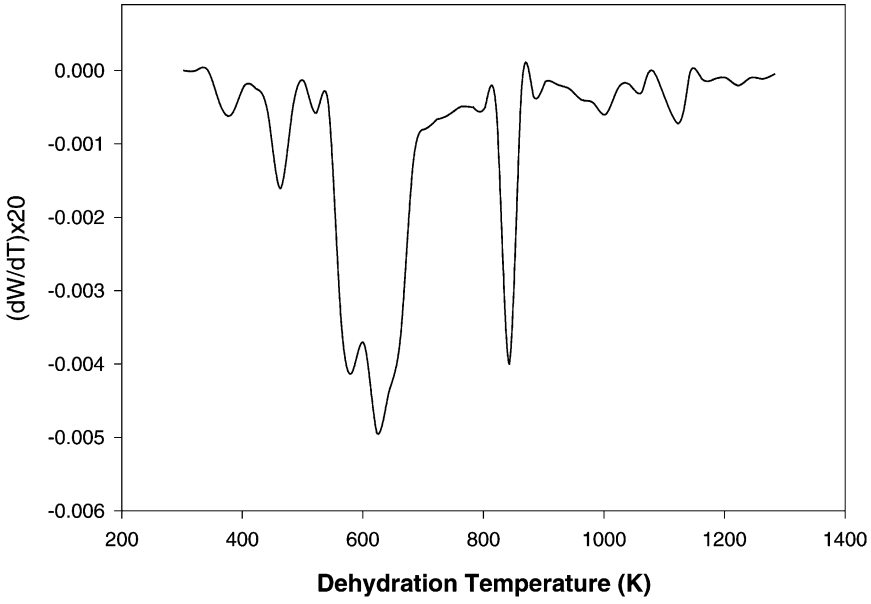

Fig. 2. DTGA diagram of the hydrated cement sample.

Table 3
Order of reactions for various stages

Temperature range (K)	R^2	n	E (KJ/mol)
325–385	0.9884	0.87	7.52
385–485	0.9879	0.90	8.48
485–525	0.9821	0.96	9.73
525–575	0.9885	1.00	17.69
575–675	0.9814	1.00	23.35
675–850	0.9865	1.15	43.87
850–900	0.9832	1.20	47.79
900–985	0.9854	1.38	14.53
985–1025	0.9871	1.42	10.87
1025–1175	0.9864	1.67	8.59

water molecules of the cement hydrate controlled the rate in this stage. Beyond 675 K, the reaction order was more than 1 and it might be due to the fact that concentration of water molecules both at the surface and inside the calcium aluminate hydrate structure plays a role.

4. Summary and conclusions

Dehydration kinetics of calcium aluminate cement, synthesized by reaction between calcium carbonate and calcined alumina powder at elevated temperature, was studied from thermo-gravimetry under non-isothermal condition. A multi-stage dehydration reaction was observed which occurred with different reaction orders at different stages. The progressive collapsing of layers as a result of dehydration probably increased the activation energy for dehydration at the initial stage, but afterwards the disintegration of the lattice at elevated temperatures caused a reduction in activation energy.

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