The use of a high-voltage electron microscope and gas reaction cell for the microstructural investigation of wet Portland cement

For both metals and ceramics relationships between microstructure and the bulk properties have been used to develop materials with new or improved properties. In the case of Portland cement, however, systematic investigations have shown that the microstructure is complex, although recently the structure has been classified into a number of types [1] and this has made characterization rather more universal. This complex microstructure is due in part to the significant variation in the composition of cement as purchased and in part to the fact that the reaction of cement with water is strongly influenced by many variables such as water/cement ratio, temperature, time and the addition of admixtures. In view of the complexity of this reaction, few serious attempts have been made to relate properties with structure for cement.

Except for the porosity, the microstructure of cement is sufficiently fine as to require electron microscope techniques for observation. Both scanning and transmission microscopes have been used, but because the specimens need to be placed in the vacuum of the microscope column, most studies [1], except for the recent work of Double and co-workers [2–4], have been of dried cement. This note describes an aspect of a current study where transmission electron micrographs were made of cement specimens which were kept moist in an environmental stage inside a high-voltage electron microscope.

Specimens were prepared by sandwiching several carbon-coated grids with the cement and water mixture between glass microscope slides and sealing them with an adhesive. After curing for the desired length of time the slides were separated and the grids carefully chipped away from the bulk cement. Although crude, and obviously a method that can both damage the cement and produce areas which are too thick for observation, it was found that almost all grids contained some areas of relatively undamaged thin sections. Unlike the technique used by Double and co-workers [2–4], this method allows realistic water/cement ratios to be observed (results reported here have $w/c \simeq 0.5$) and it produces a thin section quickly and without the necessity of drying. The time taken between breaking the specimen open and placing it in the EM 7 microscope is less than 2 min, while the lifetime of a specimen in the microscope can be 1 to 2 h.

The gas-reaction specimen stages were designed by Swann and Tighe [5]. Either air or argon, saturated with water vapour, is fed into the central part of the specimen stage and it is pumped away

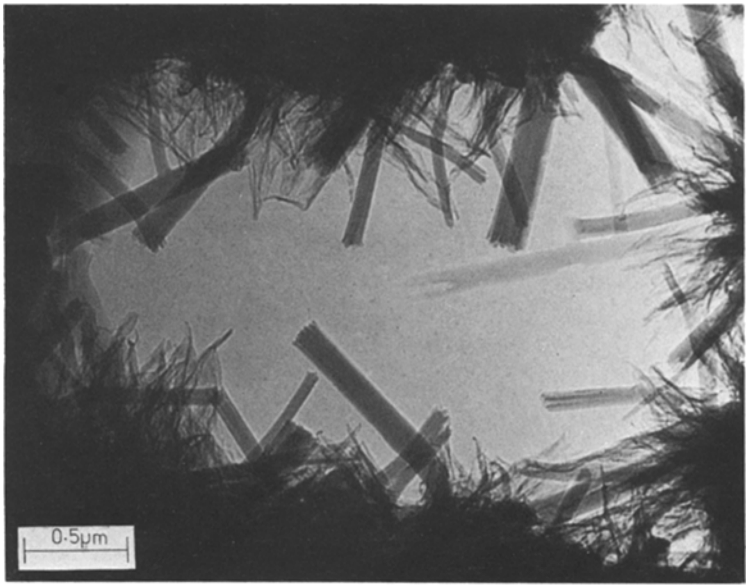

Figure 1 Specimen hydrated for 5 days at 20° C. The angular large needles contain aluminium, sulphur and calcium, and are probably ettringite while the sheet-like material is calcium silicate hydrate.

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through special apertures just above and below the specimen. The pressure at which the specimen can be maintained is, therefore, a function of the differential pumping ability. Two stages have been used, one which enters through the side of the microscope in exactly the same way as the ordinary stage and one which drops down between the pole pieces. The second design incorporates much larger pumping ducts which allow a higher operating pressure to be maintained at the specimen. In the first case the specimen is exposed to about 200 Torr and in the second case the specimen can be maintained at atmospheric pressure whilst in the microscope column. In both cases the overall water content of the specimen is kept about constant (suggesting a possible technique for observation of biological specimens) at least during the initial period of observation. In the side-entry design, however, the reduced pressure appears to allow some drying particularly in specimens observed over a long period of time.

This technique has been used together with an analytical electron microscope, to obtain some new observations of the reaction of cement with water. Fig. 1 shows two important microconstituents commonly found in ordinary Portland cement. The square-ended fibres contain aluminium and sulphur along with calcium and often some silicon, and are probably ettringite. Examination shows a hollow structure, particularly near their ends, suggesting that they are fibre bundles which are beginning to dehydrate, possibly due to electron beam damage and/or the passage of time. The thin sheet-like foils on the other hand are calcium silicate hydrate and they are believed [6] to be growing by an exfoliation process as the silicon-rich solid reacts with calcium-rich liquid. The micrograph is quite typical of the specimens observed in the wet stage; photography under wet conditions is difficult and somewhat statistical but when the structure can be seen, the calcium silicate hydrate is normally in this sheet-like form. The structure is very delicate and often not even observed (due to the innate poor quality of the fluorescent screen) until the film is processed and printed. It is easily damaged by the electron beam and therefore photographs must be taken at the lowest possible beam current. Finally, small hexagonal crystals which are probably calcium hydroxide can be seen near the thick black grains of cement.

Structures which have been variously described as plates, flakes, foils and thin sheets have been observed by other workers in hydrated cements. For example the early electron microscope work of Grudemo [7] showed a sheet-like structure for calcium silicate hydrate which had been mechanically dispersed on microscope grids. Although subsequent observations [8–11] have confirmed a sheet-like structure, the difficulty in preparing specimens for transmission electron microscopy has resulted in most of the recent studies [12, 13] using a scanning electron microscope to study the fracture surfaces of cement. Here, networks of needles or fibres have been observed, particularly in the early stages of hydration in dilute systems and around porosity. The suggestion has been made [14] that properties such as strength develop as the fibres grow together into tangled networks. Our observations suggest that although fibres are observed under certain conditions, it is the sheet-like structure of calcium silicate hydrate which is fundamental to cements of a realistic water/cement ratio. However, particularly in the early stages, this structure is difficult to observe.

The sheet-like structure appears a little coarser in specimens hydrated at 55° C and Fig. 2 shows a sequence of photographs of specimens of $w/c = 0.5$ hydrated for 4 days at 55° C, which were taken at approximately 10 min intervals. The sheet-like hydrate material is seen to "roll up" to form a fibrous structure. These photographs were taken in the side-entry stage where drying with time, particularly under the influence of the electron beam, is very possible. The final photographs show hollow open-ended fibres and we believe that most of the fibrous calcium silicate hydrate traditionally observed growing into pores of cement of realistic water/cement ratio are, in fact, these rolled-up thin sheets. Analytical microscopy has shown that the fibres which form in this way are the only ones observed to contain silicon and calcium exclusively. This sheet-like nature of calcium silicate hydrate is consistent with chemico-physical data such as surface-area development [7, 15] in the early stages of hydration. Furthermore, the rolling up of sheets which are growing into porosity is consistent with the surface-area changes which occur during the initial drying of cement [16]. In thicker sections with more restricted pores (Fig. 3), the calcium

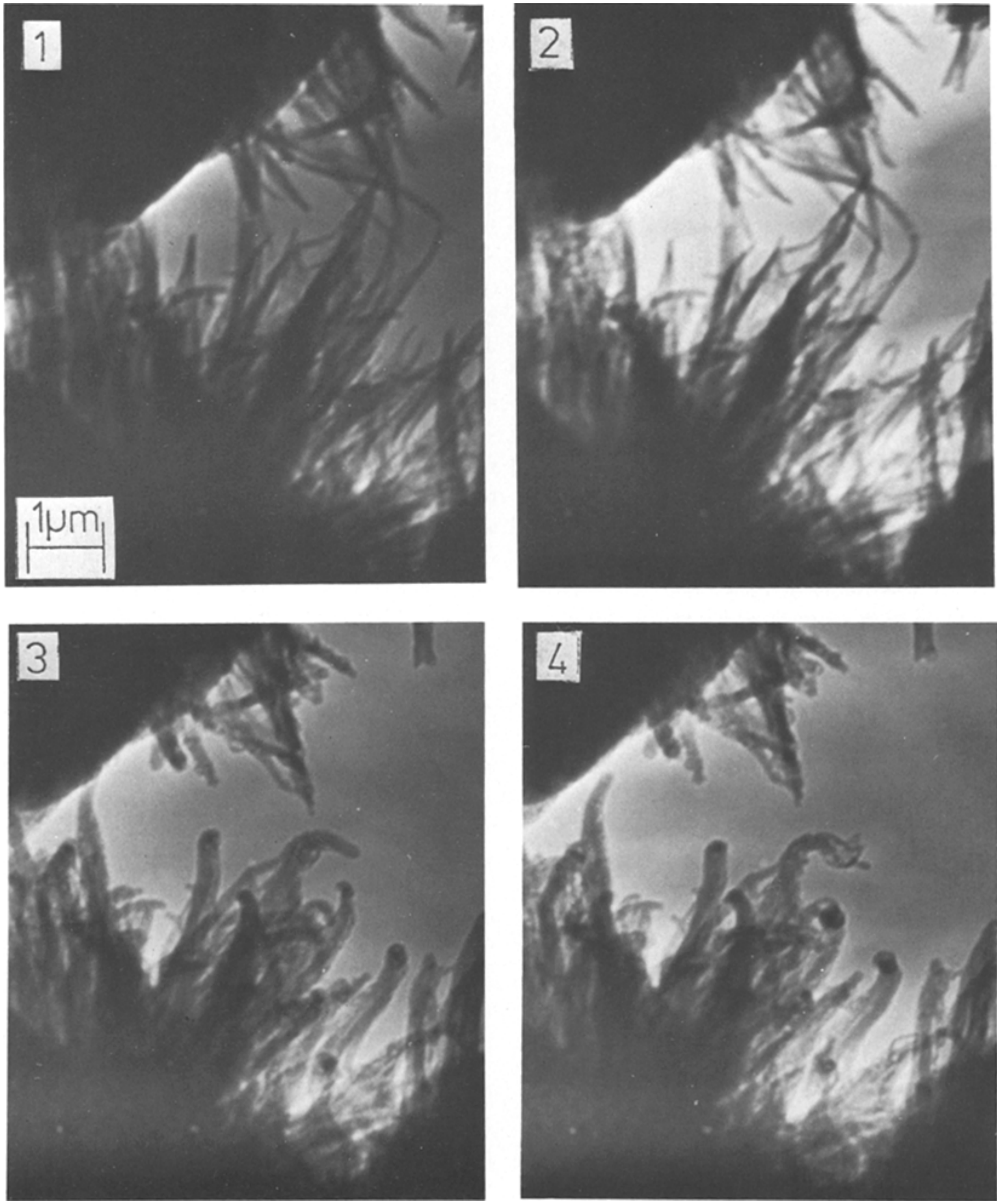

Figure 2 Specimen hydrated for 4 days at 55° C, w/c = 0.5. Sequence of photographs showing transition of thin sheets into needles. Photographs were taken at approximately 10 min intervals.

silicate hydrate does not appear to roll up but instead intertwines and interlocks. As the weakest link, these interlocking sheets must be responsible for the rigidity and strength of the coherent mass. Interestingly, a sheet-like structure has been proposed to explain observations associated with creep [17].

A determined effort to find an undamaged sheet-like structure in dried specimens, otherwise prepared in the same way, has made it clear that

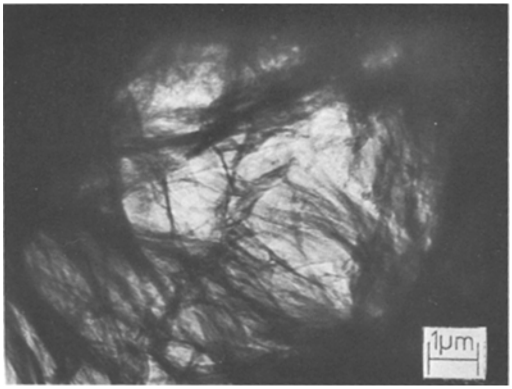

Figure 3 Specimen hydrated for 4 days at 55° C; w/c = 0.5. Calcium silicate hydrate forming an interlocking network.

this delicate structure is not generally seen except when the specimen is kept wet. However, its existence does provide a very important clue to the mechanism of formation of the calcium silicate hydrate found in set cement.

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Solid-solution hardening in b c c metals

The similarities between the movement of screw dislocations by double-kink propagation in pure b c c metals [1], on the one hand, and, on the other, of edge dislocations in concentrated ($c > 1$ at.%) f c c solid-solutions [2, 3], suggests that edge dislocations rather than screws may determine the CRSS in concentrated b c c solid-solutions.

This inversion of the roles of the two types of dislocations in the b c c alloys compared with their behaviour at low temperatures in the pure metals, might be expected to set in at concentrations of the alloying element at which the pinning of the edge dislocations rendered them less mobile than the screws; although the Peierls force for the latter is higher than for edges, the screws, by contrast, would be less susceptible to pinning by the alloy atoms.

To examine the possibility that the CRSS in concentrated b c c alloys was determined by the mobility of edge dislocations, we considered it of diagnostic value to attempt representing suitable data, e.g. those on the CRSS of alloys of niobium single crystals containing either 5 to 16 at.% Mo or 5 to 9 at.% Re, studied in the range 77 to 350 K by Statham and Christian [4], as if the edge dislo-

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