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Microstructural Development During Hydration of Cement

EDITORS
Leslie J. Struble
Paul W. Brown

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EDITORS:

Leslie J. Struble
National Bureau of Standards, Gaithersburg, Maryland, U.S.A.

Paul W. Brown
National Bureau of Standards, Gaithersburg, Maryland, U.S.A.

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Microstructural Development During Hydration of Cement

TEM STUDIES OF CEMENT HYDRATION

G.W. GROVES
Department of Metallurgy and Science of Materials, Oxford University, Parks Road, Oxford OX1 3PH, U.K.

ABSTRACT

The application of transmission electron microscopy to the study of the early stages of hydration C_3S and the microstructure of very mature C_3S paste is reported. In the former case the effect of water-cement ratio appears to be very important. In the latter, a detailed evaluation of the microstructures of inner C-S-H, outer C-S-H and CH is possible and the relationship of these to models of cement hydration is discussed.

INTRODUCTION

Microscopy has played an important role in shaping ideas about cement hydration. Amongst the various electron microscopy techniques, scanning reflection electron microscopy of fracture surfaces has been by far the most widely applied. It has the advantages of great convenience and good resolution of such morphological detail as may be exposed by the fracture path. It suffers from the drawbacks of not necessarily giving a representative view of the microstructure and of failing to give information about relatively dense regions where the fracture surface is flat. A technique which does not have these drawbacks is backscattered electron imaging of polished sections of cement pastes or concretes and this holds much promise, especially for quantitative phase analysis [1]. However the technique which has the greatest potential for high resolution, both of microstructural detail and of microanalysis, is transmission electron microscopy (TEM). In this paper we consider the application of this technique to hydration at two extremes. Observations of very early stages of hydration of C_3S are discussed and the microstructure of a very mature, 26 year old C_3S paste is evaluated.

EARLY HYDRATION

Many observations have been made of hydrate gel formed during the early stages of C_3S hydration. Double and Hellawell [2] observed gel coatings formed after 3 hours on grains in a wet cell in a HVEM, and this was taken as evidence for a membrane surrounding the grain and halting further reaction until disrupted by osmotic pressure at the end of the induction period [3], an idea developed also by Birchall et al [4] and originally suggested by Powers [5]. In this experiment the water-cement ratio was high, probably in excess of 10. Copious reaction product on C_3S thin foils immersed in the supernatent liquid of a 2:1 water-cement paste was reported by Groves [6]. Ings et al [7] observed a 5 μm thick hydrate layer formed on a single crystal of C_3S after 30 mins in a water-cement ratio of 2. This crystal, however, appeared to be unusually reactive and a suspicion of enhanced reactivity also rests on the thin foils observed by Groves, since they were prepared by ion-beam thinning, which might activate the surface of the C_3S. Thin flakes or foils were observed in a HVEM wet cell after 3 hours hydration by Jennings et al [8] at a water-cement ratio of 0.47, but it is not clear whether a continuous coating or membrane existed. It appears that the majority at least of the observations indicating a copious continuous coating refer to a relatively high water-cement ratio. Analysis of the solution

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present during early stages of hydration by Brown et al [9] led to the conclusion that the amount of C_3S reacted increased very markedly indeed with increasing water-cement ratio. Since the silica concentration in solution quickly falls to very low values even at high water-cement ratios, this would imply that much more hydrate gel is formed when the water-cement ratio is high. To check this point, C_3S particles were hydrated at two extreme water-cement ratios, 0.5 and 50, filtered and washed with isopropyl alcohol after 30 mins and collected by dispersion in isopropyl alcohol on a carbon film for observation by TEM and SEM. The amount of hydrate visible at the particle surfaces was very much greater for the particles from the 50:1 water-cement ratio. TEM observations shown in Fig. 1 and the SEM observations confirmed that whereas the 50:1 particles were smothered in gel, only occasional patches were seen on the 0.5:1 particles (the fibrous morphology of the gel in Fig. 1 is likely to be the result of drying shrinkage). This does not disprove that a continuous coating at some stage existed on the 0.5:1 particles. Such a coating could have been disrupted, especially in view of the fact that the thickness, if continuous, would be expected to be only on the order of 10 nm, on the basis of the small amounts of reaction found by Brown et al [9] for a concentrated paste. However the great influence of water-cement ratio on the total amount of hydrate gel formed is confirmed. The model of hydration during the induction period being arrested by the presence of a gel membrane or coating whose permeability controls the rate of further reaction does not appear to account for this observation in a simple way, even though the apparent equilibrium between the solution and C-S-H has been taken as evidence that the solution is isolated in some way from the C_3S grain surface [10]. The hydrate gel on the 50:1 particles was sufficiently copious for microanalysis in the TEM. Eight regions analyzed gave an average C:S ratio of 1.7 although a wide range from 1.12 to 2.27 was found. This may in part be due to the relatively low counts obtained from very thin regions, but there may also be real variation depending on the composition of the solution from which the particular area of hydrate formed. There is nothing distinctive in the appearance of early gel, or, from limited initial measurements, in its composition, that can be related to the distinctive structure as revealed by solid-state NMR measurements [11].

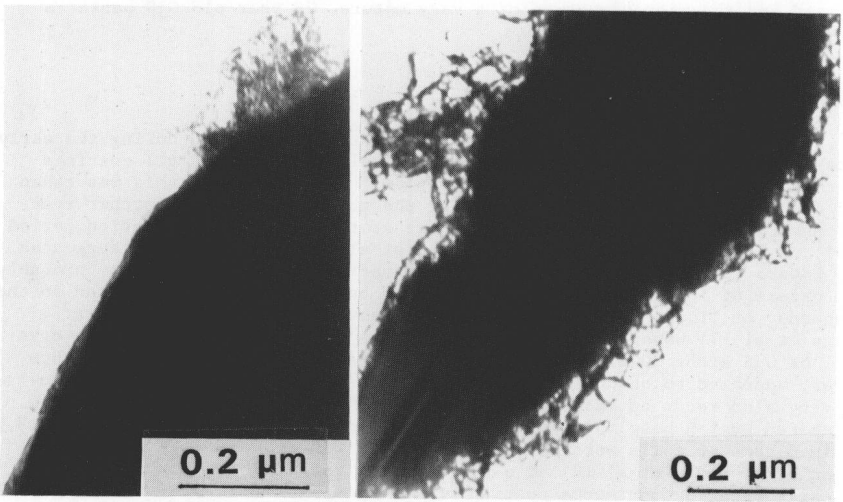

Figure 1. C_3S grain after 30 min hydration at w/c = 0.5 and w/c = 50.

LATE HYDRATION

Cement pastes of various types, containing C_3S or alite as the major component, have now been observed in section in the TEM. For example "macro-defect-free" polymer-modified portland cement paste of low water-cement ratio [6,12], normal portland cement pastes of low water-cement ratio [12], portland cement paste with microsilica additions [13] and portland cement paste hydrated at 120°C [14] have all been examined, as well as C_3S pastes of various ages [8] and one year old C_3S paste [15]. The general picture emerging is that the paste microstructure can always be divided into three broad regions. These are residual unhydrated material, outer hydration products (including CH) forming in the space between the original cement grains, and inner hydration product, formed within the boundaries of the original C_3S grains (without there necessarily being any exact correspondence between the positions of the outer boundaries of product and grains). Whereas the outer products vary greatly depending on the type of paste, the inner hydration product does not vary greatly in appearance from one cement to another, generally being very homogeneous and fine-grained. The existence of inner hydration product was of course noted in earlier SEM observations of fracture surfaces, for example by Williamson [16]. It appears to be identical to Diamond's Type IV C-S-H gel [17]. It has been suggested that this material could more accurately be described as "late product", but we prefer the original term because of its long standing (according to Williamson [16] the term was first used by Taplin in 1959) and also because "late product" might be taken to suggest a product forming only near the end of the hydration process, which is not the case. In fact a major difference in the impressions of the overall microstructure of pastes obtained by SEM of fracture surfaces and TEM of sections of mature paste lies in the prevalence of inner product as a feature of the microstructure. Areas of inner product are not very frequently identified clearly by SEM observations, whereas from TEM it is clear that inner product forms the bulk of C-S-H in mature C_3S pastes [8]. This is particularly striking in the case of a very mature C_3S paste, 26 years old and completely hydrated, which we have examined. The paste was made at the Portland Cement Association in 1960 with a water-cement ratio of 0.45. TEM specimens were prepared by grinding sawn slices to a thickness ~30 μm on dry silicon carbide papers, followed by ion-beam thinning at moderate beam currents to limit heating of the specimens. Examination was carried out in a high voltage electron microscope (1 MV) giving extra penetration of thick areas, except for some microanalysis which was carried out on a 200 KV microscope. The microstructure is very clearly divided into three phases: inner product C-S-H, outer product C-S-H and CH crystals. Inner product was always clearly distinguishable from adjacent outer product (Fig. 2). This is in contrast to the finding of Rayment and Majumdar [18] that in fully hydrated mature portland cement pastes inner and outer hydrates become impossible to distinguish by surface observations. Thin section observations show the clear difference in porosity and hydrate morphology between inner and outer product. The suggestion of Dalgleish and Ibe [19] that fibers interlocked during growth to form the dense inner product, or sub-layer as they termed it, does not appear plausible from our observations, which always show a distinct rather than a gradual transition. An important question is whether the inner product ever contains channels which could have led from the hydrating grain to the outside regions forming short circuits for material transport. This was never observed. Occasionally what were apparently originally small grains appeared to have developed a less dense inner core, as in Fig. 3. This individual observation could be explained as the effect of sectioning on a particle having a concave surface, but this would appear rather implausible as a general explanation. Larger particles were not observed with hollow centers; generally the section showed a uniform structure throughout. Calcium hydroxide was never observed within inner hydrate