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THERMAL ANALYSIS OF HYDRATED CALCIUM ALUMINATES

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Abstract

Differential scanning calorimeter (DSC) has been used to study the dehydration characteristics of hydrated calcium aluminates such as CA, CA_2 and $C_{12}A_7$ where C and A stand for CaO and Al_2O_3 respectively. Dehydration of CAH_{10} and C_2AH_8 (where $H=H_2O$) occur ˜ at 160–180°C and 200–280°C respectively. These two phases are unstable and ultimately get transformed to AH_3 and C_3AH_6. Dehydration of AH_3 and C_3AH_6 occur between 290 and 350°C and overlap at lower scanning rate. The activation energy for dehydration of the stable AH_3 and C_2AH_6 phases has been found to be 107.16 and 35.58 kJ mol^{-1} respectively. The compressive strength of the hydrated calcium aluminates has been determined. The result shows that in the case of CA, almost 90% of ultimate strength has been attained in 1 day whereas in CA_2, ultimate strength has been attained in 14 days and in $C_{12}A_7$ in 1 day. DSC results have been correlated with the rate of strength developments.

Keywords: calcium aluminates, cement, DSC

Introduction

Calcium aluminate cement is considered to be the most hydraulically setting cement used for bonding refractory castables. The $CaO–Al_2O_3$ binary equilibrium diagram [1] provides useful informations regarding the existence of various calcium aluminates which are the important hydraulic phases of calcium aluminate cement having wide refractory application. The mineralogical composition of some commercially available calcium aluminate cement shows that it typically contains 2–6% $C_{12}A_7$, 37–46% CA, 13–30% CA_2 and 20–44 % α-Al_2O_3 where C and A stand for CaO and Al_2O_3 respectively [2]. When water is added in it, various hydrated phases form leading to changes in both physical and chemical properties of the cement. Water converts various anhydrous calcium aluminates into different hydrated phases. Formation of these phases depend on both hydration temperature [2–7] and time [2, 7]. Different hydrau-

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lic phases are mainly responsible for the setting properties of these castables. During firing this hydrated products are recrystallized and the required setting properties are obtained at a temperature which is much below the temperature required for anhydrous calcium aluminates. So the knowledge of formation of different hydrated phases and their dehydration characteristics are necessary for any field application.

Recently, hydration reaction process of calcium aluminate cement has been studied [8–11] using DSC. In comparison to TG, this method reflects more precisely the cement hydration process. Therefore, an attempt has been made in the present work to study the hydration of three different calcium aluminates namely CA, CA_2 and $C_{12}A_7$ using differential scanning calorimeter.

Sample preparation

Reagent grade BDH quality $Al(OH)_3$ and $Ca(OH)_2$ were used in the present work. These raw materials were intimately dry mixed in the stoichiometric ratio. Small balls were then prepared using water as binder. These balls were dried and heated in a furnace at 1500°C (2 h soaking) for CA and CA_2 and at 1380°C (2 h soaking) for $C_{12}A_7$. The materials after heating were crushed and ground to a fineness of about 0.32 to 0.34 $m^2 g^{-1}$ without any foreign contamination. Briquettes were made from the prepared calcium aluminate using 12.5% water at room temperature (25–30°C). These were cured in the moist atmosphere of about 90% humidity for 10–12 h within the mould and then kept in water for hydration.

Experimental

Calorimetric study was made after different days of hydration using differential scanning calorimeter (DSC-7, Perkin-Elmer, USA). 8–12 mg of hydrated sample were taken for this study. Heating rate was maintained at 10°C min^{-1}. Higher heating rates (20, 30°C min^{-1} and so on) were used for the determination of activation energy of different phases.

Prepared calcium aluminates were mixed with –20+60 BS size fraction of IS-8 fireclay refractory aggregate in the proportion of 1:3 by weight for compressive strength measurement. Compressive strength was measured in a specially made miniature hydraulic press [7].

Results

X-ray diffraction patterns of anhydrous CA, CA_2 and $C_{12}A_7$ are shown in Fig. 1(a), (b) and (c) respectively. It appears from these figures that anhydrous monocalcium aluminates contain CA as major and CA_2, α-Al_2O_3 as minor components. Calcium dialuminate contains CA_2 as a major with minor amounts of CA and α-Al_2O_3. $C_{12}A_7$ contains major amount of $C_{12}A_7$ with CA and CA_2 as minor phases.

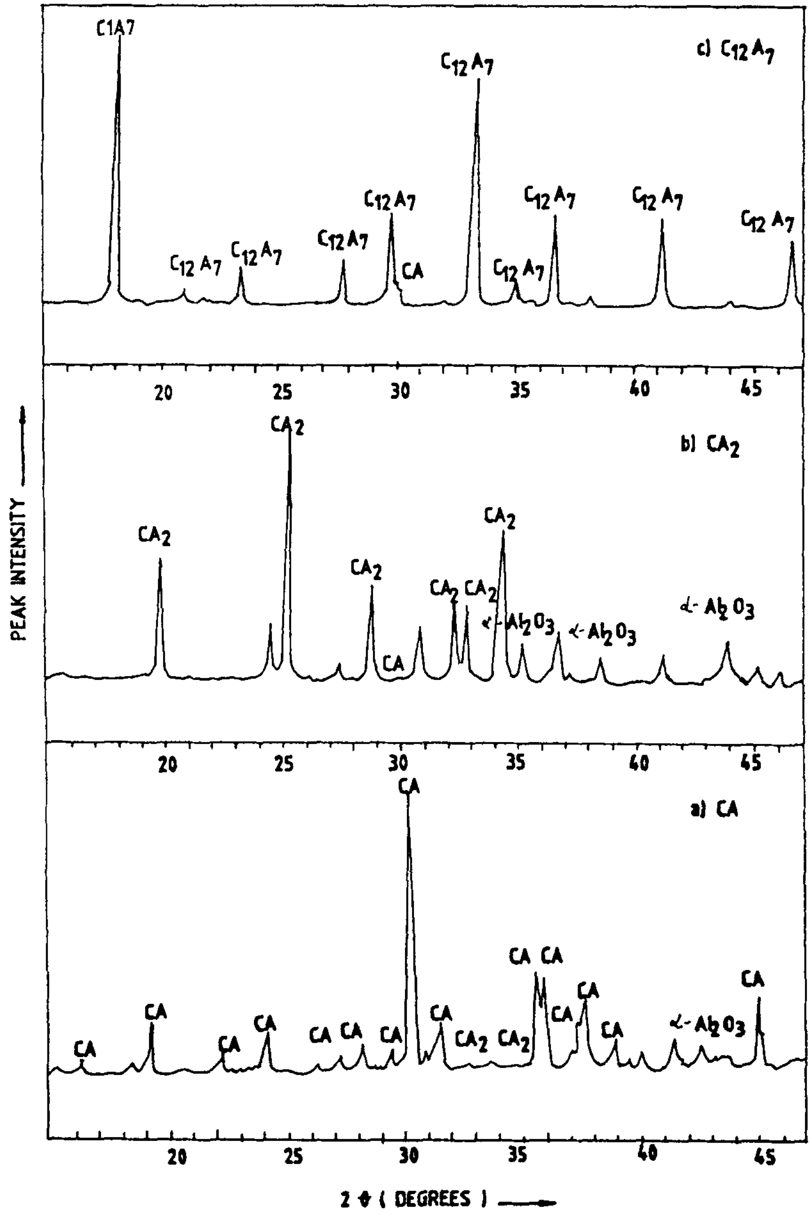


Fig. 1 X-ray diffractogram of anhydrous calcium aluminates a) CA, b) CA_2 and c) $C_{12}A_7$

Hydration reaction starts just after addition of water in anhydrous calcium aluminate. Initially, only a small portion of the cement takes part in the hydration reaction. The hydrate first nucleates and then grows with time leaving the rest of the anhydrous cement dissolved in water. Figure 2(a), (b) and (c) represent the amount of heat flow for hydrated CA, CA_2 and $C_{12}A_7$ respectively after different days of hydration at 10°C min^{-1}. Endothermic peak corresponds to the dehydration of different hydrated phases. Figure 3(a), (b) and (c) show the total amount of heat absorbed during the transformation of hydrated phases of CA, CA_2 and $C_{12}A_7$ respectively. Dehydration characteristics of CA samples have also been measured at different scanning rate (Fig. 4). The overall compressive strength after different days of hydration are shown in Fig. 5.

Discussion

Hydration of CA

Three characteristic temperatures are observed when CA is heated after 1 day of hydration. Endothermic peaks observed at 175 and 300°C are easily identified as dehydration of CAH_{10} and AH_3 gel respectively [2]. The peak which appeared at 275°C after 1 day of hydration may be due to the formation of a complex C_2AH_8 phase. This phase finally transformed to simple C_2AH_8 phase which is indicated by the presence of the peak at 230°C after 28 days of hydration. With the increase of hydration period C_3AH_6 phase starts growing. Formation of this phase which is dehydrated at 320°C is quite prominent after 7 days of hydration. As the strength of non-hydraulic phase C_3AH_6 is very low, the strength of hydrated CA starts decreasing with the formation of considerable amount of C_3AH_6 (Fig. 5). CAH_{10}, C_2AH_8 and AH_3 gel phases are metastable. Vanishing of dehydration peak at around 170°C after 28 days of hydration and decrease of the amount of heat absorbed with the hydration period for the dehydration of C_2AH_8 (Fig. 3a) indicate the unstability of these two phases. AH_3 gel changes to AH_3 crystalline with hydration. As the dehydration of AH_3 gel and crystalline occur almost at the same temperature, calorimetric method is not suitable to identify these two forms. However, microstructural study and XRD reveal the formation of AH_3 crystalline and C_3AH_6 phases after 28 days of hydration [7}. As dehydration of AH_3 and C_3AH_6 occur at a very close tempe- rature and the heat energy for dehydration of AH_3 is much higher than that for the dehydration of C_3AH_6, these dehydration peaks get overlapped at slow scanning rate (say, 10°C min^{-1}). So the total heat energy for the dehydration of AH_3 and C_3AH_6 phases are plotted together (Fig. 3a). These two dehydration peaks are well separated in DSC at higher scanning rates (Fig. 4). Increase of the total heat energy, evolved for the dehydration of $(AH_3+C_3AH_6)$, indicates the in-

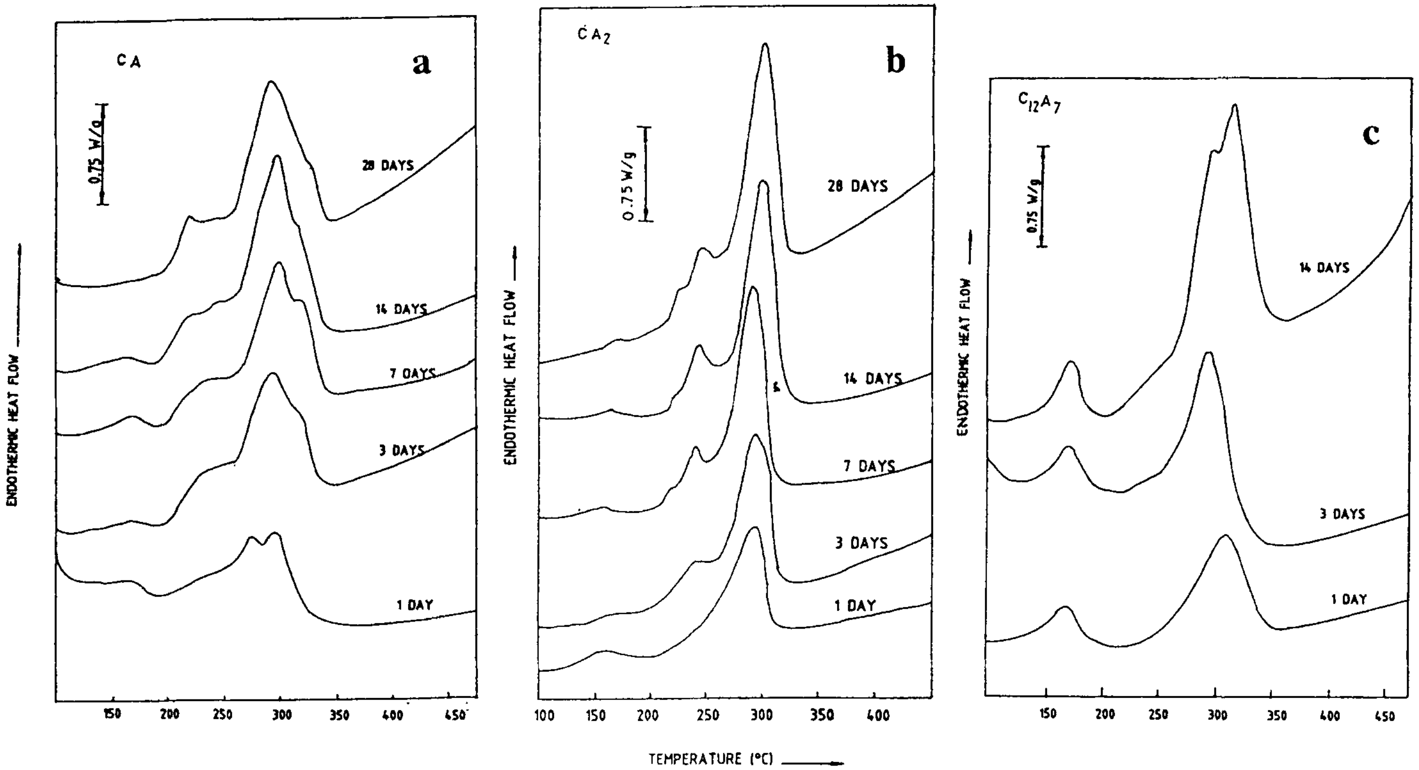


Fig. 2 Calorimeter output of hydrated CA after different days of hydration (a); Calorimeter output of hydrated CA_2 after different days of hydration (b); Calorimeter output of hydrated $C_{12}A_7$ after different days of hydration (c)

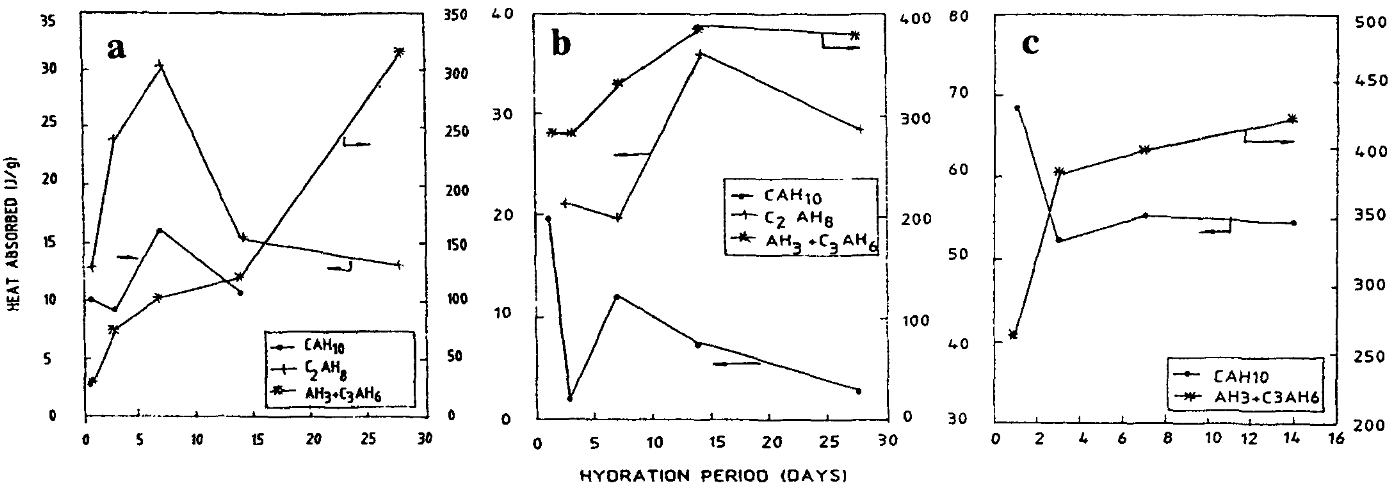


Fig. 3 Plot of total heat energy absorbed during dehydration of each phases of hydrated CA against the hydration period (a); Plot of total heat energy absorbed during dehydration of each phases of hydrated CA_2 *vs.* the hydration period (b); Plot of total heat energy absorbed during dehydration of each phases of hydrated $C_{12}A_7$ *vs.* the hydration period (c)

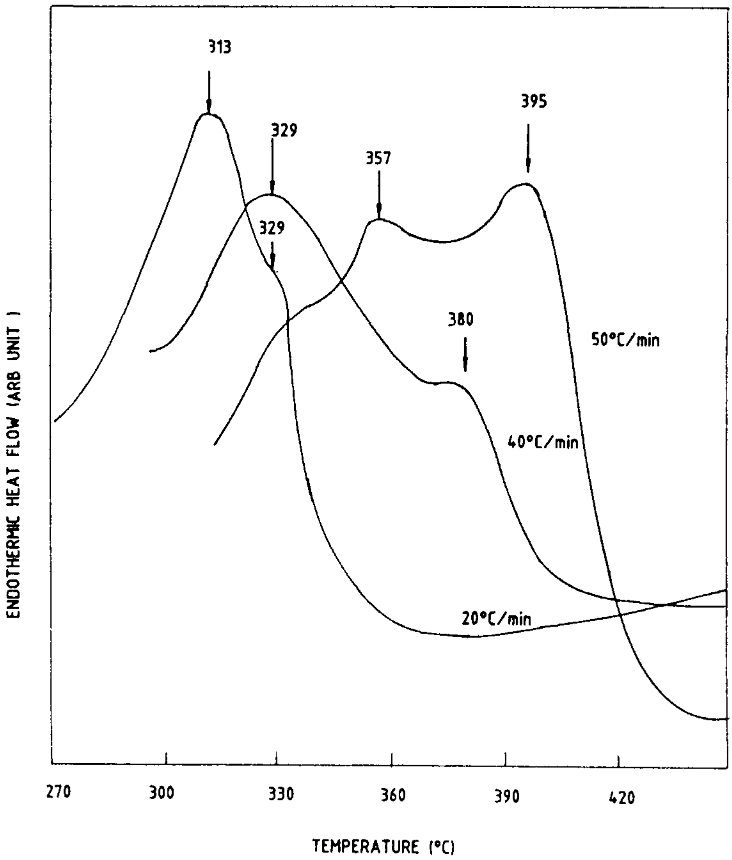


Fig. 4 Calorimeter output of hydrated CA at different scanning rate after 28 days of hydration

crease of these two phases with the hydration period. The schematic reaction for the hydration of CA can be written according to the present study as,

$$CA \xrightarrow{+H} CAH_{10} + (C_2AH_8)_{complex} + (AH_3)_{gel} \xrightarrow{+H} CAH_{10} +$$
$$C_2AH_8 + (AH_3)_{gel} \xrightarrow{+H} CAH_{10} + C_2AH_8 + (AH_3)_{gel} +$$
$$(AH_3)_{cryst.} + C_3AH_6 \xrightarrow{+H} (AH_3)_{cryst.} + C_3AH_6.$$

Activation energy (E_a) for the dehydration of AH_3 and C_3AH_6 have been calculated from the DSC curves at different scanning rates using Kissinger's relation [12]

$$\frac{V}{T_m^2} = \exp(-E_a/RT_m) \quad (1)$$

where E_a=Activation energy, V=Scanning rate, T_m=Peak transition temperature, R=Gas constant.

Kissinger's relation is plotted in Fig. 6 for the dehydration of AH_3 and C_3AH_6. The slope of the line give an estimation of the activation energy and was found to be 107.16 kJ mol^{-1} and 35.58 kJ mol^{-1} for the dehydration of AH_3 and C_3AH_6 respectively.

Hydration of CA_2

Figure 2b gives the DSC curves after different days of hydration of CA_2. Only CAH_{10} and AH_3 phases are found after 1 day of hydration which are dehydrated around 165 and 295°C respectively. Appearance of C_2AH_8 is prominent after 3 days of hydration. Higher heat energy involved during the dehydration of AH_3 (Fig. 3b) indicates that the formation of AH_3 phase in hydrated CA_2 sample is much more than that in CA. This is expected as CA_2 contain more Al_2O_3. The strength of hydrated CA_2 is found to increase (Fig. 5b) up to the highest measured hydration period (14 days). This behavior of CA_2 suggests that a mixture of CA and CA_2 is good for practical application. Hydrated calcium aluminate ultimately get transformed to the stable C_3AH_6 as AH_3 crystalline phase. But in the present DSC study of CA_2, there is no indication of the formation of C_3AH_6. This may be due to the slow reaction process and/or the presence of small

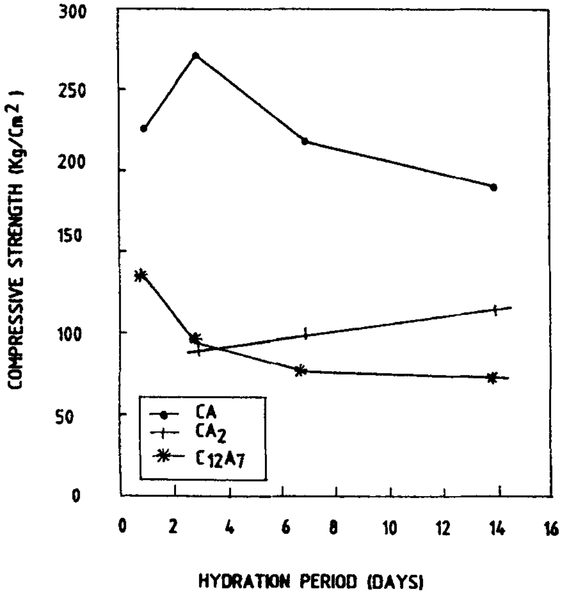


Fig. 5 Compressive strength of hydrated CA, CA_2 and $C_{12}A_7$ after different hydration using IS-8 as aggregate

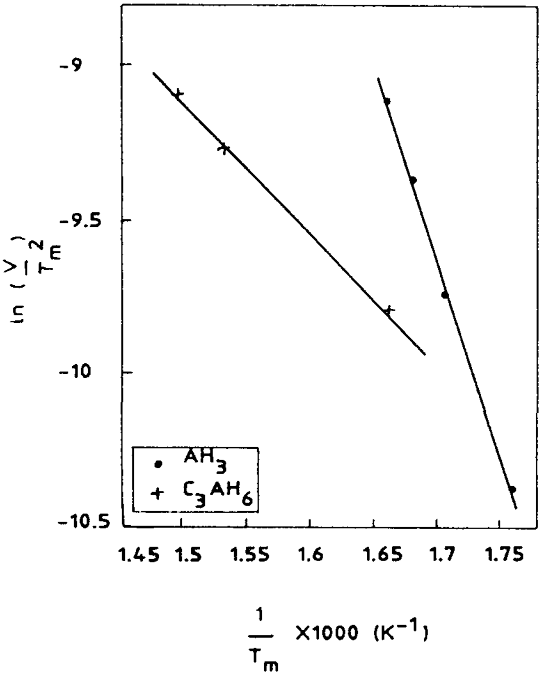


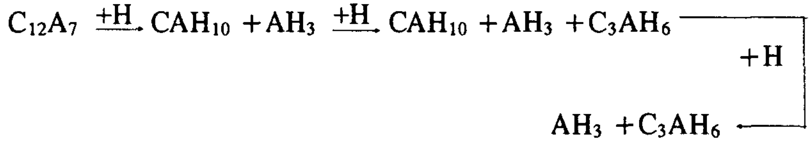
Fig. 6 Kissinger's plot for determination of activation energy for dehydration of AH_3 and C_3AH_6 phases

amount of C_3AH_6 whose dehydration peak is overshadowed by the presence of higher amount of AH_3 and CA_2 contain higher amount of Al_2O_3. Continuous increase in strength for hydrated CA_2 up to the measured hydration period also indicate that nonhydraulic C_3AH_6 phase is not prominent for hydrated CA_2 in the present study. The dehydration reaction scheme for CA_2 can be written as,

$$\begin{aligned}&CA_2 \xrightarrow{+H} CAH_{10} + (AH_3)_{gel} \xrightarrow{+H} CAH_{10} + C_2AH_8 + (AH_3)_{gel} \xrightarrow{+H}\\ &C_3AH_6 + (AH_3)_{cryst.} \xleftarrow{+H} C_2AH_8 + (AH_3)_{gel} + (AH_3)_{cryst.} \longleftarrow\end{aligned}$$

Hydration of $C_{12}A_7$

DSC curves of different hydrated $C_{12}A_7$ are shown in Fig. 2(c). Broadening of dehydration peak at 310°C indicates that C_3AH_6 together with AH_3 phases are formed within 1 day of hydration. The peak at 170°C corresponds to the dehydration of CAH_{10}. A considerable amount of C_3AH_6 phase is formed after 14 days of hydration. The decrease of strength after 1 day hydration is expected as the nonhydraulic C_3AH_6 phase is formed within 1 day of hydration. The reaction scheme for the hydration of $C_{12}A_7$ is as follows,



$$C_{12}A_7 \xrightarrow{+H} CAH_{10} + AH_3 \xrightarrow{+H} CAH_{10} + AH_3 + C_3AH_6 \xrightarrow{+H} AH_3 + C_3AH_6$$

Conclusion

Hydration characteristics of three high alumina cements namely CA, CA_2 and $C_{12}A_7$ have been studied using differential scanning calorimeter. The major hydraulic phases for calcium aluminates are CAH_{10}, C_2AH_8, AH_3 and C_3AH_6. Out of these, CAH_{10} and C_2AH_8 are metastable. Dehydration of CAH_{10} and C_2AH_8 occur in between 160–180°C and 200–280°C respectively. The activation energy for the dehydration of stable AH_3 and C_3AH_6 phases are respectively 107.16 kJ mol^{-1} and 35.58 kJ mol^{-1} respectively. Hydration of CA_2 is very slow compared to the hydration of CA and $C_{12}A_7$ is highly reactive. Compressive strength measurement shows that almost 90% of the ultimate strength is attained after 1 day of hydration of CA whereas in CA_2 a continuous increase in strength is observed up to the measured duration of hydration (14 days). In case of $C_{12}A_7$ strength starts decreasing within 1 day of hydration. The formation of nonhydraulic C_3AH_6 phase is responsible for the strength reduction.

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