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# ESEM evidence for through-solution transport during brownmillerite hydration

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In portland cements, there are two non-silicate clinker minerals which contain aluminum: calcium aluminate $C_3A$ and calcium aluminoferrite, having the approximate composition of the mineral brownmillerite $C_4AF$ (here we use the standard notation $C = CaO$, $A = Al_2O_3$, $\bar{S} = SO_3$, $H = H_2O$). In oil well cements, which are iron-rich, the aluminoferrite is always the predominant and usually the only aluminum-containing phase [1, 2]. Brownmillerite has frequently been used as a model of the aluminoferrite phase in cements. When placed in contact with water, brownmillerite forms solid hydration products within a few minutes [3]. The hydration of brownmillerite has been widely studied, yet only a handful of direct microscopic observations of the hydration products have been made [4, 5]. In the absence of any other phases, the hydration of brownmillerite appears to be similar to the hydration of the iron-free $C_3A$, in which a C-A-H gel first coats the $C_3A$ grains from which metastable hexagonal C-A-H plates then develop within 10 min [4, 6–8]. The plates eventually convert to the hydrogarnet $C_3AH_6$ over a period of minutes [7, 9] to hours [4, 8]. Most authors have concluded that brownmillerite is less reactive than $C_3A$ [10, 11].

The formation of C-A-H can produce a rapid undesirable stiffening of the wet portland cement paste, and therefore sulphate minerals (principally gypsum $C\bar{S}H_2$) are invariably added to clinkers in cement manufacture. The presence of gypsum suppresses the formation of C-A-H phases by producing tri- and monosulphate hydrates instead. When gypsum and $C_3A$ are hydrated together ettringite ($C_6A\bar{S}_3H_{32}$) forms in a C-A-$\bar{S}$-H gel that coats the $C_3A$ within 10 min of hydration [4, 8]. It is commonly assumed that ettringite can form by both solid-state diffusion and through-solution mechanisms [12, 13]. Direct evidence of through-solution diffusion and precipitation is difficult to obtain as the hydrates are normally seen nucleating on the aluminate [4–6, 8]. Ettringite crystals have been observed to grow in voids between $C_3A$ grains [8], but this is not conclusive evidence for a through-solution mechanism since the nature of the nucleation sites is unclear. Hence direct observational evidence of a through-solution diffusion and precipitation mechanism for the formation of ettringite is tenuous.

When $C_4AF$ hydrates, the sequence of reactions is similar to that of $C_3A$. However the hydration products are assumed (more often than not) to incorporate some iron [14–17]. The exact Al/Fe ratios of the products are as yet debatable but it is generally accepted that the Al/Fe ratio of the product is greater than in $C_4AF$ itself [18]. However, iron almost certainly does not enter the solution during hydration [19] and it is assumed that an iron-rich residual phase is formed as hydration proceeds [15]. Carlson [18] suggests that this residue is an amorphous iron hydrate containing some calcium. Scanning electron microscopy has been used to identify such iron-rich phases [4] and recent energy dispersive diffraction work [3] corroborates the theory that this product is indeed amorphous, as no Fe-rich crystalline phases are observed during $C_4AF$ hydration. As there has been much discussion as to whether secondary phases formed during hydration of $C_4AF$ contain iron, it was decided that a two-track approach could be taken towards this problem. First, environmental scanning electron microscopy (ESEM) allows us to observe hydration reactions without the need for stopping hydration with solvents. Furthermore, the low vacuum aqueous atmosphere prevents desiccation of the sample and dehydration of individual phases. Second, chemical analysis of the solution in contact with hydrating $C_4AF$ with or without sulphate yields information about mobility of ions during hydration. The combination of results from these two techniques should allow us to determine whether through-solution mechanisms occur during the hydration of $C_4AF$ and if so what the likely products should be.

A Philips-FEI XL30 field emission gun environmental scanning electron microscope (FEG-ESEM) was used to avoid preparation artefacts in common standard SEM [8]. Construction Technology Laboratories (Skokie, IL) supplied the $C_4AF$. Reagent grade gypsum was used as a sulphate source. A very small amount of sample ($<1$ mg) was placed in a specially designed steel cup which was then mounted on a Peltier stage in the ESEM. The pump-down sequence and condensing method of Meredith *et al*. [8] were used to hydrate

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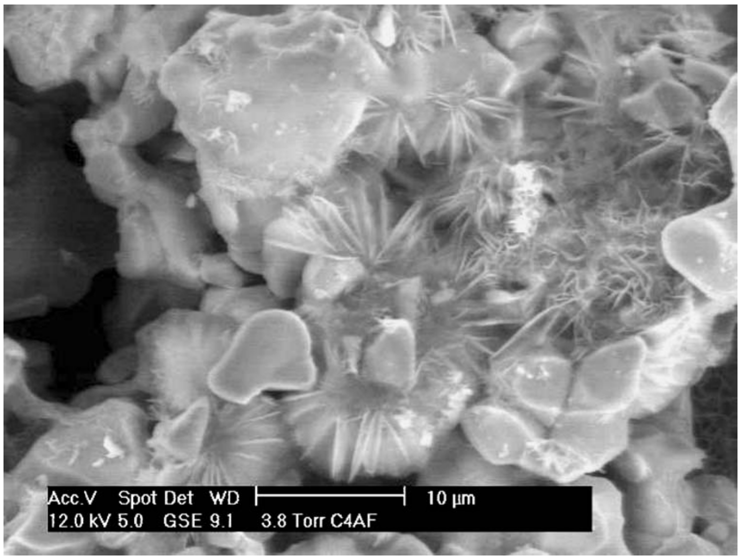

*Figure 1* $C_4AF$ after 13 min hydration. Plates of metastable hexagonal calcium aluminate hydrates are growing on the surface of $C_4AF$ grains. Larger plates are approximately 5 $\mu$m diameter and appear to grow radially from a common point.

the sample. Where more than one reagent was used, approximately equal amounts of each reagent were placed on the cup 'by eye'.

$C_4AF$ alone was hydrated for 13 min. Clusters of plates were observed on the surfaces of $C_4AF$ grains and in between them (Fig. 1). Networks of C-A-H plates were also observed on the surface of the steel sample cup (Figs 2 and 3). No cubic phases were present after 13 min hydration. In the presence of gypsum, elongate hexagonal ettringite crystals were seen growing both on the surface of $C_4AF$ grains and the walls of the steel cup (Fig. 4) within 8 min.

To determine the amount of iron in the solution during brownmillerite hydration, 60 g of water was added to 5 g of $C_4AF$ (water:solid ratio, $W/S = 12$) and blended using an IKA overhead stirrer at 500–600 rpm for 30 s. The stirring speed was then reduced to $\sim$120 rpm to prevent settling of the solids. Aliquots of approx. 7 mL were taken at roughly 1, 30, 60, 90, 120, 150 and 180 min intervals and the slurry suspension vacuum filtered through a 0.45 $\mu$m nitrate membrane filter. Five mL dil. HCl (800 mL water + 6 mL concentrated HCl) was added to the extracted liquid to prevent carbonation, and the sample further diluted by ten before analysis by inductively coupled plasma atomic emission spectroscopy (Thermo Jarrell Ash IRIS). The experiment was repeated to ensure reproducibility. The iron content of the solution was negligible, with values always $<$1 ppm and often below the detection limit of 0.06 ppm (Table I). The iron content of the solution did not appear to be altered by the addition of 2 per cent gypsum by weight of $C_4AF$ (Table I).

The presence of both C-A-H and ettringite phases on the surface of the steel cup clearly shows that a through-solution ion diffusion and precipitation mechanism is at work. While some topotactic growth cannot be ruled out, it appears that the predominant method of hydrate formation must involve mass transport through the

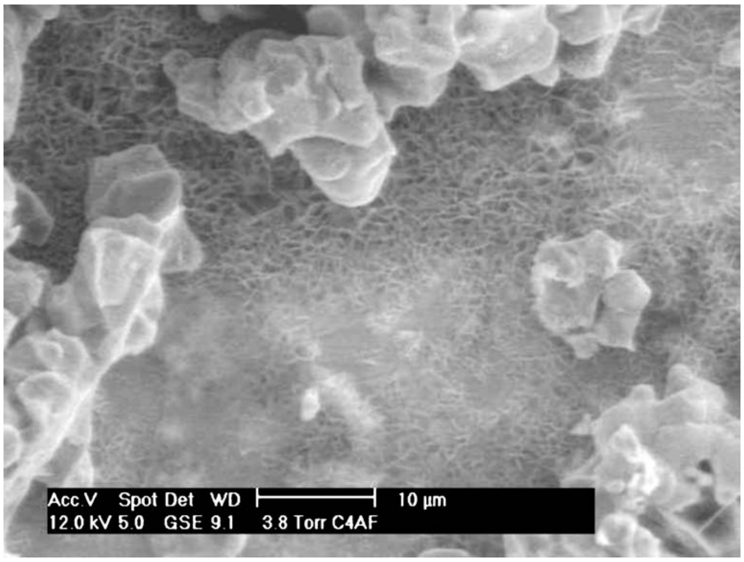

*Figure 2* $C_4AF$ after 13 min hydration. Fine-scale networks of small C-A-H plates growing on the walls of the steel cup. The plates have an inter-connected habit rather the radial habit observed when grown in contact with the $C_4AF$ (Fig. 1). The larger particles are $C_4AF$ grains.

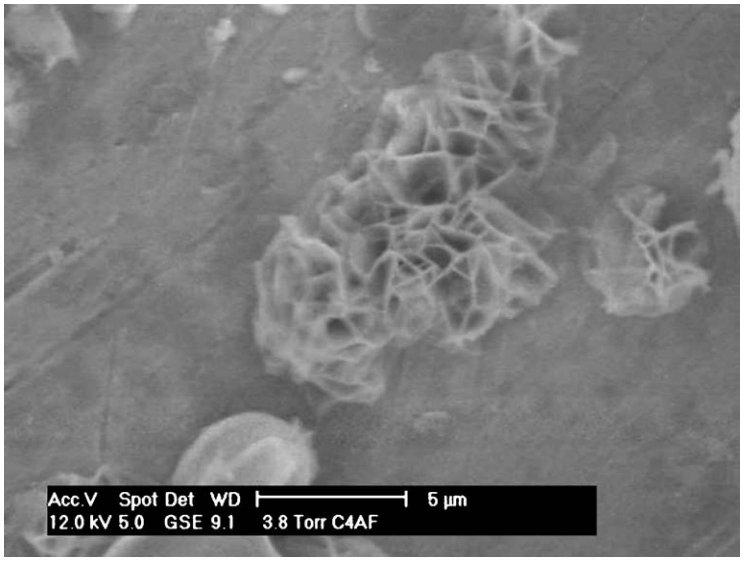

*Figure 3* $C_4AF$ after 13 min hydration. Growth of larger C-A-H plates nucleated on the walls of the steel cup showing inter-connected network.

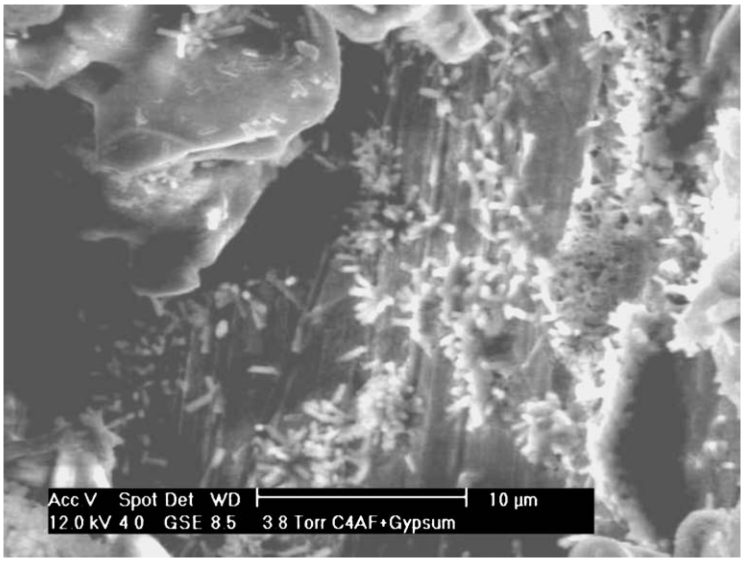

*Figure 4* $C_4AF$ and gypsum after 8 min hydration. Ettringite crystals, 1–2 $\mu$m long, growing on the surface of the steel wall of the sample cup. The crystals are elongate, apparently nucleating on the steel and then growing outwards from the steel surface.

water as predicted by previous authors for ettringite [8]. This is the first time this has been unequivocally observed for ettringite and the first time it has ever been noted for hexagonal C-A-H plates.

X-ray microanalysis in the ESEM chamber cannot be used to determine the composition of either the hydrate in contact with $C_4AF$ or that in contact with the steel cup. The 'skirt effect' in an environmental chamber generates X-ray lines from much more surrounding material than the point analyses possible in a vacuum chamber. This is also enhanced by the uneven topography of the sample: hence the beam samples surrounding material as well as the point of interest. Therefore analyses of hydrates would pick up lines from adjacent $C_4AF$ or from the steel. In both cases iron would be detected, and so we cannot use X-ray microanalysis in an environmental chamber to determine whether iron has travelled through the solution. However the liquid phase data presented above can be combined with ESEM observations to determine the composition of secondary hydrates not in contact with $C_4AF$. The liquid phase data suggest that minimal iron goes into the solution, in agreement with the findings of Brown [19] and Carlson [18]. Since iron does not readily enter the solution, we conclude that hydrate products nucleated on the steel wall are almost certainly iron-free.

TABLE I Iron content (ppm Fe) in the liquid phase in contact with $C_4AF$ (with or without gypsum) during hydration. Values below the detection limit (0.06 ppm) are listed as not detected (*n.d.*)

| Hydration time (min) | C4AF only | | C4AF + gypsum | |
|---|---|---|---|---|
| | Experiment 1 | Experiment 2 | Experiment 1 | Experiment 2 |
| <2 | 0.17 | *n.d.* | 0.13 | 0.12 |
| 30 | 0.07 | 0.12 | 0.12 | 0.06 |
| 60 | 0.09 | *n.d.* | *n.d.* | 0.13 |
| 90 | *n.d.* | 0.47 | 0.10 | *n.d.* |
| 120 | 0.15 | 0.07 | *n.d.* | *n.d.* |
| 150 | 0.14 | *n.d.* | *n.d.* | *n.d.* |
| 180 | 0.07 | *n.d.* | *n.d.* | *n.d.* |

In conclusion we can say that the metastable hexagonal C-A-H and ettringite can form by interdiffusion of calcium and aluminate ions moving through the solution away from the source mineral. In the case of $C_4AF$ the iron content of solid products formed in this way is negligible as iron does not go into the solution during hydration. It should be noted that the experiments here have high water-to-solid ratios: hence there are large fluid volumes in which soluble ions may move around freely. The situation in a dense paste is somewhat different. What is certain is that the hydration products of $C_4AF$ do not necessarily nucleate on the surface of hydrated $C_4AF$ but may grow on the surface of other clinker or hydrate phases.

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