

Crystal morphology of calcium aluminates hydrated for 14 days

S. K. DAS, S. KUMAR, S. K. DAS*

FRP Division and *MTC Division, National Metallurgical Laboratory, Council of Scientific and Industrial Research, Jamshedpur 831 007, India

P. K. DAS PODDAR

Department of Chemical Technology, Calcutta University, 92 APC Road, Calcutta 700 009, India

The active phases during early hydration of calcium aluminate cement are CA ($C = CaO$; $A = Al_2O_3$) and $C_{12}A_7$, but CA_2 seems to be fairly inactive before the massive precipitation [1]. The phenomenon of strength degradation of calcium aluminates as related to the phases transformation, i.e., conversion of metastable transition phase CAH_{10} ($H = H_2O$) into unstable C_2AH_8 and finally stable C_3AH_6 phase [2–4]. Many researchers [5–7] have investigated the development of these hydrated phases by electron microscopy. The effects of crystal morphology on the hydration characteristics and setting time have also been studied by some workers [8–9]. The aim of the work reported here is to investigate exactly what the crystal habit and morphology are on the fourteenth day of hydration of calcium aluminates, and what their role is in the development of compressive strength of the hydrated samples.

Calcium aluminates such as CA, CA_2 and $C_{12}A_7$ were synthetically prepared from the reagent grade $Al(OH)_3$ and $Ca(OH)_2$ raw materials using the same method adopted by the present authors in other work [10–12]. Cubic briquettes of 1.25 cm sides were prepared from a mortar consisting of calcium aluminates (individual and mixes) and calcined bauxite aggregate adopting the method followed by Parker [13]. The following combinations were selected for the present work: (a) CA; (b) CA_2 ; (c) $C_{12}A_7$; (d) $CA_2:CA = 1:1$; (e) $CA_2:CA:C_{12}A_7 = 2:1:1$; (f) $CA_2:CA:C_{12}A_7 = 8:1:1$.

The size fraction of the aggregate was maintained at $-20 + 60$ BS sieve. Calcium aluminate cement powder and aggregate were used in the mortar in the proportion of 1:3 by weight and the water-to-cement ratio was 0.50. The briquettes were allowed to undergo hydration under water at room temperature (around 25 °C) for 14 days. The compressive strength of the hydrated briquettes were measured using manually operated hydraulic press. The briquette specimens hydrated for 14 days were subjected to scanning electron microscopy (SEM) studies. The instrumental parameters for the SEM studies were as follows: JEOL model JSM 840 A, Japan, microscope; range, 40 kV; resolution, 4 nm. The photomicrographs were taken on the specimen after it had been gold coated by ion sputtering. The coating thickness was between 150 and 200 Å.

Fig. 1 shows the histogram of compressive strength data of calcium aluminates hydrated for 14 days. The following order of strength develop-

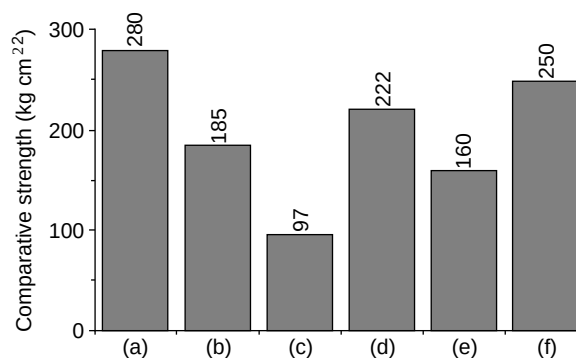


Figure 1 Histogram of compressive strength of calcium aluminates hydrated for 14 days: (a) CA; (b) CA_2 ; (c) $C_{12}A_7$; (d) 1:1 $CA_2:CA$; (e) 2:1:1 $CA_2:CA:C_{12}A_7$; (f) 8:1:1 $CA_2:CA:C_{12}A_7$.

ment at 14 days may be observed from the histogram:

CA . 8:1:1 $CA_2:CA:C_{12}A_7$. 1:1 $CA_2:CA$.

CA_2 . 2:1:1 $CA_2:CA:C_{12}A_7$. $C_{12}A_7$

From the above sequence, it is revealed that CA phase attains a maximum and the $C_{12}A_7$ phase attains a minimum strength after hydration for 14 days. Addition of active phases such as CA and $C_{12}A_7$ improved the strength of CA_2 in certain cases.

The microphotograph of briquettes hydrated for 14 days and with the CA phase only is shown in Fig. 2. Most of the crystals attain the shape of cubes, spheres or hemispheres because of the presence of all three equal crystallographic axes, which are perpendicular to each other. The cubes, pyritohedra and other combinations of the isometric system are densely packed and reinforced strongly with AH_3 gel matrix, giving rise to the highest strength. All these cubic or spherical forms belongs to the C_3AH_6 phase. Fig. 2b shows the hexagonally shaped crystal with two faces; the one in front can be easily identified. These basal pinacoids of the hexagonal system belong to the CAH_{10} phase. Since the composition contains only CA_2 , the rate of transformation was very slow; thus only crystals of metastable CAH_{10} formed together with excess of AH_3 gel, and more time is required to obtain complete conversion into the C_3AH_6 phase. Because of the poor packing of crystals, the strength is also poor.

It is difficult to identify the crystal form in Fig. 2c as the orientation and morphology are not clear but, as the sample contains only $C_{12}A_7$, it can be

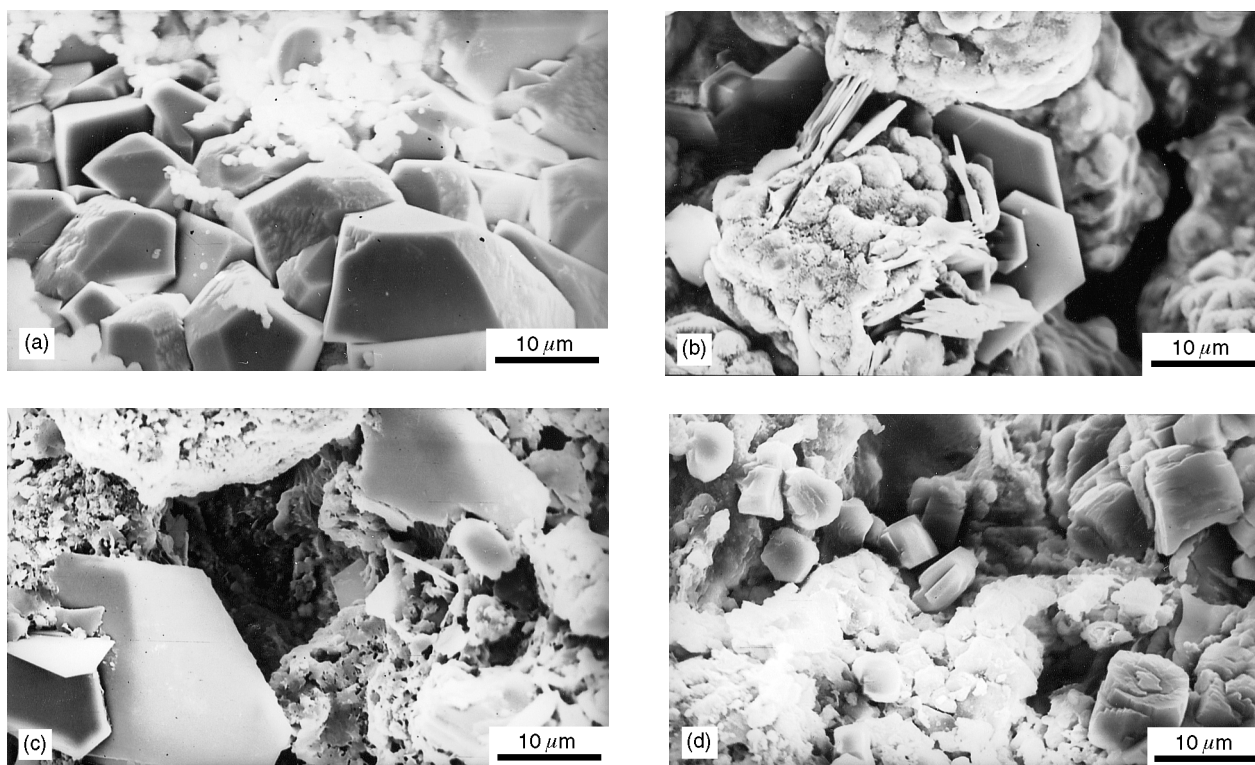


Figure 2 SEM photomicrographs of calcium aluminates hydrated for 14 days: (a) CA; (b) CA_2 ; (c) $C_{12}A_7$; (d) 1:1 CA_2 :CA; (e) 2:1:1 CA_2 :CA: $C_{12}A_7$; (f) another region of 2:1:1 CA_2 :CA: $C_{12}A_7$; (g) 8:1:1 CA_2 :CA: $C_{12}A_7$; (h) another region of 8:1:1 CA_2 :CA: $C_{12}A_7$.

surmised that complete transformation has occurred. The poor strength may be due to scattered crystals and the presence of numerous pores. The sample with 1:1 CA_2 :CA is shown in Fig. 2d. The presence of the C_3AH_6 phase in the form of a semicubic or spherical shape can be easily identified. The dense packing of these semicubic or spherical crystals gives rise to better strength.

The presence of fine needles of gibbsite (AH_3) in Fig. 2e is observed in the case of the 2:1:1 CA_2 :CA: $C_{12}A_7$ sample as also reported by Midgley [2]. Because of more CA_2 , slow hydration took place and the presence of basal pinacoids of a hexagonal system which belongs to CAH_{10} phase is noticed. Another rhombohedron form of the hexagonal CAH_{10} phase (Fig. 2f) is also seen in the other region of the same sample. Fig. 2g shows some well-developed isometric forms such as pyritohedrons, cubes and spheres. Similar forms were also reported by George [4] who termed these crystals the spherical cubic C_3AH_6 phase. The same crystal was studied at a higher magnification and the photomicrograph is shown in Fig. 2h. More precisely, these crystals may be termed pyritohedra as they are bound by 12 faces (six in front and six at the back), each of which is a pentagon. One edge is larger than the other four similar edges. These crystals belong to the C_3AH_6 phase and are densely packed with each other, leading to better strength.

In conclusion, the morphology of hydrated calcium alumina crystals, their textural arrangements and packing with alumina gel have a role in the development of compressive strength. The morphology of one hydrated phase changes in the presence of other phases.

Acknowledgement

The authors are grateful to Professor P. Ramachandra Rao, Director, National Metallurgical Laboratory, Jamshedpur, India, for his kind permission to publish this paper.

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Received 13 September
and accepted 4 December 1996