

Chemistry of Cement Hydration

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Chimie d'Hydratation du Ciment

SUMMARY: Recent advances in the chemistry of hydration of portland cement without extenders are critically reviewed under the following headings. 1, Introduction. 2, C-S-H gel: electron optical studies of composition, silicate anion structure, water content, density, thermal behaviour, structure at the nanometre level. 3, Other hydration products: AFm, Aft and hydrogarnet phases, hydration products of the ferrite phase, calcium hydroxide. 4, Quantitative phase determinations, mass balance, indirect determinations of C-S-H composition, volume fractions. 5, Microstructural development: early, middle and late periods of reaction. 6, Hydration reactions: aluminate and ferrite phases, action of gypsum, theories of the induction period, reaction mechanism in the late period. 7, Reactivities of clinker phases. 8, Solution compositions and equilibria: CaO-SiO₂-H₂O system, aluminate and sulphate systems, pore solutions in cement pastes. 9, Admixtures: inorganic admixtures, organic retarders. 10, Kinetics and modelling of the hydration process.

SUMÁRIO: Avanços recentes na química de hidratação do cimento portland sem adições são revistos criticamente nas seguintes seções: 1. Introdução. 2. Gel do C-S-H: estudos eletro-ópticos da composição, estrutura iônica dos silicatos, conteúdo de água, densidade, comportamento térmico, estrutura ao nível nanômetro. 3. Outros produtos de hidratação: AFm, Aft e fase hydrogarnetos, produtos de hidratação da fase férrica, hidróxido de cálcio. 4. Determinações quantitativas das fases, balanço de massa, determinações indiretas da composição do C-S-H, frações volumétricas. 5. Desenvolvimento microestrutural: períodos iniciais, médios e finais da reação. 6. Reações de hidratação: fases de aluminato e férricas, ação do gesso, teorias do período de indução, mecanismo de reação no período posterior. 7. Reatividades das fases do clínquer. 8. Composição e equilíbrio das soluções: o sistema CaO-SiO₂-H₂O, sistema de aluminatos e sulfatos, solução nos poros das pastas de cimento. 9. Aditivos: aditivos inorgânicos, retardadores orgânicos. 10. Cinética e modelo do processo de hidratação.

1 INTRODUCTION

This paper critically reviews investigations into the chemistry of cement hydration since the Paris Congress in 1980. The early sections deal with the products, excluding those formed during the first hours of reaction, and the later ones with reaction processes, including early products and effects of admixtures. Microstructural development is considered only to the extent needed to understand reaction mechanisms, as other aspects are dealt with in another Principal Report. Other topics omitted for the same reason include gel structure above the nanometre scale, pastes containing fly ash or other extenders, and effects of aggregates on hydration reactions or products. Investigations discussed relate to pastes with w:c ratios of 0.3 - 0.7 and hydrated at 15° - 25°C unless otherwise stated.

2 C-S-H GEL

2.1 ELECTRON-OPTICAL STUDIES OF COMPOSITION

2.1.1 TECHNIQUES: EPMA AND SEM MICROANALYSIS

The techniques of microanalysis with the electron probe (EPMA) or scanning electron microscope (SEM) differ from each other only in minor respects. In both cases, the electron beam is properly directed at a polished surface. The volume analyzed is 1 - 10 μm^3 and increases with the accelerating voltage. Analyses of fracture surfaces by this method are, except possibly under very special conditions, only semi quantitative (1) and will not be discussed. Interpretation of results for the C-S-H of cement or calcium silicate pastes is complicated by two effects. First, observed Ca/Si ratios increase with the accelerating voltage (2,3). Second, the spread of ratios in individual analyses for a given specimen and accelerating voltage is considerably greater than is found for more normal substances, such as anhydrous clinker phases; in a typical case, for the C-S-H of a C_3S paste, examined at 10 kV, the range of Ca/Si ratios was approximately 1.5 - 2.0, with a mean of 1.72 (3).

Rayment and Majumdar (2) considered that the increase in apparent Ca/Si ratio with accelerating voltage occurred because, as the latter increased, it became progressively more likely that the region analyzed would contain unreacted C_3S (in a paste of that compound), or CH, or both. They concluded that the best estimate of the true mean value was that obtained at the lowest possible voltage, which they considered to be 6 kV. Employing similar reasoning, Chatterji (4) and Chatterji and Thaulow (5) concluded that, for analyses at 15 kV, the best estimate of the true mean ratio was near to the bottom end of the observed range. Both these methods gave values of 1.4 - 1.6 for C_3S pastes.

EPMA and SEM analyses can give absolute contents of elements and not merely ratios; for a pure calcium silicate paste, if oxygen equivalent to the Ca and Si is added, the deficiency from 100 % should, in theory, be attributable to water. From data for pastes dried by heating or under reduced pressure, the $\text{H}_2\text{O}/\text{Ca}$ ratio under the conditions of an electron optical analysis is most unlikely to exceed about 0.85; this corresponds to an anhydrous oxide total of 86 %. The observed totals are almost always less than this (2,3,6-9). Taylor and Newbury (3) found that the totals of individual analyses tended to increase with the Ca/Si ratios, from ca. 60 % at Ca/Si = 1.5 to ca. 80 % at Ca/Si = 1.9.

Taylor and Newbury (3) accepted the possibility that Ca/Si ratios above 1.5 in C_3S pastes arose from mixtures with C_3S or CH, but noted two objections to

this hypothesis. First, the majority of indirect determinations of Ca/Si ratio (i.e., from the contents of CH and unreacted C_3S , if any) have given values of 1.7 - 1.8. Second, the existence of CH intimately mixed with the C-S-H has been convincingly demonstrated only in cement pastes of unusually low w:c ratio (10). Replying to a comment by Chatterji (11), they pointed out that admixture with phases of higher Ca/Si ratio was not the only possible source of error; more specifically, there could be errors tending to make the observed ratio low. Any effect that retarded the incident electrons and was not fully corrected for would do this, as it would decrease the output of Ca X-rays more than that of Si X-rays; the observed ratios would decrease with decreasing voltage, and low ratios would be associated with low totals. They considered it likely that some such effect operated, and that the true value of the mean Ca/Si ratio in C_3S pastes was 1.7 - 1.8, both higher and lower values in individual analyses being explainable as artifacts. Compositional variability on a sub micrometre scale was not excluded.

The transport of electrons through highly microporous materials, such as C-S-H gel, is not well understood, and various effects might cause unexpectedly great retardation of the incident beam. One arises from the possible presence in the pores of carbonaceous matter originating either from pump oil vapour or from organic liquids used in drying, sawing or polishing; at 6 kV, very little on or immediately below the surface would markedly lower the output of Ca X-rays. Internal charging is another possibility. The best compromise in voltage for analyses of pure calcium silicate pastes is probably 10 kV; for cement pastes, if heavier elements are being analyzed for, 15 kV may be preferable. The observed deficiencies in the totals are unlikely to be due solely to water. Further study of sources of error in EPMA or SEM analysis of such materials is needed.

2.1.2 TECHNIQUES: ANALYTICAL ELECTRON MICROSCOPY

In this method (AEM), the specimen is examined in transmission. The volume analyzed is much smaller than in EPMA or SEM analysis and is not primarily affected by the accelerating voltage. The specimen thickness must not exceed 20 to 30 nm; this can be achieved by grinding and redispersing, or by ion thinning. All results yet reported for hydrated cements are for redispersed samples. The method gives atomic ratios, but it is normally impracticable to obtain absolute contents of elements.

Even wider variations in composition between individual analyses from the same specimen have been observed than in EPMA or SEM analyses, e.g., Ca/Si ratios of 1.2 - 2.0 for the C-S-H of C_3S pastes (12). Lachowski and Diamond (13) found such variations, not only between particles, but also between points ca. 2 μm apart, within particles. There has been some discussion of possible sources of error in the analysis of C-S-H gel and other cement hydration products by this method (11,14-17). Provided the (stringent) conditions for analysis are met, individual analyses are probably reliable, but the possibility of sampling errors cannot be ignored, because of the small size of the specimen ($\ll 1 \mu\text{g}$) and the way in which it is isolated by grinding and redispersing. It is impossible to tell which part of the grosser microstructure a given particle comes from. Because of the extreme compositional variation, Lachowski and Diamond (13) concluded that earlier studies may have concentrated unduly on mean values, and the writer agrees. Attempts to prepare analyzable specimens by ion thinning have so far been rather discouraging.

and the method would not necessarily yield any more representative a sample, as the areas thinned are small and thinning may be selective.

2.1.3 RESULTS: CALCIUM SILICATE PASTES

For the C-S-H of C_3S pastes, recent EPMA and SEM analyses have given reported Ca/Si ratios of 1.5 - 2.0 (2-5,18). Taking into account the accelerating voltages used, and the possible sources of error discussed above, the most probable mean value appears on present evidence to be ca. 1.7. The only such analysis of a β - C_2S paste (3) gave a ratio of 1.78. The earlier AEM studies gave mean values of 1.43 - 1.66 for C_3S pastes (12,19) and 1.37 - 1.41 for β - C_2S pastes (20), but later work on C_3S pastes gave 1.7 - 1.8 (21). The earlier results are probably too low. The EPMA, SEM and AEM results together cover a range of w:s ratios, and hydration times from 1 day to 30 years, and neither of these variables appears to have any marked effect on the Ca/Si ratio.

2.1.4 RESULTS: CEMENT PASTES

EPMA and SEM analyses of the C-S-H in cement pastes have been reported (6-9,22,23). In some, distinction was made between "inner" and "outer" products, where "inner" product denotes either rims around partly reacted cement grains, or relicts of fully reacted grains, and "outer" product denotes material formed in what was originally water filled space. At the resolution available in X-ray microanalysis, it is probably impossible to distinguish outer product from inner product of the smaller cement grains, and "undesigned" product would be a better description. The inner product of alite and belite appears to be pure C-S-H; mean or median Ca/Si ratios of 1.7 (6,8,22), 1.7 - 2.0 (7) and 1.9 - 2.0 (9), and a bimodal distribution with centroids at 1.75 and 1.95 (23), have been reported for it. Ratios of other elements to Ca found for this product have been: Na, ca. 0.01; Mg, 0.01 - 0.08; Al, 0.04 - 0.08; S, 0.01 - 0.03; K, 0.01 - 0.02; Fe, 0.01 - 0.03 (6-9,23). The pastes to which the above data refer were made from cements of various compositions, at w:c ratios of 0.3 - 0.6, and hydrated for times from 3 days to 23 years. Taken as a whole, the results suggest that the composition does not vary greatly with either time or w:c ratio within these limits, apart from a possible decrease with time in the S/Ca ratio. The composition probably depends to some extent on that of the cement, or perhaps more directly on that of the alite and belite it contains. This is especially true of the Mg/Ca ratio, which appears to reflect that of the alite, and in turn, that of the cement.

Rayment and Majumdar (7) could distinguish inner and outer products only in cements containing unreacted alite. In cases where distinction was possible, the outer or undesigned product had a mean Ca/Si ratio of 2.6 - 2.7, and Al/Ca and S/Ca ratios higher than those of the inner product. The authors regarded the outer product as C-S-H, and, noting that the $(Ca + Mg)/(Si + Al + S + Fe)$ ratio was less variable than the Ca/Si ratio, concluded that Mg could replace Ca and that Al, S and Fe could replace Si in the C-S-H structure. By using X-ray images, Taylor and Newbury (8) distinguished inner and outer products in an essentially fully reacted, 23 year old paste. They obtained results similar to those of Rayment and Majumdar (7), but interpreted them differently. Plotting $(Al + Fe)/Ca$ ratios against Si/Ca ratios for individual analyses, they noted that the great majority of points lay within a triangle whose apices represented the compositions of C-S-H, CH and hydrogarnet, which was the principal hydrated aluminate phase (Fig. 1). They concluded

that points not lying near the corners of this triangle represented mixtures. Harrison et al. (9) obtained similar results for younger pastes, in which the major hydrated aluminate phase was AFm. Neither of the last two investigations indicated that the inner and outer product C-S-H differ in Ca/Si ratio if the presence of other phases in the outer product is allowed for. There were indications that they differ in contents of minor elements; notably, Mg appears to be low or absent in the outer product.

AEM analyses of C-S-H from cement pastes have given somewhat erratic results for the mean Ca/Si ratio, values of which have ranged from 1.4 to 2.7 (13,19,24,25). An early observation that this ratio decreases markedly with time (19) was not confirmed in later work (25). A comparison study of EPMA and SEM results for the same pastes gave good agreement between the two methods, with mean Ca/Si ratios by AEM of 1.75 - 1.85 (23). The ratios of minor elements to Ca, for which data were first obtained by AEM (24), agree reasonably well with those found from EPMA and SEM analyses. As with the C-S-H of calcium silicate pastes, the mean Ca/Si ratios are of uncertain reliability, and values below about 1.7 are probably incorrect. The results of individual analyses may be more significant.

Lachowski and Diamond (13), studying compositional variation within particles at the micrometre level by AEM, reported Ca/Si ratios varying locally between 0.89 and just over 3. Ratios of other elements to Ca also varied widely, and, in agreement with Rayment and Majumdar (7), the authors found the ratio of $(Ca + Mg)$ to $(Si + Al + S + Fe)$ less variable than that of Ca to Si. Examination of their individual analyses shows that the higher Ca/Si ratios, where not attributable to presence of CH, are usually associated with high Al/Ca and S/Ca ratios. As with the EPMA and SEM results described earlier, these compositions probably arise from mixtures of C-S-H with AFm phase, supporting the conclusion that this can occur at or below a micrometre level. Both C-S-H and AFm phase have layer structures, and a close mixture within the gel is structurally reasonable.

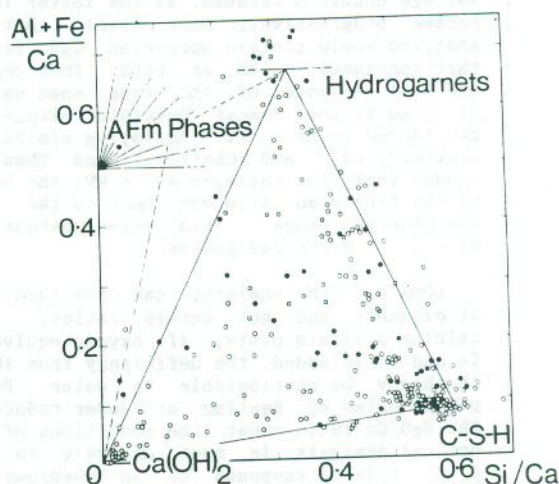


Fig. 1. Results of SEM microanalyses for a 23-year old cement paste (8).
 Open circles: Mg/Ca < 0.20, S/Ca < 0.04.
 Filled circles: Mg/Ca < 0.20, S/Ca \geq 0.04.
 Open squares: Mg/Ca \geq 0.20, S/Ca < 0.04.
 Filled squares: Mg/Ca \geq 0.20, S/Ca \geq 0.04.

2.2 SILICATE ANION STRUCTURE

2.2.1 NATURE OF THE ANIONS

By the time of the Paris Congress, a number of conclusions about the silicate anions in C_3S pastes appeared to have been established, based largely on results of trimethylsilylation (TMS) studies. The contents of monomer (SiO_4) were largely or wholly attributable to unreacted C_3S . The C-S-H contained substantial amounts of dimer (Si_2O_7) and of larger species, collectively if loosely called polymer, but little or no trimer or cyclic tetramer. The average anion size increased with time. Some information existed about the nature of the polymeric ions, based largely on gel permeation chromatography (GPC) of their TMS derivatives; at all ages, the most important single component was a relatively small one, possibly a tetramer or pentamer, but the precise nature of these ions was not established. For cement pastes, the data were less detailed. In general, the position appeared similar to that for C_3S pastes, but there were indications that the hydration products included monomer and that the proportion of the Si present in polymeric ions was less than for comparable C_3S or β - C_2S pastes.

Several subsequent studies have dealt primarily with TMS techniques (26-29). Dent Glasser et al. (29) examined the TMS derivatives of the C-S-H of cement pastes by high pressure liquid chromatography, thin layer chromatography, mass spectrometry and IR spectrometry. The results showed that the major low molecular weight anion larger than dimer was linear pentamer (Si_5O_{16}). Various larger species were found, but could have been artifacts.

A major advance has come from the use of ^{29}Si NMR (30-33), which complements the TMS approach in two respects. First, it is a purely physical method, in which there is no possibility of altering the anion structure through chemical side reaction. Second, it gives slightly different information, relating directly, not to the specific anions present, but to the environments of the Si atoms. The terms Q^0 , Q^1 , ..., Q^4 denote the connectivities of the silicate tetrahedra, i.e., the numbers of other such tetrahedra with which they share oxygen atoms. For C_3S and cement alike, the results showed that, after a few hours, the content of Q^0 begins to decrease, and that Q^1 begins to form, accompanied later by Q^2 ; neither Q^3 nor Q^4 has been detected. Q^0 can only be monomer, Q^1 without Q^2 , Q^3 or Q^4 can only be dimer, and Q^1 plus Q^2 in the absence of Q^3 and Q^4 can only occur in single chains, possibly including dimer, or in a mixture of these with single rings. Most importantly, the absence of Q^3 and Q^4 shows that three dimensional clusters or other highly connected species are absent. Clayden et al. (32) found high correlations between estimates of the degree of hydration from the relative intensities of the Q^0 and Q^1 peaks in the NMR spectrum, the amount of CH, and the cumulative heat evolution.

These results made possible a more detailed interpretation of the results of TMS/GPC studies. For alite pastes, Hirljac et al. (34) showed that the chromatograms could be accounted for if the major species in the C-S-H were dimer, linear pentamer, and linear octamer; at late ages, especially in pastes cured much above room temperature ($65^\circ - 70^\circ C$), larger species were also present. This suggests that the anions in the C-S-H of C_3S pastes are chains with 2, 5, 8... ($3n-1$) tetrahedra.

Data for cement pastes continue to be less detailed than those for C_3S or alite pastes, but recent

studies (35,36) confirm that the silicate anions are closely similar to those in C_3S pastes. The similarity between the GPC curves for the TMS derivatives shows that the sequences of anion sizes are the same, at least from dimer upwards. So far as either the TMS or the NMR method is concerned, atoms replacing Si are not parts of the anion. It follows that, if other atoms replace Si, they can not do so at all of the Si sites, as this would cause the purely silicate parts of the chain to include sections not belonging to the ($3n-1$) series. Substitution permissible only in every third site is not excluded.

Another interpretation of TMS results has recently been proposed (37), involving formation of three dimensional cluster ions. This is incompatible with both the NMR evidence (30-33) and the observed mean connectivities of 1.6 - 2.0 that have been found by the TMS method for the polymer ions (35,36). If derivatives of such anions are formed, they presumably result from side reactions.

Opinions have differed as to whether the hydration products contain monomer, for both C_3S and cement pastes. Stade et al. (38) concluded that the C_3S hydration product contained substantial amounts, even after 28 days at ordinary temperature. In contrast, several groups of workers using TMS have concluded that, for C_3S or alite pastes, the amounts of monomer found could be largely or wholly attributed to unreacted starting material (34,35,39,40). Wu et al. (39) considered that the monomer content could be used to determine the degree of hydration. Neither TMS nor molybdate methods are sufficiently accurate to show whether monomer is completely absent in the products, especially at low degrees of hydration. Cross polarization NMR, which can distinguish between Si atoms near to H atoms and ones that are not, shows that, in C_3S pastes, the product formed up to the end of the induction period contains only monomeric silicate, and that dimer begins to form only after the induction period is over; large amounts of monomer are never present in the product (33).

2.2.2 QUANTITATIVE STUDIES

Detailed, quantitative interpretation of TMS results is rendered somewhat uncertain by the fact that total recoveries of Si are typically only 80 - 90 %, and because it is probably impossible to completely eliminate interconversion of anionic species through side reactions. For tricalcium silicate or alite pastes hydrated for 28 days at $20^\circ - 25^\circ C$, estimates of the fractions of the total Si recovered, based on results of several TMS studies (35,36,41), are: monomer, 0.25 - 0.30; dimer, 0.30 - 0.45; polymer (> 5 Si), 0.15 - 0.25. Corresponding data for 180 days are: monomer, 0.10 - 0.15; dimer, 0.40 - 0.60; polymer, 0.25 - 0.35. Another investigation (34) gave similar results for dimer and polymer, but higher ones for monomer (0.44 at 28 days, 0.32 at 180 days). The amount of dimer passes through a maximum at about 180 days, but even after 30 years, this species accounts for about 40 % of the total Si (35). A study using the molybdate method for times up to 28 days gave relatively larger amounts of polymer (38).

The amounts of different anionic species within the polymer have been determined, from GPC of the TMS derivatives. For alite pastes, Hirljac et al. (34) found that pentamer accounted for about 75 % of the Si in the polymeric ions at 7 days, 60 % at 28 days, and 45 % at 180 days. At ordinary temperatures, anions containing more than 11 Si atoms were formed in appreciable quantities only after 1 year. Mohan and Taylor (35) and Uchikawa and Furuta (41) gave

results as number average and weight average sizes, which appear to indicate somewhat higher proportions of the larger species. After 22 years, the proportions of these species are considerable, but pentamer is still an important component (35).

Results for cement are not very different from those for C_3S . Massazza and Testolin (36) found that the amount of Si present as polymer relative to that present as dimer increases less rapidly in cement than in C_3S pastes. For a 28 day old cement paste, they recovered about 36 % of the total Si as dimer and 20 % as polymer; for a corresponding C_3S paste, the respective values were about 31 % and 26 %. In cement pastes, the amounts of Si present as dimer and as polymer are about equal at 1 year (35,36). $B-C_2S$ pastes have also been studied (36,42).

2.2.3 EFFECTS OF TEMPERATURE AND OTHER VARIABLES

The rate of polymerization increases markedly with temperature (34,38,43). For an alite paste hydrated for 100 days at 50°C, Hirljac et al. (34) recovered about 53 % of the total Si as dimer and 15 % as polymer. At 25°C, the corresponding recoveries were dimer, 42 %, and polymer, 24 %, while at 65°C, they were dimer, 34 % and polymer, 31 %. The distribution within the polymer is also markedly displaced to larger sizes with increase in temperature. Comparison of the TMS/GPC results for alite pastes hydrated for 1 year at 65°C (34) with those of pastes hydrated for up to 30 years at ordinary temperatures (35) suggests that the ultimate distribution of anion size may not vary greatly with temperature in the 50°C - 65°C range for which data are available.

The effects of accelerators and retarders have been studied. Changes in the nature of the products have been claimed (44), but neither Hirljac et al. (34), using TMS, nor Clayden et al. (31), using NMR, could find any effect other than that on the rate of reaction. Prolonged drying, and change in w:c ratio, are reported to have only minor effects on the course of polymerization (45). Polymerization is reported to be increased if the paste is heated before being loaded mechanically, while loading itself is reported to increase polymerization in young specimens and to decrease it in mature specimens (46).

2.3 WATER CONTENT, DENSITY AND THERMAL BEHAVIOUR

2.3.1 GENERAL

The literature shows some confusion regarding the density of C-S-H gel, and also regarding the porosity, which is a closely related quantity. The following considerations are relevant.

First, the density depends on the water content, which in turn depends on how the specimen has been equilibrated or dried. For any meaningful discussion of density in relation to structure at a chemical level, it is essential to know the total water content of the material in the state to which the density value relates. By "total water content" is meant the total amount of water lost up to ca. 1000°C, corrected for contributions from other phases. So long as this point is recognized, a wide range of density values can be equally meaningful for the same sample. Data in the literature, beginning with those of Powers and Brownyard (47) and of Feldman (48), indicate densities of C-S-H gel, corrected for other phases, in the region of 1900 - 2000 $kg\ m^{-3}$ for saturated material, 2300 - 2400 $kg\ m^{-3}$ for material equilibrated at 11 % rh, and 2500 - 2700 $kg\ m^{-3}$ for material dried at 110°C or D-dried. The corresponding H_2O/Ca ratios, similarly corrected, are approximately 2.3 - 2.5, 1.3 - 1.4, and 0.8 - 0.9, respectively.

Second, the density of a solid material is a meaningful concept only to the extent that there is a sufficiently well defined boundary between it and the surrounding medium. Any fluid (liquid or gas) in which the solid is immersed in order to measure the density must itself be of known and uniform density, penetrate at all points up to but not beyond the boundary, and not alter the solid volume of the material when brought into contact with it. These conditions are normally easily met for non porous, solid bodies of macroscopic dimensions, but for a material such as C-S-H gel, the position is more complex. Atoms do not have sharp boundaries; if this cannot be ignored, the density may depend on the properties of the surrounding medium, and the densities of separated layers may differ from those of the same layers in contact with each other. These considerations are especially relevant to C-S-H gel that has been dried at humidities below about 11 % rh, or at temperatures much above ambient, and may explain observations that observed values depend on the fluid used to determine them.

2.3.2 NEW DETERMINATIONS

Relis and Soroka (49) reported that the densities of cement hydration products increased with the degree of hydration; for a typical cement, values of ca. 2550 $kg\ m^{-3}$ at 20 % hydration and 2650 $kg\ m^{-3}$ at 40 % hydration were obtained, and by extrapolation, a value of 2720 $kg\ m^{-3}$ for complete hydration was suggested. There was discussion as to the validity of these conclusions (50).

Feldman and Ramachandran (51) determined the densities of mature cement pastes from which the CH had been leached. Using He on pastes that had been equilibrated at 11 % rh, and allowing time for the gas to flow in, a value of 2350 $kg\ m^{-3}$, uncorrected for other phases, was obtained. Data were also obtained for pastes that had been further dried. The results showed that removal of the CH did not alter the properties of the C-S-H, but that with further leaching, the structure was partly destroyed.

Juhász (52) followed changes in dielectric constant and other properties of pastes heated at temperatures up to 1000°C as a method of studying water binding. Parrott et al. (53) reported a study of alite pastes that included density and TG determinations. For pastes that had been treated with methanol to replace the pore water and then dried over silica gel, the density, corrected for other phases, was 2375 $kg\ m^{-3}$. It did not change with hydration time between 1 and 203 days. "Bound water", defined as that lost on TG between 100°C and 750°C, was 0.235 g per g of C_3S for a fully reacted paste; this value is not corrected for CH. The authors found 0.39 g of CH to be formed per g of C_3S on complete reaction. These data imply that the C-S-H has a Ca/Si ratio of 1.8 and an H_2O/Ca ratio of 1.0; its water content can also be expressed as 0.14 g per g of tricalcium silicate reacted. It was also found that the loss on TG at 100°C to 200°C was proportional to that at 200°C to 400°C throughout hydration, providing further evidence that the product does not change. The 100°C to 200°C loss was about 15 % greater than that at 200°C to 400°C.

Taylor (54) and Taylor et al. (25) calculated various quantities for cement pastes, including porosities and amounts and specific volumes of non evaporable and gel water, from estimates of quantitative phase composition. In order to obtain results agreeing with ones in the literature for broadly similar pastes, the following values for the density and water content of the C-S-H were assumed

in the later and more definitive work (25): Saturated conditions, density, 1950 kg m^{-3} , $\text{H}_2\text{O}/\text{Ca}$, 2.5; Equilibrated at 11 % rh, density, 2300 kg m^{-3} , $\text{H}_2\text{O}/\text{Ca}$, 1.4; Dried at 110°C , density, 2650 kg m^{-3} , $\text{H}_2\text{O}/\text{Ca}$, 0.85. A standard TG curve was given for the C-S-H gel. The data were expressed as molar ratios of H_2O retained in the C-S-H to Ca in the C-S-H for each of a series of temperatures, some typical values being 0.28 at 425°C (immediately below the CH step), 0.70 at 200°C , and 1.00 at 150°C . There were indications that the C-S-H in cement pastes retains some of its water on TG to higher temperatures than that of C_3S pastes, perhaps because substituents impede the crystallization of anhydrous phases. The results of Parrott et al. (53) appear to indicate a somewhat greater loss of water between 200°C and 400°C , but this could depend on the TG conditions used.

2.4 C-S-H AND RELATED PHASES FORMED OTHER THAN IN CEMENT OR CALCIUM SILICATE PASTES

Of the various studies reported, we shall consider only a few that are especially relevant to cement hydration. Some others, concerned chiefly with solution compositions or equilibria, are considered later.

Stade et al. (55,56) studied the incorporation of Al^{3+} and Fe^{3+} into C-S-H preparations made in suspension. NMR studies showed that preparations with Ca/Si ratios of 1.0 - 1.5 and Al/Si ratios of ca. 0.07 contained both tetrahedrally and octahedrally coordinated Al, the proportion of the latter increasing with Ca/Si ratio; at a ratio of 1.5, all the Al was octahedrally coordinated. Electron spin resonance and Mössbauer studies showed that Fe, which could be incorporated up to a level of at least 0.18 atoms per atom of Si, was almost all octahedrally coordinated. Neither Al nor Fe substitution had much effect on the distribution of silicate anion size, and it was concluded that these elements do not replace Si in the structure. As noted elsewhere in this review, there are indications that part of the AFm phase in cement pastes is closely mixed with the C-S-H. A similar explanation could perhaps account for the above results.

A new crystal structure determination of 1.1 nm tobermorite ($\text{C}_5\text{S}_6\text{H}_5$ approx.) is reported (57). The results confirm those of Megaw and Kelsey (58) and provide some additional detail. Jennite ($\text{C}_9\text{S}_6\text{H}_{11}$) has been synthesized in suspensions at 80°C from CH and either fumed silica, silica glass, or volcanic glass (59,60). An Al-bearing jennite was also prepared, which had slightly different cell parameters, behaved differently on heating, and was less crystalline.

2.5 C-S-H GEL STRUCTURE AT THE NANOMETRE LEVEL

The term "nanometre level" is preferred to "crystal structural level" because of the low degree of crystallinity. We shall assume that, at the coarser pore structural level, the structure is adequately described by the model of Feldman and Sereda (61), perhaps as modified by Daimon et al. (62). The question to be addressed concerns the nature of the individual layers. Early XRD work, reviewed by Bernal (63), indicated a layer structure and further suggested that this was closely related to that of 1.1 nm tobermorite. The name "tobermorite gel" was widely used for some years, but later rightly fell into disuse because of lack of evidence together with marked differences in composition, degree of crystallinity and silicate anion structure. Structural relationships to jennite were also suggested (64).

Recently, Taylor (65) has suggested that many properties of C-S-H gel can be accounted for if most of the layers are structurally imperfect ones of jennite, and a smaller proportion are similarly related to the more highly hydrated, 1.4 nm form of tobermorite ($\text{C}_5\text{S}_6\text{H}_9$). Both jennite and 1.4 nm tobermorite have structures that can be described in terms of alternating main layers and interlayers. The constitutional formula of 1.4 nm tobermorite, somewhat idealized, is $[\text{Ca}_4\text{Si}_6\text{O}_{18}\text{H}_2] \cdot \text{Ca} \cdot 8\text{H}_2\text{O}$, where square brackets enclose the contents of the main layer. The latter is based on a central, Ca-O sub layer, all the O atoms of which are shared with silicate chains of empirical formula $\text{Si}_3\text{O}_9\text{H}$. The constitutional formula of jennite, similarly expressed, is $[\text{Ca}_8\text{Si}_6\text{O}_{18}\text{H}_2(\text{OH})_8] \cdot \text{Ca} \cdot 6\text{H}_2\text{O}$. The main layers are again based on central, Ca-O portions, but in this case only some of the O atoms are shared with $\text{Si}_3\text{O}_9\text{H}$ chains, the rest being parts of OH groups. The layers differ sufficiently in structure that it is unlikely that one structure could merge into the other within a single layer, but layers of both types might well coexist within a poorly ordered structure.

Taylor (65) suggested that, in C-S-H gel, numerous silicate tetrahedra were missing from both types of layer, in a way that would fragment the chains into lengths containing 2,5,8... $(3n-1)$ tetrahedra. In the tobermorite type layers, one third of the Si and an equivalent amount of O was missing, giving them the formula $\text{Ca}_5\text{Si}_4\text{O}_{14}\text{H}_2 \cdot 8\text{H}_2\text{O}$; in the jennite type layers, up to one third was missing, giving the formula $\text{Ca}_9\text{Si}_{4+n}\text{O}_{14+2n}\text{H}_2(\text{OH})_8 \cdot 6\text{H}_2\text{O}$, where $0 \leq n \leq 2$. For each type of layer, it was possible to calculate the Ca/Si ratio for a given chain length (Fig. 2). A jennite type layer with an average chain length of 5 would have a Ca/Si ratio of 1.8; this is approximately that of C-S-H gel, and would account for the high proportion of pentamer formed in the material.

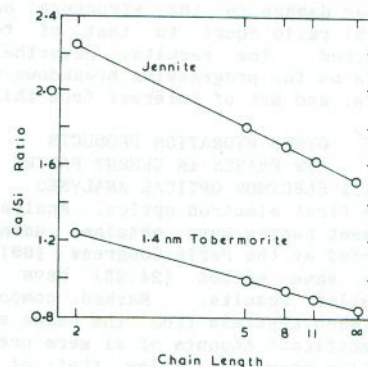


Fig. 2. Calculated Ca/Si ratio as a function of chain length in the jennite and tobermorite structures (65).

The evidence cited comprised conditions of formation, silicate anion structure, $\text{H}_2\text{O}/\text{Ca}$ ratios and densities for three different drying conditions, TG curves, XRD pattern, selected area electron diffraction patterns, and the range of Ca/Si ratios observed in AEM analyses. The observed mean Ca/Si ratio of 1.7 - 2.0 could arise in various ways. At early ages, a mixture of tobermorite type and jennite type layers was formed, both with purely dimeric anions, and having Ca/Si ratios of 1.25 and 2.25, respectively. At later ages, jennite type layers containing larger anions, especially pentamer, became increasingly important. Since they contained fewer missing tetrahedra, these were thermodynamically more stable;

this could explain the occurrence of the polymerization process.

It was suggested that, in C-S-H gel equilibrated at 11% rh, the layers had the H_2O/Ca ratios of jennite and 1.4 nm tobermorite. In material that had been dried at 110°C or D-dried, they were similarly related to the known dehydration products of these phases, namely metajennite ($C_9S_6H_7$) and 1.1 nm tobermorite. In saturated material, they had the H_2O/Ca ratios of jennite and 1.4 nm tobermorite, and the micropores described by Daimon et al. (62) and others were full of water. In each case, this explained the observed H_2O/Ca ratio and density. Attention was drawn to the early work of McConnell (66) on a naturally occurring C-S-H gel, known as plombierite; this had some close similarities to the material in cement pastes, including the H_2O/Ca ratio both under saturated conditions and at lower humidities.

Two other structures for C-S-H gel at the nanometre level have recently been proposed. Grudemo (67) suggested a structure, based on XRD evidence, closely related to that of CH. The silicate ions were separate tetrahedra, and the structure is thus incompatible with the TMS and NMR evidence. In a long series of papers, Shebl et al. (68) developed the hypothesis that the final product of hydration of C_3S or $\beta-C_2S$ is 1.1 nm tobermorite, "identical with the natural and synthetic mineral." This conclusion was largely based on extraction experiments using a modified Franke solvent, supported by IR evidence. The CaO extracted was categorized as "free", "interlayer" and "bound"; for 1 mole of fully reacted C_3S , the amounts of these were 1.0, 0.5 and 0.67 moles, respectively. The conclusion that the product is identical with 1.1 nm tobermorite is untenable; it does not give a tobermorite XRD pattern, and differs in anion structure and other respects. Moreover, the work of Feldman and Ramachandran (51) shows that major damage to the structure occurs well before a Ca/Si ratio equal to that of tobermorite has been reached. The results, nevertheless, provide much data on the progressive breakdown of the C-S-H structure, and are of interest from this point of view.

3 OTHER HYDRATION PRODUCTS

3.1 AFM PHASES IN CEMENT PASTES

3.1.1 ELECTRON OPTICAL ANALYSES

The first electron optical analyses of AFM phases in cement pastes were obtained using AEM and were reported at the Paris Congress (69). Later studies by the same method (24,25) have given substantially similar results. Marked compositional variations between crystals from the same specimen were found; significant amounts of Si were present, and mean S/Ca ratios were well below that of monosulphate. The deficiencies in sulphate were not compensated by the contents of silicate, and it was assumed that some of the interlayer anion sites were occupied by hydroxide; hydroxoaluminate was also believed to be present, to an extent that increased as hydration proceeded. These substitutions are equivalent to solid solution with C_4AH_x and C_2AH_x , respectively.

Harrison et al. (9) have reported SEM microanalyses of AFM phases in cement pastes elsewhere in these Proceedings. In pure portland cement pastes, regions of AFM phase free from other phases had, typically, Al/Ca ratios near 0.5 and Si/Ca ratios near 0.05. S/Ca was rather variable and, most commonly, 0.10 - 0.15. They were low in other elements, including Fe. AFM phase closely mixed with C-S-H, occurring in the outer product, was similar in composition to the above, but tended to have a higher

S/Ca ratio, which was sometimes as high as 0.25, the theoretical value for monosulphate. In a very few cases, AFM phase containing little or no S was found. There was no positive evidence that any of the AFM phase contained much Fe, or that its Al/Ca ratio deviated far from 0.5, the latter indicating that little or no hydroxoaluminate was present in the interlayer sites. As noted earlier, some of Rayment and Majumdar's results (7) of outer product can also be interpreted as being of mixtures of C-S-H with AFM phase, and this is also true of some AEM analyses, which relate to much smaller volumes of material.

3.1.2 COMPARISON WITH XRD AND IR EVIDENCE IR
XRD evidence, beginning with that of Copeland et al. (70), shows that typical cement pastes more than a few days old, that have not been strongly dried and that have been protected from carbon dioxide before and during examination, give peaks corresponding to AFM phases with layer thicknesses of approximately 0.89 nm and 0.78 nm. Several studies on the pure C-A-S-H system have shown that a miscibility gap exists in the $C_4AH_n-C_4ASH_n$ series; Roberts (71) concluded that it extended from S/Ca = 0 to S/Ca = 0.125, and reported layer thicknesses for the solid solution varying from 0.877 nm at S/Ca = 0.125 to 0.896 nm at S/Ca = 0.25 (monosulphate). Substantial replacement of the SO_4 in monosulphate by 2 OH can thus occur with only minor effect on the layer thickness. Substitution of silicate for sulphate probably has little effect on the layer thickness (72). The peak at 0.78 nm can reasonably be assigned to C_4AH_x ; this assignment is supported by the fact that mild attack by CO_2 causes a peak at about 0.82 nm to appear. The XRD evidence thus indicates the presence in typical portland cement pastes of two kinds of AFM phase, one of which is C_4AH_n , and the other having a S/Ca ratio that could be anywhere between 0.125 and 0.25, with possible partial replacement of sulphate by silicate.

From IR evidence, Bensted (73) concluded that the AFM phase in cement pastes differed from pure monosulphate. It was less crystalline, and its sulphate content decreased as hydration proceeded.

The SEM analytical results (9) are, in the main, compatible with these results. If replacement of sulphate by silicate is assumed, the compositions mostly fall into the range that would be expected to give an X-ray peak at about 0.89 nm. One might, however, have expected to have found more particles containing little or no S, to account for the peak at 0.78 nm. The close admixture of much of the AFM phase with C-S-H could well explain the IR evidence of poor crystallinity.

It is more difficult to reconcile some of the AEM results with the other evidence. This applies most strongly to those analyses giving Al/Ca ratios well above 0.5, which imply presence of interlayer hydroxoaluminate, and to the finding by AEM of occasional crystals relatively high in Fe. As with AEM analyses of C-S-H, the individual analyses may be valid, but sampling may present a serious problem, and the significance of mean ratios found by this method must be considered uncertain.

3.2 AFT AND HYDROGARNET PHASES IN CEMENT PASTES

The electron optical analysis of AFT phases is especially difficult because of the ease with which decomposition and probable loss of material occur in the electron beam. As with the AFM phases, AEM analyses were reported at the Paris Congress (69); they indicated compositions significantly different

from that of ettringite, notably in showing lower S/Ca ratios and significant contents of Si. Later studies by the same method have given broadly similar results (24,25,74); the most recent (74) showed that deficiencies in both S and Al were common, but were usually though not always balanced by Si. Fe/Ca ratios were usually below 0.01. No EPMA or SEM analyses have been reported. Bensted (73) concluded from IR evidence that the AFt phase in cement pastes, like the AFm phase, was relatively poorly crystalline.

Taylor and Newbury (8) reported EPMA analyses of the hydrogarnet which was the principal hydrated aluminate phase in a 23 year old cement paste. The mean composition was near to $\text{Ca}_3\text{Al}_{1.2}\text{Fe}_{0.8}\text{Si}_{0.12}\text{H}_8$, but Mg was also present, and it was not clear how much, if any, was in the hydrogarnet. This composition is near to that suggested by Copeland et al. (70) from XRD evidence.

3.3 AFm, AFT AND HYDROGARNET PHASES FORMED OTHER THAN IN CEMENT PASTES

As with C-S-H, we shall only consider studies that are particularly relevant to cement hydration; some dealing mainly with solution compositions or equilibria will be discussed later. Fischer and Kuzel (75) reexamined phases in the system $\text{C}_4\text{AH}_n\text{-C}_4\text{A}\bar{\text{C}}\text{H}_n$ system, using single crystal and powder XRD. The phases were:

C_4AH_n with $n = 19$ (2 polytypes), 13, 11 and 7;

$\text{C}_4\text{A}\bar{\text{C}}\text{O}.5\text{H}_n$ with $n = 12, 11.25, 10.5,$ and 6.5 ;

$\text{C}_4\text{A}\bar{\text{C}}\text{H}_n$ with $n = 11, 9 - 9.95,$ and 6 .

C_4AH_{13} was shown to have a 12-layer structure and its unit cell was determined. New XRD, thermal and IR data were given for many of the phases. Fischer et al. (76) described two naturally occurring specimens of hydrocalumite.

Gessner et al. (77) studied C_2AH_8 by NMR; they found that all the Al was octahedrally coordinated. This does not support the interlayer anion structure proposed by Scheller and Kuzel (78), and the constitution $[\text{Ca}_2\text{Al}(\text{OH})_6][\text{Al}(\text{OH})_3(\text{H}_2\text{O})_3]\text{OH}$ was suggested. An AFm phase containing sulphite was described (79), but an attempt to prepare one containing sulphide was unsuccessful, though a compound with S/Ca = 2 was obtained (80).

Several studies on the formation, stability or thermal dehydration and rehydration of ettringite have been reported (81-83). Others, dealing mainly with ettringite morphology or with the possible existence of amorphous or quasi crystalline precursors to AFm or Aft phases, are considered later. Other studies on Aft phases concern refinement of the thaumasite crystal structure (84,85), thermal decomposition of thaumasite (86) and naturally occurring Aft phases containing Cr(III) or borate (87-89). Among studies on hydrogarnets (90-93) is one that includes a crystal structure refinement and a formula relating cell parameter to composition (91). Murat (94) reviewed thermal properties (mainly DTA) of hydrated calcium aluminate phases.

3.4 HYDRATION PRODUCTS OF THE FERRITE PHASE

Uncertainty persists as to the hydration products of the ferrite phase in cement pastes. Copeland et al. (70) concluded from careful XRD studies that it yielded a hydrogarnet phase, but subsequent XRD studies on pastes of other cements do not appear to have shown this, except with cements hydrated for long times or at elevated temperatures. In agreement with several earlier workers, Teoreanu et al. (95) found that hydration of C_4AF or C_2F by itself gave an iron hydroxide, together with AFm and hydrogarnet phases. Fortune and Coey (96) similarly concluded

from a Mössbauer and XRD study that hydration of C_4AF by itself at 72°C gave a hydrogarnet and an FH_x gel, the latter giving a weak, broad X-ray band centred at 0.44 nm. Relatively little of the iron entered the hydrogarnet, and none at all if gypsum was present. In contrast, Harchand et al. (97,98) concluded from Mössbauer and IR studies on cement pastes that no FH_x gel was formed, and that the Fe entered the AFm phase. Bensted (99) agreed, and considered it unlikely that FH_x would form in presence of CH. Evidence from X-ray images in the SEM indicates that, when the interstitial phases hydrate, the Fe does not migrate away from the resulting relicts (8), and this conclusion is supported by results at higher resolution obtained from backscattered electron images (100). Mass balance calculations suggest that the amounts of Fe present in the AFm phase and C-S-H are insufficient to account for all the Fe supplied by the clinker phases that have reacted (25). SEM microanalyses of pastes by Harrisson et al. (9) showed no regions high in Fe that were not also high in Ca, Al, Si and, sometimes also, in Mg, and could be interpreted as indicating that the Fe was present in a separate phase that was mixed at or below the micrometre scale with C-S-H, AFm phase low in Fe and, sometimes, a phase high in Mg. Several other studies have been reported (101-103).

The problem is not solved, though the balance of the existing evidence seems to favour the view that, when the ferrite phase hydrates in a cement, the space it occupied is filled with a close mixture of C-S-H, AFm phase low in Fe, a hydrated phase high in Fe, and often, another one high in Mg. Such a mixture can have a bulk composition quite close to that of the hydrogarnet that has sometimes been found (8,70), which could thus readily form from or instead of it under favourable conditions. More work is, however, needed. Studies on C_4AF by itself are only of background relevance, even if CH and gypsum are added, because the ferrite phase in cement is normally closely mixed with aluminate phase, hydrates in an environment dominated by the silicate phases, and has a composition that is not even close to the $\text{C}_2\text{A-C}_2\text{F}$ series, but is typically near to $\text{Ca}_2\text{AlFe}_{0.6}\text{Mg}_{0.2}\text{Si}_{0.15}\text{Ti}_{0.05}\text{O}_5$ (104). X-ray microanalysis in the EPMA or SEM probably does not give sufficient resolution, but backscattered electron imaging may provide further useful data.

3.5 CALCIUM HYDROXIDE

The existence, or otherwise, of amorphous or cryptocrystalline CH has received attention. Marchese (105) could detect CH in some 12th century lime mortars by thermal methods but not by XRD, and concluded that it was amorphous. Neal and Stanger (106) reported that CH occurred in nature in both crystalline and amorphous forms. Vitkovskii (107) considered that the CH in cement pastes included amorphous material. Groves (10) examined cement pastes of low w:c ratio (0.15) by TEM of ion thinned sections. He found parallel clusters of CH platelets about 10 nm thick, rotated through various angles around their common c-axis and embedded in gel; the larger crystals common in normal pastes were not observed. Abo-El-Wafa and Al-Wakeel (108) concluded from IR evidence that the CH in alite pastes was poorly crystalline, especially at low w:s ratios. On the other hand, Rayment and Majumdar (7) concluded from their EPMA study that microcrystalline CH was not present in cement pastes of normal w:c ratio.

The possibility of ionic substitutions in CH has been examined. AEM results (24) supported earlier conclusions that the CH in cement pastes contained

significant amounts of foreign ions, especially silicate and sulphate. Shpynova et al. (109,110) calculated the effects that substitutions in interlayer sites, balanced by omission of H, would have on the XRD powder pattern, and concluded from experimental observations that CH modified by such substitutions could be prepared. The C-S-H structure suggested by Grudemo (67) is based on a similar concept. In contrast, some other studies, summarized by Barker (111), suggest that CH largely avoids incorporating foreign ions, and the AEM evidence could possibly be explained by the existence of inclusions.

Barker et al. (112) made an XRD study of strain in CH crystals, including ones grown in presence of colloidal silica. Brindley and Kao (113) discussed crystal structures and IR spectra of brucite type hydroxides, including CH. Barker (111) and Barker and Barnes (114) reviewed aspects of the growth of CH in cement pastes and its role in the development of strength.

4. QUANTITATIVE PHASE DETERMINATIONS, MASS BALANCE AND VOLUME FRACTIONS

4.1 EXPERIMENTAL METHODS OF PHASE DETERMINATION

4.1.1 UNREACTED CLINKER PHASES

Quantitative X-ray diffraction analysis (QXDA) is probably the only practicable method at present for determining the unreacted clinker phases individually in a cement paste. The problem is similar to, though more complex than, that of determining the phases in an unreacted clinker, and will not be discussed here. Gutteridge (115) recently described a least squares procedure and applications to anhydrous cement systems. Determinations in pastes are of low precision; Odler and Dórr (116) estimated the precision at not better than $\pm 3\%$ for unreacted alite in alite pastes, and for cement pastes, even this would be difficult to achieve (25). Analysis of backscattered electron images obtained in the SEM is a rapidly developing technique, and may prove a more effective method, both for unreacted clinker phases and for CH (117).

4.1.2 CALCIUM HYDROXIDE

Many recent papers have dealt with determination of CH in cement or calcium silicate pastes. Thermal methods used have included thermogravimetry (TG) or differential thermogravimetry (DTG; 25,53,54,116,118-123), semi isothermal DTG (124), thermal evolved gas analysis (TEGA; 124,125) and differential thermal analysis (DTA) or differential scanning calorimetry (DSC; 118,125-128). QXDA has been used (54,67,116,118-121,125,126), as has IR (129). Chemical extraction methods have included the use of aqueous CaCl_2 (4) or aqueous CH (126), and of Franke solvent or related organic media (68,116,118,125). Some of the investigators have found significant differences between the results of thermal methods and QXDA, with QXDA usually giving lower results (116,118,119,125,126), but others have reported no differences outside experimental error (25,120). There is broad agreement that extraction methods give higher results than either thermal methods or QXDA (116,118,125,126). It has been suggested that QXDA gives low results due to presence of amorphous CH (126); some workers consider that this may also apply to thermal methods, either for the same reason (116), or because of CH that is adsorbed on the C-S-H (125) or present as interlayer CH (68). Sources of error in the determination of CH by TG have been discussed (54).

The following conclusions are suggested. First, adsorbed or interlayer Ca^{2+} and OH^- are not CH, but parts of the C-S-H. Second, part of the CH in some

or all cement pastes could be intimately mixed with C-S-H. There is no convincing evidence for the presence in cement pastes of amorphous CH, or, except in pastes of unusually low w:c ratio (10), of cryptocrystalline CH, but the present evidence probably does not exclude the possibility of mixture within the gel at or approaching a single layer level. Ultimately, the differences may be ones of how C-S-H is defined. CH mixed with C-S-H at or near a single layer level would not be recognized as a separate phase by EPMA or SEM analysis, and possibly not by QXDA or thermal methods, but it might well be counted as CH by extraction methods or AEM. Further investigation is needed; structural and analytical studies of ion-thinned sections probably offer the best hope of providing definitive evidence.

Day (130) found that if either cement paste or CH was soaked in methanol, an increase in weight loss occurred on DTG in nitrogen in the 700°C region. He considered that methanol, or some reaction product, was retained in the paste and reacted with CH to produce a carbonate like material. This conclusion, which is of much interest because methanol or other organic liquids are often used to stop hydration, was challenged (131), but nevertheless appears worthy of further investigation. It is not inconceivable that small organic molecules could be strongly sorbed and then pyrolyse giving CO, which in the presence of active CaO could yield CaCO_3 and C. If such a process does, in fact, occur, it has important implications for the determination of CH by TG, and might also account for an observation (25,54) that the loss on TG above the CH step exceeds the CO_2 content found in a separate, chemical determination, as the samples studied had previously been soaked in acetone, which might have a similar effect.

4.1.3 HYDRATED SILICATE AND ALUMINATE PHASES

The literature is conflicting as to the possibility of determining the hydrated aluminate phases in cement pastes by thermal or X-ray methods. Uchikawa et al. (128) found it possible using (DSC) to determine monosulphate, C_4AH_x and C_3AH_6 , but not ettringite or C-S-H. Later, however, they reported ettringite contents determined by a modified TG-DSC method (132). Millet et al. (133) found that QXDA gave false results for ettringite due to effects of grinding; DTA was better in this respect, but the need for grinding still caused problems. Ogawa and Roy (82) found it possible to determine ettringite either by QXDA or by DSC, and Bensted (134-137) reported ettringite contents determined by DTA. Crammond (138) determined ettringite, thaumasite and gypsum by QXDA. Odler and Abdul-Maula (139) found that Aft phase could best be determined by DTA, as the peak area scarcely depended on composition or crystallinity, though care was needed to avoid interference from C-S-H. For AFm phase, QXDA was probably the best method; however, though very sensitive, it gave only semi quantitative results. Grudemo (67) reported C-S-H contents found by QXDA.

From the foregoing results, it appears that thermal methods and possibly QXDA may be used for determining Aft phase, but it is doubtful whether the direct determination of either C-S-H or AFm phase in pastes has been successfully achieved. The very close admixture of much of the AFm phase with C-S-H, together with its variable composition and imperfect crystallinity, explains the difficulty. Least squares fitting of observed and calculated TG curves probably offers the best possibility, but better standard data and a fuller understanding of AFm compositions and how they affect the thermal behaviour are required.

4.2 MASS BALANCE AND INDIRECT DETERMINATION OF C-S-H COMPOSITION

4.2.1 CALCIUM SILICATE PASTES

Many studies have been reported over a long period with the object of determining the Ca/Si ratio of the C-S-H in calcium silicate pastes indirectly, from the contents of unreacted starting material, if any, and of CH. Some indicated marked changes in this ratio as hydration proceeds. The most recent studies do not confirm this, except perhaps for the very early stage of reaction. Odler and Dörr (116) reported Ca/Si ratios in C₃S pastes of 1.60 using an extraction method for CH, or of 1.99 using TG, with an uncertain but lower value for the product of the first 1 - 2 % of reaction. LeSueur et al. (120) reported values of 1.7 ± 0.1 and 1.8 ± 0.2 for C₃S pastes made with and without CaCl₂, respectively, both substantially independent of the degree of reaction. The difference between these values was not considered significant. Parrott et al. (53) obtained closely similar results, discussed in Section 2.3.2, which gave a value of 1.8 for an alite paste. For β -C₂S pastes, the results of Kantro and Weise (140) and of Fujii and Kondo (141) indicate values around 1.8 at complete hydration. Shibata et al. (142) described the preparation and hydration of an unstabilized β -C₂S that gave virtually no detectable CH on hydration, and which thus gave C-S-H with a Ca/Si ratio close to 2.0.

Taken as a whole, these results agree well with the conclusions derived from electron optical analyses, discussed earlier. There are several indications that β -C₂S tends to give a product with a slightly higher Ca/Si ratio than that formed from C₃S, and the results of Shibata et al. (142) provide an extreme example of this. Small experimental errors have a disproportionate effect on Ca/Si ratios determined indirectly, especially at low degrees of reaction. It is now reasonably certain that the Ca/Si ratio of the C-S-H reaches its final value not later than the end of the induction period.

4.2.2 CEMENT PASTES

For typical portland cements, CH contents, referenced to the ignited weights, are typically 18 - 25 % after times of 3 - 12 months (25,118,122,126). Contents of AFt phases appear to have been determined only for short hydration times; Uchikawa et al. (128) and Bensted (134 - 137) quote values of, typically, 2 - 4 % for normal cements at 4 h.

Taylor et al. (25) reported contents of C-S-H and hydrated aluminate phases determined by a difference method. The amounts of unreacted clinker phases, CH and CaCO₃ were determined by approximate QXDA, TG and a chemical method, respectively; the compositions of the clinker phases were known from SEM microanalyses; the nature of the hydrated aluminate phases (AFm or AFt or both) was established by XRD; their mean compositions and that of the C-S-H were determined by AEM. Knowing also the bulk composition of the cement, the amounts of CaO, SiO₂, Al₂O₃ and SO₃ present in the hydrated silicate and aluminate phases were obtained by difference. A linear, simultaneous equation was set up for each of the oxides mentioned, having the compositions of the hydrated phases as coefficients, the amounts of those phases as unknowns, and the quantity of the oxide to be accounted for as the right hand side. These equations were then solved by least squares to find the most probable amounts of the hydrated silicate and aluminate phases. The results were tested in three ways. First, using standard data for each phase, a simulated TG curve was calculated and

compared with the observed one. Second, quantities such as porosities were calculated, which could be compared with typical data from the literature for comparable cements. Third, the discrepancies between the total amounts of all the oxides present, both major and minor, were compared with those accounted for by all the anhydrous and hydrated phases.

The results of the first two of these tests were reasonably satisfactory, but the mass balance test showed some systematic discrepancies: on the average, 2.5 % of CaO (referenced to the ignited weight) and 0.7 % of Fe₂O₃ were unaccounted for, and the calculated content of SiO₂ was 1.1 % too high. Suspicion fell on the C-S-H compositions, determined by AEM, which were mostly between 1.6 and 1.7; higher values would have improved the agreement. It was also suggested that the presence of an iron rich gel, perhaps containing some Ca, could account for the discrepancy for Fe₂O₃ and contribute to that for CaO. Subsequently, SEM analyses of the hydration products of one of the same cements were carried out (9), and gave a Ca/Si ratio of ca. 2.0 for the C-S-H. Substitution of this value in the calculations greatly improves the agreement for CaO.

The effect on mass balance of varying the Ca/Si ratio assumed for the C-S-H is shown by the following hypothetical calculation for a fully reacted cement:

- (i) Assume the cement composition to be: Na₂O, 0.2; MgO, 1.3; Al₂O₃, 5.4; SiO₂, 20.6; SO₃, 2.7; K₂O, 0.4; CaO, 65.3; TiO₂, 0.3; Fe₂O₃, 3.0; Misc., 0.7; Total, 99.9 %.
- (ii) Assume the CH content, referenced to the ignited weight, to be 23.8 %; this is at the upper end of the probable range.
- (iii) Assume the atom ratios in the C-S-H, relative to Ca, to be: Mg, 0.02; Al, 0.05; Si, 0.50; S, 0.01; Fe, 0.015 (Ca/Si = 2.0).
- (iv) Assume those in the AFm phase to be: Mg, 0.02; Al, 0.50; Si, 0.02; S, 0.18; Fe, 0.03.
- (v) Assume 0.9 % of CO₂, present as calcite.
- (vi) Set up and solve two simultaneous equations to determine C-S-H and AFm phase, using the contents of Al₂O₃ and SiO₂, and thus making the mass balance complete for these components and concentrating the principal discrepancies into the result for CaO.

This gives a calculated total of 65.3 % for CaO, in excellent agreement with the amount present in the cement; other totals are: MgO, 0.7 %; SO₃, 2.6 %; Fe₂O₃, 1.2 %. If the calculation is repeated assuming a Ca/Si ratio of 1.7 for the C-S-H, the calculated total for the CaO is 60.1 %, which is 5.2 % below the amount in the cement. If a lower content of CH is assumed, it is necessary to assume that the C-S-H has a Ca/Si ratio greater than 2.0 if balance for the CaO is to be obtained. These results support the view that, for some cements at least, the Ca/Si ratio of the C-S-H is closer to 2.0 than to 1.7. They also indicate that not all the Fe₂O₃ in the hydration products is present in the AFm phase and C-S-H, and the same is probably true of the MgO.

4.3 VOLUME FRACTIONS

Volume fractions in pastes depend on drying conditions and are subject to the same considerations as densities and water contents, discussed in Section 2.3.1. For an alite paste with w:s 0.6, treated with methanol and then dried over silica gel, Parrott et al. (53) reported experimental data which, extrapolated to complete reaction, give: CH 0.20; C-S-H, 0.35; pores < 50 nm, 0.25; pores > 50 nm, 0.20. For

cement pastes, Taylor et al. (25) calculated volume fractions and some related quantities from the amounts and densities of phases, using procedures and data quoted in Sections 2.3.2 and 4.2.2. Porosities were obtained by difference. For a paste with w:c = 0.5, hydrated for 1 year and equilibrated at 11 % rh, the volume fractions were: Unreacted clinker phases, 0.05; CH, 0.11; CaCO₃, 0.01; C-S-H, 0.37; AFm, 0.15; micropores (≤ 5 nm), 0.13; capillary pores, 0.18. Interlayer space was counted as part of the C-S-H. The Ca/Si ratio assumed for the C-S-H in such calculations has little effect on the resulting porosities, but the volume fraction of C-S-H is liable to change by up to 0.04, with corresponding change in that of AFm phase. These two sets of results are approximately compatible if due allowance is made for differences in composition, w:s ratio and divisions between C-S-H, micropores and larger pores.

5 MICROSTRUCTURAL DEVELOPMENT

5.1 INTRODUCTION

Knowledge of microstructural development in cement pastes has greatly increased since the Paris Congress. The contributions of P.L. Pratt and his co-workers at Imperial College, London, have been especially important, and the writer is much indebted to him and to Dr. K.L. Scrivener for helpful discussions, on which this section is largely based. The advances were possible because several techniques were used. With any one technique for studying cement paste microstructure, there are inevitably questions concerning the representative nature, or otherwise, of the fields examined, and the extent to which the microstructure has been altered during specimen preparation or examination. No one method is likely to answer all such questions satisfactorily but from the use of several methods and critical comparison of the results, a reasonably clear picture has begun to emerge.

The most important, relatively new methods are high voltage transmission electron microscopy (HVEM) with environmental or "wet" cells to reduce water loss (143-145), scanning transmission electron microscopy (STEM) of ion thinned sections (146), and backscattered electron imaging (BEI) of polished sections in the SEM using detectors designed to maximize contrast due to compositional differences and to minimize that associated with topography (117). Scrivener and Pratt (147) have concisely described the uses of these techniques. Other methods have included X-ray imaging in EPMA (8), SEM examination of matched fracture surfaces (148), and SEM using a cryo stage to avoid dehydration (149). Microstructural development in C₃S or alite pastes differs in important respects from that in cement pastes, and we shall consider it separately. Following Jennings et al. (150), we shall refer to the early, middle and late periods of microstructural development, with boundaries at ≈ 3 h and 20-30 h for typical cements at 20°C, and to the corresponding products.

Unless a wet cell or cryo stage is used, extreme dehydration occurs in any electron optical investigation, and it has been shown (100,150) that this can have drastic effects on the fine microstructure. However, drying begins as soon as the rh falls below saturation, and any paste at lower humidities will contain regions in which water is in varying degrees deficient. The water is lost initially from the wider pores, which appear in electron micrographs as the most open parts of the structure. One would expect them to be disproportionately represented on fracture surfaces.

5.2 CEMENT: THE EARLY PERIOD

The period up to 3 h comprises the pre induction and induction periods. The anhydrous cement has a wide particle size distribution, with, typically, 15 % < 5 μ m and 10 % > 50 μ m (151). BEI indicates that most grains are polymineralic (Fig. 3a; 100,117). If surface active admixtures are absent, the grains tend to flocculate in water. HVEM with wet cells shows that, at high dilutions, a gelatinous layer or membrane forms over the grain surfaces soon after mixing (143,145). A product of similar appearance, though not necessarily of the same composition, has been observed on the surfaces of C₃A hydrated in presence of gypsum (152). There appears to be no unequivocal, direct evidence for the formation of a gel layer during the first minutes of hydration in cement pastes of realistic w:c ratio, but the observed behaviour of C₃A plus gypsum, together with evidence from concentrations in solution, strongly suggests that one is formed, and that it is probably amorphous, colloidal, and rich in Al and Si but also contains significant amounts of Ca and SO₄ (100).

Dalgleish et al. found that, after 1 h, stubby rods of Aft phase, typically 250 nm long and 100 nm thick, were formed (153-155). Later studies by Scrivener and Pratt (100,147,152), using both wet cells in the HVEM and ion thinned sections in the STEM, showed that these can occur at some distance from the cement grains, suggesting that they have nucleated either in the solution, or on the outer surface of a thin layer of gel (Fig. 3b). On drying, they fall back on to the grain surfaces, on which they are unevenly distributed, possibly reflecting compositional differences in the underlying grains.

The first study using a wet cell, made at high w:c ratios, showed tubular growths radiating from the cement grains, which were believed to have formed by a "silicate garden" mechanism (143). It was later shown that they were rich in Ca, Al and S, and were not formed if C₃S was substituted for cement (156). They have not been observed in the more recent studies made at normal w:c ratios, and do not appear to be a significant feature of normal cement hydration.

5.3 CEMENT: THE MIDDLE PERIOD

5.3.1 FORMATION OF C-S-H AND CH

The period from 3 h to 20-30 h comprises the acceleratory and early deceleratory periods, during which some 30 % of the cement reacts. It is characterised by the rapid formation of C-S-H and CH. Many observers studying fracture surfaces have reported the formation during this period of C-S-H as fibres apparently radiating from cement grains (Type I of Diamond, 157). Honeycombs or reticular networks (Diamond Type II) have also often been seen. Rosettes of fibres $\approx 2\mu$ m in diameter forming bulges on larger surfaces could result from reaction of small cement grains adhering to larger ones (100). There are several indications that the C-S-H when wet consists of foils, and that the fibres or honeycombs are, at least in part, produced on drying (100,147,158).

The C-S-H forms a thickening layer or shell around the cement grains (154,158), which engulfs and possibly nucleates on the framework of Aft rods (Fig. 3c; 152). A significant amount has formed in 3 h, and the particle surfaces are entirely covered by 4 h (154). The shells grow outwards; by about 12h, they are 0.5-1.0 μ m thick, and inter shell cohesion is sufficient that fracture sometimes occurs through the shells and not between them. This stage, which corresponds approximately to the maximum in heat evolution rate, was termed the cohesion point; the structure of

interconnected shells around the larger grains was considered to play an important part in determining the mechanical and other properties, which thus depend on the particle size distribution (154,158).

From studies using wet cells, BEI and ion thinned sections, Scrivener and Pratt (100,147,152) showed that spaces develop between the shells and the anhydrous grains; they are detectable at 5 h in ion thinned sections, and by 12 h are up to $0.5\ \mu\text{m}$ wide. They were believed to contain solutions with high concentration gradients and possibly colloidal material. Initially, therefore, the shell grows outwards and by becoming less porous, rather than inwards, and the spaces widen as the anhydrous material, primarily alite and C_3A , is consumed. The mode of growth shows that the shells are, at this stage, permeable and that reaction occurs through solution. This last conclusion is reinforced by the observation that C-S-H also grows on fly ash surfaces, if present, before any detectable reaction of the fly ash has taken place (159).

The same studies showed that, before the end of the middle period, C-S-H begins to deposit also on the inner surfaces of the shells, and that the spaces between the latter and the anhydrous cores begin to fill up (Fig. 3d). Cement grains were shown to differ in behaviour depending on their size, phase composition, and internal microstructure. Ones smaller than $\approx 3\ \mu\text{m}$ dissolved completely by the end of the acceleratory period, giving almost entirely outer product, which was often absorbed in the shells surrounding larger grains. Grains containing high proportions of C_3A might develop larger spaces within their shells. The behaviour of the larger grains is considered in Section 5.4.

Partly or completely empty shells, called "Hadley grains" and up to at least $10\ \mu\text{m}$ across, were first observed on fracture surfaces (160). Pratt and Ghose (158) noted that it would be difficult to reconcile any widespread occurrence of such cavities in a mature paste with the density of the material, and concluded that they were temporary phenomena. The separations between shell and core observed in BEI or ion thinned sections are typically $< 3\ \mu\text{m}$, but can be larger around C_3A (100,158). Scrivener (100) observed that large, empty shells often result from cores having fallen out on fracture.

CH forms during the middle period, as hexagonal plates in the water filled space, and makes a major contribution to the filling of space between the shells (158).

5.3.2 FORMATION OF AFm AND AFT PHASES

Many observers have reported the outward growth of long, thin needles of Aft phase in pastes about 1 day old. Their formation, which is a renewed one of this phase, was shown to occur at 16 h and to coincide with a shoulder on the downward slope of the main heat evolution peak (Fig. 3d; 153,158). The length of the needles is, typically, $1-2\ \mu\text{m}$, but can reach $10\ \mu\text{m}$. The heat evolution may well be associated chiefly with the renewed dissolution of C_3A , and perhaps also of ferrite phase. Both Aft and AFm phase can also form inside the shells. The latter become less permeable as more product is formed, causing the solution inside them to become isolated and low in sulphate; AFm phase therefore tends to form inside, and Aft phase outside the shells (100, 152,158).

Locher (161) considered that recrystallization of ettringite played a major part in setting. The

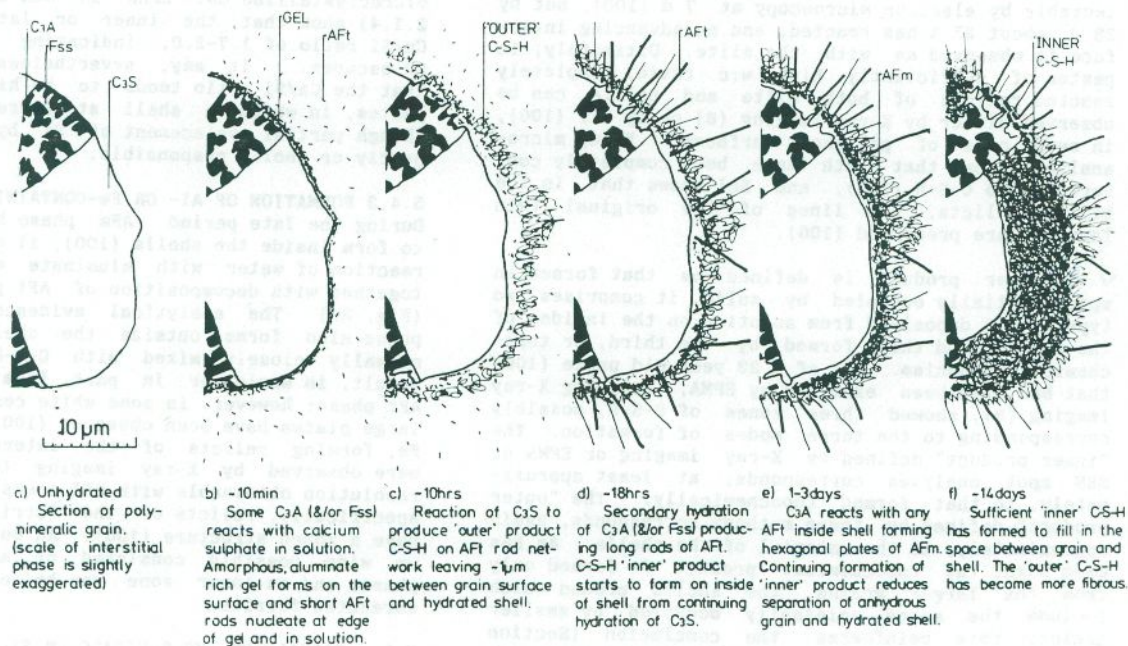


Fig. 3. Microstructural development during the hydration of portland cement (Scrivener, 100).

observations described in the previous sections do not support this view, the early formation of Aft phase occurring before initial set, and the later formation after final set. From quantitative determinations of ettringite with parallel ones of setting times, Bensted (137) concluded that setting was directly associated with loss of mobility of water, and that in normal setting, this in turn was primarily caused by formation of C-S-H. In agreement with this view, Dalglish et al. (155) considered that initial set was associated with the beginning of rapid C-S-H formation, and final set with completion of coverage of the cement grains by C-S-H.

5.4 CEMENT: THE LATE PERIOD

5.4.1 FORMATION OF C-S-H

The late period is one of increasingly slow reaction, beginning at 20-30 h. In it, C-S-H forms by three, distinct mechanisms, the first two of which have started earlier (100,152,158). In the first, the shells grow outwards and become less porous, adding to the outer product. SEM of fracture surfaces (158) and BEI of polished surfaces (100) showed that their thickness reaches 8-10 μm in 7-14 d. In the second, they grow inwards. The anhydrous phases meanwhile dissolve, and the spaces between them and the surrounding shells continue to grow at first, until at 4 d those around the silicates are up to $\approx 3 \mu\text{m}$ wide. Gradually, the growth of C-S-H overtakes the retreat of the anhydrous surface, and the gaps close up; in the larger grains, they disappear by 7-14 d (Fig. 3e and f; 100). Grains smaller than 15-20 μm hydrate completely before the space has been entirely filled, leaving cavities up to 5 μm in diameter that have been observed on fracture surfaces (158) and even on polished surfaces of pastes up to 23 years old (100).

Both the above mechanisms occur through solution. The third probably does not. After the spaces have been filled, the alite continues to react, and the interface between it and the surrounding C-S-H moves slowly inwards. Reaction of the belite is undetectable by electron microscopy at 7 d (100), but by 28 d, about 25 % has reacted, and an advancing interface is observed as with the alite. Ultimately, in pastes of sufficiently high w:c ratio, completely reacted relicts of both alite and belite can be observed either by X-ray imaging (8) or by BEI (100), in each case of polished surfaces. X-ray microanalyses show that both have been completely converted into C-S-H (8,9), and BEI shows that, in the belite relicts, the lines of the original twin lamellae are preserved (100).

✓ If inner product is defined as that formed in space initially occupied by solid, it comprises two types: that deposited from solution on the insides of the shells, and that formed by the third, or topochemical mechanism. BEI of a 23 year old paste (100) that had also been examined by EPMA, including X-ray imaging (8), showed three zones of C-S-H, possibly corresponding to the three modes of formation. The "inner product" defined by X-ray imaging or EPMA or SEM spot analyses corresponds, at least approximately, to that formed topochemically. The "outer product" defined by these methods corresponds, again approximately, to the material of the shells. As has been seen, the topochemical product is formed only from the larger grains, the shells around which include the space originally occupied by smaller grains; this reinforces the conclusion (Section 2.1.4) that "undesigned product" would be a more exact description. Jennings et al. (150) suggested that "late product" was a term preferable to "inner product", and a good case can be made for this. It is

uncertain whether the C-S-H deposited inside the shells from solution is compositionally identical with that formed topochemically, i.e., pure C-S-H, or with the outer product, which consists of C-S-H often closely mixed with AFm phase. The spatial resolution of X-ray microanalysis is probably inadequate to settle this question.

The topochemical product can possibly be identified with Diamond's (157) Type IV C-S-H. His Type III C-S-H (equant grains) presumably includes all but the most porous parts of the shell material, and possibly also that deposited on the insides of the shells. The microstructure of Type III C-S-H was clarified by the work of Jennings et al. (150), who showed that material that fitted this description when examined in reflection appeared when examined by STEM of ion thinned sections to consist of interleaved and interlocked thin foils. These and other morphological varieties of C-S-H gel are, almost certainly, not distinct categories, but points in a continuum of forms, all derived from sheets which tend to roll, crumple or shred in a preferred direction. The way in which they do this, and the extent, appear to depend largely on the amount of space available, perhaps together with such other factors as the mechanism or rate of formation, or the presence of admixtures, and can be further modified by drying, fracture, or other processes after formation.

5.4.2 FORMATION OF CH

CH continues to form in the water filled space during the late period of reaction, and is readily observed on fracture surfaces (157), X-ray images (8), or BEI (117). The thin plates seen earlier give place to large crystals or dense masses up to tens of μm in size that can engulf other phases. This change presumably results from the decrease in available space.

Scrivener and Pratt (152) suggested that the continued hydration of alite in the enclosed regions within the shells must lead to formation there of microcrystalline CH. EPMA and SEM analyses (Section 2.1.4) show that the inner or late product has a Ca/Si ratio of 1.7-2.0, indicating that most of the CH escapes. It may, nevertheless, be significant that the Ca/Si ratio tends to be higher than in C₃S pastes, in which a shell structure does not form, though partial replacement of Si by Al may also be partly or wholly responsible.

5.4.3 FORMATION OF Al- OR Fe-CONTAINING PHASES

During the late period, AFm phase has been observed to form inside the shells (100); it could result from reaction of water with aluminates or ferrite phase, together with decomposition of Aft phase, if present (Fig. 3e). The analytical evidence shows that AFm phase also forms outside the shells, where it is normally closely mixed with C-S-H (9), and may result, in whole or in part, from decomposition of Aft phase; however, in some white cements, relatively large plates have been observed (100). Areas high in Fe, forming relicts of the interstitial material, were observed by X-ray imaging (8). The higher resolution obtainable with BEI shows them to be, more specifically, relicts of the ferrite phase, and to have a zoned structure (100). An outer zone, about 1 μm wide, possibly consisted of an iron hydroxide phase, and an inner zone was believed to consist of unreacted ferrite.

5.5 TRICALCIUM AND β -DICALCIUM SILICATES

5.5.1 C₃S AND β -C₂S : EARLY PRODUCTS

Ménétrier et al. (162-164) and Jawed and Skalny (165) extended earlier studies using high resolution SEM,

ESCA and solution analyses, in which pellets of C_3S or $B-C_2S$ were dipped in water or aqueous solutions. No protective coatings were observed; the surfaces of the crystals were attacked unevenly, and within a few minutes, minute particles of product were deposited. Subsequently, films, honeycombs or fibres of C-S-H, and later also CH, were observed. Several other workers have reported broadly similar results. Groves (166), studying ion thinned specimens of C_3S that had been dipped in water or aqueous solutions, found that at 3-6 h, a layer of amorphous material had been formed. Jennings et al. (150), using a wet cell with HVEM, observed the formation during the induction period of thin flakes or foils, which they called "Type E" C-S-H. Scrivener (100) made a similar observation, and noted that on drying, the foils either collapsed or crumpled to form fibres. Le Sueur et al. (120), in an SEM study of C_3S pastes, reported that after 30 m, an amorphous looking layer had been formed. Stewart and Bailey (167) found the first substantial product of C_3S hydration visible in an SEM examination to consist of thin flakes or foils. Possibly all these observations are consistent with the hypothesis that the first product consists of foils or flakes exfoliating from the surface, which can change in various ways on drying.

Ings et al. (168) placed single crystals of C_3S in an alite slurry (w:s = 2), later removing them for SEM examination. A layer of apparently structureless product built up to a thickness of 5 μm in 30 m, together with cryptocrystalline CH; later, it shrank, with formation of acicular outgrowths. Calorimetric evidence showed that the single crystals were highly reactive, but the product layer contained Al, and had thus formed in part also from the alite. The authors concluded that an initial, transient hydrate was formed, which served as a barrier layer, and that its subsequent transformation ended the induction period.

5.5.2 C_3S AND $B-C_2S$: MIDDLE AND LATE PRODUCTS

As with cement, the middle period is that of rapid formation of C-S-H and CH, and several early studies showed the formation of Diamond Type I material, together in the outer product with massive CH (157). Jennings et al. (150), using a wet cell, found that the period began with the formation of an apparently structureless layer of gel, which they called "Type 0" C-S-H, and which grew to a thickness of $\approx 0.5 \mu m$ over several days. It changed, rather slowly, to give acicular particles where space was freely available, or crumpled and interlocked foils where it was not. As noted in Section 5.4.1, the latter product, when seen in reflection, resembled Diamond Type III C-S-H, and a less porous component, which could have been the inner or late product, was also present. These changes were encouraged by drying or ageing.

Stewart and Bailey (167), in the SEM examination reported earlier, obtained results varying with the structural modification of the C_3S . With a monoclinic modification, the foils that had grown previously lifted and peeled, giving crumpled sheets, but with triclinic or rhombohedral preparations, needle like outgrowths were formed. All three specimens eventually gave similar structures, in which needle like outgrowths were bridged by crumpled foils. Studies using a cryo stage indicated that the outgrowths were not an artifact of drying (149).

Scrivener (100), studying alite pastes with HVEM and a wet cell, found that the product at 1 d consisted of crumpled foils in places where it was thin enough for the structure to be observed, with no evidence of fibrillar outgrowths. Fibrils were,

however, produced if the paste was allowed to dry; in a paste not cured in water, this could apparently happen through local exhaustion of water. There was no indication of more than the one, basic morphological type of C-S-H, though the inner or late product would not have been observed. Pastes of C_3S mixed with C_3A were studied by BEI (100,152); with the C_3A particles, large spaces developed between the anhydrous cores and the surrounding hydration products, but with those of C_3S , no spaces were observed. This contrasted markedly with the behaviour of the alite in cement, and supported the view that the spaces and shell structure in cement pastes are caused by the presence of the aluminate phase.

5.5.3 C_3S AND $B-C_2S$: CONCLUSIONS

The following conclusions are suggested from the above observations. On mixing, the C_3S begins to dissolve, and C-S-H precipitates as foils, which peel off or exfoliate. The resulting layer becomes progressively thicker and more tightly packed, but at no stage is there convincing evidence of any continuous film or membrane. The foils very readily change into acicular forms or honeycombs on drying, which is bound to occur locally under any conditions other than saturated. As noted by Pratt and Ghose (158), the absence of a shell structure and of spaces between the anhydrous material and the product are very important differences from cement, for which C_3S is therefore of limited value as a model. CH is deposited in the outer product, as with cement.

5.6 COHESION AND THE EFFECT OF WET CURING

In both C_3S and cement pastes, cohesion probably results primarily from the coming together of foils, which transforms an essentially particulate gel into a continuous one, but in the more open parts of the structure, where local drying would be most likely to occur, this process might be confined to the crossing points of foils rolled or shredded into fibres and thus barely if at all distinguishable from an interlocking process. An effect of wet curing is to prevent or at least minimize the changes in C-S-H morphology that occur on drying. These changes are probably, at least in part, irreversible.

5.7 TRICALCIUM ALUMINATE AND THE FERRITE PHASE

Scrivener and Pratt (152) studied the paste hydration of these phases using a wet cell with HVEM. In the absence of calcium sulphate, C_3A yielded initially a filmy, amorphous looking product, similar to that seen earlier in SEM by Breval (169). The films appeared crumpled and sometimes peeling from the surface, and it was thought unlikely that they could inhibit reaction. Later, hexagonal plates and icositetrahedra were seen. If gypsum was present, an amorphous layer was again formed, but it appeared denser and more coherent. Its formation was followed by that of rods of AFT phase on the outer edge of the layer and in the solution; they were easily damaged by the beam. If the sample was dried, the rods remained, but the amorphous layer could no longer clearly be seen. If hemihydrate was substituted for gypsum, the early microstructure was dominated by secondary gypsum, which made it impossible to see whether an amorphous layer had been formed; AFT crystals again formed, and were shorter and thicker than those formed in the paste made up with gypsum. The difference in morphology was attributed to the higher degree of supersaturation obtained with hemihydrate. Pastes of C_4AF with gypsum or hemihydrate behaved in a way broadly similar to those of C_3A with the same admixtures, but the amorphous layer seems to have been less evident. The two samples of C_4AF used differed greatly in reactivity.

6 HYDRATION REACTIONS

6.1 C₃A AND C₄AF IN THE EARLY AND MIDDLE PERIODS6.1.1 C₃A

Jawed and Skalny (170) studied the early hydration of C₃A using electron spectroscopy for chemical analysis (ESCA). The Ca/Al ratio in the surface layer increased to ≈ 2.0 in 2 s and then decreased to ≈ 1.7 in several minutes, thereafter remaining steady for several hours. These results suggest that calcium aluminate hydrates, and not an Al rich layer, are being formed. In contrast, Glasser and Marinho (171) found that the Ca/Al ratio in solution was > 1.5 after 30 s, and concluded that an Al rich layer was formed. They, and also Shin and Glasser (172), made similar studies on Na doped forms of C₃A.

Hampson and Bailey (173,174) found from SEM and TEM studies that the first product of C₃A hydration in presence of gypsum was a disordered phase with an irregular platelet morphology similar to that of the calcium aluminate hydrate observed by Brevet (169). At high pH values (≈ 12.5) of the surrounding medium, short rods of a structurally imperfect Aft phase were produced, and could form a coherent coating on the C₃A grains; in the presence of CH, this coating was eventually ruptured, and longer rods of ettringite, which had grown at lower pH beneath the coating, were observed. From solubility data, the authors concluded that the ionic activity products of synthetic ettringite preparations varied with the pH. This was attributed to the existence of major structural defects in the crystals formed at the higher pH values, which also accounted for their morphology. Initially, these defects were believed to be vacancies in Al sites, balanced by additional H (173), but it was later considered more likely that they were Ca and SO₄ vacancies (175). Vacancies of this latter type were also considered to exist in the larger crystals precipitated at lower pH values, when these were first formed. Tubular particles of ettringite, formation of which had been reported in cement suspensions (143,176), were not observed; their formation from cement was attributed to the presence of alkalis in the aluminate phase in the latter case. Scrivener (100) found that reaction of Na-doped C₃A in presence of gypsum gave a dense mass of tangled, irregular rods, which tended to bubble under the electron beam. This suggests that hollow fibrils could result from dehydration.

Brown et al. (177) studied the kinetics of reaction of C₃A with solutions containing various combinations of Ca, Na, SO₄ and OH ions. Four C₃A samples differing in specific surface area were used. The rates of loss of Ca and SO₄ from the solution depended on the initial composition of the solution, but the rate of sulphate uptake per unit surface area of C₃A was constant. Ca and SO₄ were not consumed in equimolar proportions, and it was concluded that formation of ettringite was accompanied by that of C₄AH_x. This interpretation was preferred to that assuming formation of an Aft phase in which SO₄ was partially replaced by OH because attempts to prepare such products had failed. It was also consistent with phase equilibrium evidence, which indicated that ettringite could not exist in direct contact with C₃A, but that an AFm phase should occur in the interfacial zone. The authors considered that, because of its needle like morphology, ettringite by itself was unlikely to be an effective diffusion barrier, but that in a composite, each would enhance the effect of the other, thus producing a barrier effect.

As noted in Section 5.7, Scrivener and Pratt (152) found that the ettringite crystals formed from C₃A

in presence of hemihydrate were shorter and stubbier than those formed with gypsum. They attributed the morphological difference to the higher degree of supersaturation which was obtained with hemihydrate.

6.1.2 C₄AF AND MIXED INTERSTITIAL MATERIAL

Fukuhara et al. (178) studied the kinetics of the hydration of C₄AF in presence of gypsum and CH in pastes with w:s = 0.5. They concluded that the retarding effect of gypsum was inversely proportional to the surface area of the C₄AF; if the amounts of gypsum per unit area in two experiments were the same, the heat liberation curves were also the same. From calorimetric data, they concluded that the products of the reaction were ettringite with minor replacement of Al by Fe, and an amorphous iron(III) hydroxide. They also found the enthalpy of the hydration reaction to be 173 cal g⁻¹ (352 kJ mole⁻¹) of C₄AF and found the rate to be diffusion controlled until the depth of reaction had reached 0.6 μ m.

Plowman and Cabrera (179) studied the hydration of a paste (w:s = 0.7) of interstitial material (a mixture of the ferrite and aluminate phases) that had been isolated from a cement. The reaction was followed by continuously monitoring the material in an X-ray diffractometer, in a carbon dioxide free atmosphere. In contrast to Locher (161), they found that both phases were consumed much more rapidly if gypsum was absent than if it was present. The rate constant for the aluminate was about 6 times as great as that for the ferrite. From their results, they concluded that retardation was due to a protective coating of AFm phase together with withdrawal of water caused by ettringite formation, and that the reaction was diffusion controlled. The maximum proportion of gypsum that they used was 56 mg to 700 mg of the interstitial starting material; this is much lower than the proportion in a typical cement, which is about 56 mg to 200 mg of interstitial material, much of which, moreover, is not accessible in the early stages of reaction.

6.1.3 SET CONTROL BY GYPSUM - DISCUSSION

The explanations of the set controlling action of gypsum given by the above investigators (173-179) agree in the conclusion that a protective layer is formed. The layer consists of short, stubby rods of Aft phase, probably together with an underlying sub stratum, and, as suggested by Brown et al. (177), both these components may play a part. It may be considered doubtful whether even poorly formed Aft crystals would, by themselves, be effective. With pure C₃A, the sub stratum appears to be of AFm composition; with cement, it probably is not, and appears to be gelatinous, though it may well have an underlying foil like morphology. Hampson and Bailey (173,174) predicted that gypsum could be effective in controlling set if the surrounding solution had a pH in the approximate range 12.3-12.8, and that admixtures shifting the pH out of this range would render gypsum ineffective; further work is probably needed to test this hypothesis. There is disagreement as to what controls the morphology of the Aft phase; Hampson and Bailey found that the short, stubby rods were produced if the pH was high, but Scrivener and Pratt's (152) observations using hemihydrate show that they can also result from a higher level of supersaturation.

Many portland cements contain small proportions of calcite, either added deliberately or present as an impurity in the gypsum. Bensted (180) found that, if gypsum was replaced by limestone, AFm and Aft phases containing carbonate ions were formed.

6.1.4 SECOND STAGE FORMATION OF ETTRINGITE

The delay of approximately 16 h before the second stage of Aft formation takes place has to be explained. Scrivener (100) noted that it occurred after the major middle period reaction giving C-S-H and CH, and suggested two possibilities. One was that the reaction of the alite rendered the gel layer unstable. The other was that a decrease in Ca concentration, caused by precipitation of CH, increased the rates of dissolution of gypsum and of C₃A. Yet another possibility is that the dissolution of the alite makes available additional surfaces of the interstitial phases.

6.2 C₃S AND β-C₂S IN THE EARLY AND MIDDLE PERIODS

6.2.1 ESCA, SURFACE AREA AND SIMS STUDIES

ESCA studies of the early hydration of C₃S (181,182) and β-C₂S (183) were reported. All show, in broad agreement with earlier results, an initial, rapid fall in surface Ca/Si ratio, followed by a rapid increase and a subsequent, slower decrease to values of 1.5-2.0. Regourd et al. (181) attributed the initial decrease to formation of a Primary Hydrate, with Ca/Si << 3. Assuming a Ca/Si ratio of 1, the layer of hydrate at this stage was 0.8 nm thick. The increase in Ca/Si ratio that followed was attributed to formation of a Secondary Hydrate, which persisted throughout the induction period; as the product layer thickened, the contribution of the underlying C₃S to the signal decreased, and with it the surface Ca/Si ratio. The Secondary Hydrate had a Ca/Si ratio of 2.0. At 4h, well after the contribution from the C₃S had disappeared, the shape of the Si_{2p} peak changed, indicating a major change in the structure of the Secondary Hydrate. This coincided with the end of the induction period, and consequent formation of Diamond Type I C-S-H, with dimeric silicate anions.

The results of Ménétrier et al. (183) for β-C₂S indicated that the thickness of the hydrate layer was ≈5 nm after 15 s and ≈15 nm after 6 h, both at 25°C. Stadelman et al. (182) made studies on C₃S with times of up to 8 h. For a pellet immersed in water at w:s = 10, results similar to those of Regourd et al. were obtained, but a second maximum in the surface Ca/Si ratio was observed, and was attributed to formation of CH. Parallel studies of surface area by Kr sorption showed that the surface area passed through a sharp maximum corresponding to the initial sharp minimum in surface Ca/Si ratio; the product after this stage, which had a relatively high Ca/Si ratio and relatively low specific surface area, was considered to act as a protective layer during the induction period. A second, broader maximum in the surface area curve was attributed to formation of CH, initially finely divided. Early hydration of cement has also been studied using secondary ion mass spectrometry (SIMS), which indicated a depth of reaction of 10-20 nm in 10 minutes (184).

6.2.2 THEORIES OF THE INDUCTION PERIOD

The mechanism and products of C₃S hydration have been reviewed in a collaborative paper (185), which includes a discussion of theories of the induction period. In one group of hypotheses, it is assumed that the initial or first stage product does not act as a barrier layer; its presence may affect the kinetics, but the ending of the induction period does not depend on its destruction. In these hypotheses, the induction period occurs because of a delay in the nucleation or growth of a second stage or major product; some workers consider that this is the CH (Hypothesis No. 1), and others that it is the C-S-H (Hypothesis No. 2). In the second group of hypotheses,

the first stage product acts as a barrier, and the induction period ends when it is destroyed because of a phase transformation or ageing process (Hypothesis No. 3), or by osmotic bursting or some related effect (Hypothesis No. 4).

We shall consider only a few recent contributions. Support for Hypothesis No. 4 rested largely on early wet cell observations at high w:c ratios (143), which have not been confirmed in the more recent studies on pastes discussed in Section 5. Ings et al. (168) considered that their results using single crystals of C₃S, described in Section 5.5.1, supported Hypothesis No. 3; however, they appear to show that a change occurs in the C-S-H, but not necessarily that this change corresponds to the destruction of a barrier layer. Other recent reports in which destruction of a barrier layer was assumed are those of Stadelman et al. (182), Ball (186), and Pommersheim et al. (187), who constructed a mathematical model of the hydration of tricalcium silicate on this basis.

An argument against any barrier layer hypothesis was advanced by Odler and Schöppstühl (188), who confirmed and extended earlier studies showing that the length of the induction period for C₃S was affected by, among other things, the concentration of defects in the C₃S. They pointed out that there was no reason to believe that this could affect the quality of the hydration product as a barrier layer.

Wu and Young (189) determined Ca and OH concentrations as a function of time in suspensions of C₃S in water or various salt solutions. The results supported previous indications that the CH nuclei are poisoned by silicate ions, with the result that CH does not precipitate until a relatively high degree of supersaturation has been reached.

Brown et al. (190) reported studies in which the precipitation of CH from supersaturated solutions obtained from C₃S hydration was followed conductimetrically. Seeding with CH, itself also obtained from hydration of C₃S, greatly accelerated the precipitation of CH, seeding with C-S-H being much less effective; however, separate experiments using conduction calorimetry showed that addition of solid CH had no detectable effect on the length of the induction period. Earlier experiments by Odler and Dörr (191) had also shown that the induction period was not significantly affected by seeding with CH, but that it was shortened by seeding with C-S-H.

Brown et al. (192) concluded that the kinetics of C₃S hydration can be explained if it is assumed that an initial hydrate forms a layer surrounding the C₃S grains, that the final product nucleates in this layer and that the kinetics during the middle period of reaction are controlled by the growth of C-S-H. This evidence, together with that in the previous paragraph, supports Hypothesis No. 2.

Jennings (193) showed that the concentrations in the bulk solution are controlled by transient equilibria with the layers of product surrounding the C₃S grains, and concluded that these layers acted as barriers that allowed high concentration gradients to exist near to the C₃S surfaces.

The evidence appears to the writer to favour the view, proposed by Sierra (194) and others, that the induction period is caused by a delay in either the nucleation or the growth of the C-S-H. The early product is a barrier in the sense that it allows high concentration gradients to exist, but the induction

period does not end because it is destroyed. It is not a necessary part of this hypothesis that more than one type of C-S-H should be involved, but there are several indications that this is the case; these include the evidence from cross polarization NMR (33) and ESCA (181), the observations of Ings et al. (168) using single crystals, and the kinetic arguments of Brown et al. (192), all of which suggest that a change occurs at the end of the induction period.

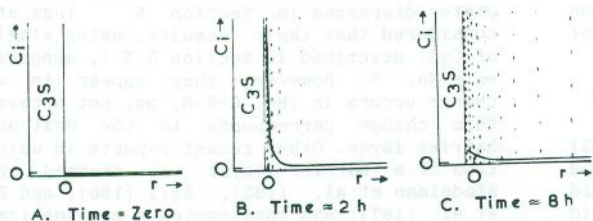


Fig. 4. Schematic plots of the analytical or total concentrations (C_i) of either CaO or SiO_2 against distance from the original position of the C_3S surface (r). Stippling represents reaction product (195).

The following discussion (195) relates to the reaction during the early and middle periods in a C_3S paste, but is applicable with some modifications to $\beta\text{-C}_2\text{S}$ or to the silicate phases in cement. The immediate factors controlling the rate at which the C_3S dissolves are its inherent reactivity and the CaO and SiO_2 concentrations close to its surface. These latter depend on the rates at which the ions are supplied and removed. Initially, both concentrations are zero, and the rate of dissolution is high (Fig. 4a). This diagram is purely schematic, and the curves serve for both oxide components. Steep concentration gradients build up close to the surface, and the rate decreases (Fig. 4b). Relatively little product is deposited at this stage, but what there is limits the rate at which ions diffuse away into the solution. The rate at which the product (at this stage, almost entirely C-S-H) is deposited increases with the amount already formed, according to a law of growth, and after a time the increased rate at which ions are removed causes the concentration gradients near to the C_3S surface to weaken, so that the rate of dissolution increases (Fig. 4c). The consequent increase in CaO concentration in the bulk solution leads to precipitation of CH. After some 12 h, the increasing quantity of product causes the concentrations near the surface to increase again, and the rate of dissolution once more decreases.

During the induction period, and also in the later part of the middle period of reaction, the concentrations close to the C_3S surface must be very much higher than those in the bulk solution; if they were not, they would have no significant effect on the rate of dissolution. One should not, therefore, necessarily expect to find any close relationships between the concentrations in the bulk solution, which alone can be measured by existing techniques, and the rate of consumption of the C_3S .

This hypothesis could readily be modified, and would indeed be strengthened, if it was shown that the type of C-S-H that forms the major product only begins to form at the end of the induction period. It applies to cement paste, with modifications arising from the shell structures surrounding the grains, from the fact that the C-S-H is, initially,

deposited close to the C_3S surface, and possibly also because the composition of the bulk solution differs greatly from that in a C_3S paste.

6.3 REACTIONS IN THE LATE PERIOD

During the late period, the anhydrous phases remaining in the larger grains are no longer in contact with water molecules other than those contained in the surrounding product, mainly in its micropores and interlayer spaces. Under these conditions, a through solution mechanism, if possible at all, is likely to be even slower than an 'in situ' or topochemical one. Many years ago, McConnell (66) found naturally occurring crystals of $\beta\text{-C}_2\text{S}$ and of a related mineral, bredigite, that had been partially converted into plumbierite (C-S-H gel), apparently by an in situ mechanism. The plumbierite was sufficiently crystalline that it was possible to show that it had been formed in a definite crystallographic orientation relative to the starting material. Funk (196) showed that, under certain conditions, $\beta\text{-C}_2\text{S}$ prepared in the laboratory behaved in the same way.

Extending an argument of McConnell (66), Taylor (197) calculated the numbers of atoms of each element in a specified volume of starting material or product (Table I). It was assumed that the product included the micropores but no capillary pores, and that it was saturated; these assumptions are consistent with the results of Powers and Brownard (47) and with the density and water content of plumbierite (66). The C-S-H composition was assumed to be $1.7\text{CaO}\cdot\text{SiO}_2\cdot 4\text{H}_2\text{O}$. The numbers of oxygen atoms are the same to within 10% in all the phases considered, but in order to replace C_3S or $\beta\text{-C}_2\text{S}$ by C-S-H, many Ca and Si atoms must be lost and H atoms gained.

TABLE I. Numbers of Atoms in $1000/N_0 \text{ cm}^3$ (197)

Phase	Density (g cm^{-3})	Ca	Si	H	O
C_3S	3.21	42.2	14.1		70.3
$\beta\text{-C}_2\text{S}$	3.30	38.3	19.2		76.6
C-S-H	2.07	15.5	9.1	72.8	70.1

A mechanism was suggested by which this could occur (197). It is shown in Fig. 5 for C_3S ; a similar mechanism is possible for $\beta\text{-C}_2\text{S}$. The microstructural evidence shows that an interface advances into the grain as reaction proceeds. There is no diffusion of water molecules through the inner or late product; H ions are transferred from one O atom (probably water

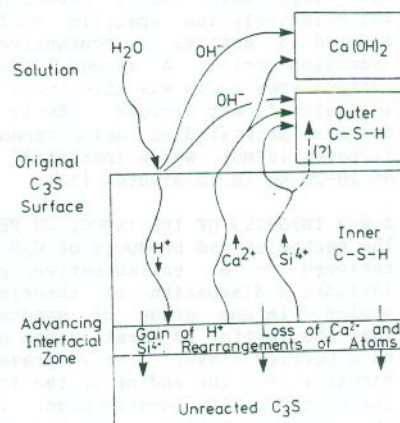


Fig. 5. Suggested mechanism for the hydration of C_3S during the late period of reaction (197).

molecule) to another within the late product, until they reach the C_3S surface, which is attacked much as if it were in contact with an aqueous solution. A narrow zone is assumed to exist at the interface, in which the substantial rearrangements of atoms needed to convert the C_3S into C-S-H take place. The Ca and Si atoms that are lost migrate outwards through the late product, and ultimately pass into the CH or outer product C-S-H. There is little or no long range movement of O atoms. It was suggested that the Si migrated by a series of movements through the faces of tetrahedra, from ones initially filled to ones initially empty, and that this same mechanism could also permit the changes in silicate anion type both during and after C-S-H formation. The movement of Si was possibly rate controlling in this stage of reaction.

Jennings (198) suggested that the porosity of the late product may be lower than assumed above. This may be so, and is indeed suggested by the results of Relis and Soroka (49). If it is, the microporosity associated with the C-S-H elsewhere in the paste would have to be greater, in order to account for the observation (47) that complete hydration is not possible at w:c ratios below about 0.38. A lower porosity in the late product would mean that less Si had to migrate, but even if this product contained no micropores at all, some Si would still have to be lost from the C_3S , and much more from the β - C_2S .

As noted earlier, C-S-H formed in situ from β - C_2S tends to adopt a preferred crystallographic orientation relative to the starting material (66,196). This may explain the persistence of relicts of twin boundaries in reacted belite grains. The numbers of Mg and of Al atoms per unit volume are roughly the same in typical alites, belites and C-S-H of cement pastes, and probably little migration of these elements occurs during the late period of reaction.

7 REACTIVITIES OF CLINKER PHASES

Barret et al. (199) suggested a mechanism for the dissolution of C_3S , based on a repeating sequence of three steps. In the first, H ions are transferred from water molecules to oxygen atoms in the C_3S surface, producing OH and hydrogen silicate ions. In the second, calcium ions pass into solution to the extent needed to cancel the unbalance of charge in both solid and solution resulting from the previous step. In the third, the remaining ions from the part of the structure already affected are dissolved. This is the most difficult process, because the cations and anions cannot move independently, and the transfer of hydrogen silicate ions was regarded as limiting the rate. A new area of surface was thus exposed, and the sequence repeated.

In this mechanism, the initial attack is by water molecules acting as Brønsted acids. This concept goes a long way towards explaining the differing reactivities of the anhydrous clinker phases. It suggests that a major factor governing reactivity is the average basicity of the oxygen atoms, i.e., the real (as opposed to formal) charges that they carry. This is greater for C_3S than for β - C_2S , because it contains oxide ions, and is greater for β - C_2S than for the less basic calcium silicates, because the latter contain oxygen atoms linked to two silicons. For a given degree of condensation, one would also predict that calcium aluminates would be more reactive than calcium silicates; this is, in fact, the case, as is shown by the very differing reactivities of C_3A and α - $CaSiO_3$, in both of which the anions are rings. The argument could be extended to explain the

inertness of granulated slag to this form of attack, and its relative susceptibility to basic attack.

The above theory does not explain the differing reactivities of β - and γ - C_2S . Jost and Ziemer (200) proposed a different hypothesis, in which they assumed that phases in which Ca-O polyhedra shared faces were reactive and those that did not were not. They showed that some earlier theories of reactivity, in which the latter was related to coordination number, distortion of polyhedra, or openness of structure did not accord with modern knowledge of the crystal structures. The calcium silicates that were hydraulically active, including β - C_2S , contained face sharing Ca-O polyhedra, and the inactive ones, including γ - C_2S , did not.

This theory is of much interest because it explains the differing reactivities of β - and γ - C_2S . However, it cannot be the main factor controlling reactivity: CaO, with no sharing of faces, is highly reactive, while corundum, in which faces are shared, is inert. It is more likely that oxygen basicity is the main factor and that this is a subsidiary one. Jost and Ziemer also considered some other crystal chemical influences on reactivity, such as twinning. These may provide a basis for understanding the many and often seemingly contradictory observations in the literature on the effects of polymorphism and ionic substitution on reactivity, especially for belites.

8 SOLUTION COMPOSITIONS AND EQUILIBRIA

8.1 THE CaO - SiO_2 - H_2O SYSTEM

Barret et al. (199) described the results of experiments in which C_3S was extracted with a rapid flow of water saturated with C-S-H. These showed that the process was one of congruent dissolution followed by precipitation of a product with Ca/Si 1. The ESCA evidence (Section 6.2.1) was interpreted in terms of removal of atoms from the C_3S structure by the mechanism described in Section 7, as opposed to precipitation of a hydrate and change in its composition as suggested by Regourd et al. (181).

Fujii and Kondo (201) studied poorly crystalline calcium silicate hydrates formed by mixing solutions of calcium nitrate and sodium silicate. Freshly precipitated C-S-H of low Ca/Si ratio, giving the XRD pattern of C-S-H(I) (quasi-crystalline tobermorite) took up CaO from solution at 20°C only until the Ca/Si ratio reached 1.5, but precipitates aged at 20°-50°C could have Ca/Si ratios up to 1.87. Solubility data at 30°C were determined, and agreed substantially with results of previous investigators. Using the Gibbs-Duhem equation, Ca/Si ratios were calculated from them; they agreed with those found experimentally. The same authors also calculated thermochemical data for C-S-H from the solubility data (202). The material was treated as a solid solution of composition $(0.833 + x)Ca(OH)_2 \cdot SiO_2 \cdot 0.917H_2O$ and for Ca/Si = 1.7, the values obtained, all for 298 K, were $\Delta H_f^\circ = -2890$ kJ/mol, $\Delta G_f^\circ = 2630$ kJ/mol, and $S^\circ = 200$ J/mol.K.

Brown et al. (203) determined the concentrations of calcium and silica in solution during the first 4 hours of hydration of C_3S at 24°C. Two samples of C_3S , differing in specific surface area, and w:s ratios of 0.7 to 20 were used. For all of the experiments, some of which were obtained at times as short as 30 s, the concentrations in the filtered solutions lay on the same curve, which was close to that found by Fujii and Kondo (201) and several other previous investigators for C-S-H preparations made in other ways. An equilibrium between the C-S-H and the

solution was thus rapidly established. For the early period, in which it was assumed that no CH had precipitated, fractions of C_3S reacted were calculated from the concentrations in solution, assuming Ca/Si ratios for the solid derived from equilibrium data in the literature; this indicated that at a w:s ratio of 0.7, about 0.3 % of the C_3S had reacted at the end of the induction period. The rate of hydration thus calculated increased markedly with w:s ratio, but was almost independent of the surface area of the C_3S .

The method of calculating the degree of reaction described above may give low results, because it ignores the probable existence of high concentration gradients close to the C_3S surface; significant amounts of material may be contained in the solution in this region, and some CH may be precipitated.

Several other recent studies have yielded plots of the analytical concentration of CaO against time in C_3S hydration (164,189,204,205). All show the concentration reaching supersaturation in CH during the induction period, but the curves vary in shape, and one (205) is unusual in showing no subsequent decrease towards saturation within 3 months.

Jennings (193) critically examined the many sets of data in the literature for the concentrations of CaO and SiO_2 in solutions in contact with C-S-H. He showed that, with few exceptions, the data points lay on one or other of two, distinct curves. Those lying on the lower of these curves (Fig. 6, Curve A) had, with few exceptions, been obtained using material prepared, not from C_3S , but by mixing solutions of sodium silicate and of a soluble calcium salt or from calcium oxide or hydroxide and silicic acid. XRD evidence for some of these preparations indicated that this curve was the metastable solubility curve of C-S-H(I) or material of similar structural type but lower crystallinity. Those lying on the upper curve, B, had all been obtained from experiments similar in principle to those of Brown et al. (203), whose results were thus among the few exceptions. Barret et al. (199) had regarded a curve close to Curve B as a "supersolubility curve" of C-S-H, but this was improbable; supersaturation would be expected to produce a scatter of points and not a distinct curve. The concentrations were much too low for it to be the metastable solubility curve of C_3S . Jennings concluded that it was the metastable solubility curve of a form of C-S-H that was produced from C_3S , which was metastable relative to C-S-H(I), but not readily converted into it. Probably without exception, the points on Curve B relate to solutions undersaturated in CH. Jennings (198) pointed out that they therefore relate to the form of C-S-H existing before the end of the induction period. As noted in Section 6.2.2, he also observed that the maintenance of metastable equilibrium conditions between the solution and the hydration product showed that the latter forms a barrier which allows high concentration gradients to be maintained near to the C_3S surface.

8.2 SULPHATE AND ALUMINATE SYSTEMS

Bailey and Hampson (206) discussed ionic and neutral species present in aqueous solutions in the part of this system relevant to the early and middle periods of cement hydration. The complex species (or ion pairs) liable to occur in significant proportions, with stability constants in square brackets, are $CaOH^+$ [25], $CaSO_4$ [204], $NaSO_4^-$ [5] and KSO_4^- [10]. Aluminate ions occur as $Al(OH)_4^-$. Solubility products given were: CH, 6.46×10^{-6} ; $CaSO_4 \cdot 2H_2O$, 2.6×10^{-6} ; gibbsite, 5×10^{-35} . These data refer to activities.

An extension of the Debye-Hückel equation was used to calculate activity coefficients for the ionic species; for the neutral species, $CaSO_4$, a different expression was used. An iterative procedure was outlined, by which it was possible to calculate the concentration and activity of each species from the analytical concentrations. Table II gives typical results for a liquid phase analysis from cement, using data of Thomas et al. (207). The concentrations of Al_2O_3 and SiO_2 were very low.

Table II. Analytical and Species Concentrations and Activity Coefficients (f) for the Aqueous Phase in a Cement Paste. [Concentrations in $m \text{ mol l}^{-1}$; K denotes (K+Na); Ref. 206]

	Ca ²⁺	SO ₄ ²⁻	OH ⁻	K ⁺	CaOH ⁺	CaSO ₄	KSO ₄ ⁻
Analytical	57	58	35	15	-	-	-
Species	24.5	30.7	27.9	13.7	7.0	25.8	1.3
f	0.42	0.35	0.76	0.77	0.77	0.87	0.77

Due apparently to errors in the data, the positive and negative charges do not balance, but the importance of the corrections is clear. The uncorrected data indicate an ionic product of 7×10^{-5} for CH, which is much above saturation; the corrected data indicate an activity product of 4.6×10^{-6} , which is below saturation. Bailey and Hampson also concluded that an early decrease in the concentrations of Ca^{2+} and SO_4^{2-} was due, not to precipitation of a calcium aluminosulphate hydrate, but to conversion of a more soluble form of calcium sulphate into gypsum.

Rechenberg and Sprung (208) presented concentration data for the CH-CaSO₄-H₂O system in presence of alkali hydroxides and sulphates, and for cement pore solutions. They concluded that increases in Ca concentrations in presence of sulphates were due, not to oversaturation in CH, but to the higher solubility of calcium sulphate. Neither the presence of complex species, nor deviations of activity coefficients from unity were explicitly considered, and it would be of interest to reexamine these results by the method used by Bailey and Hampson.

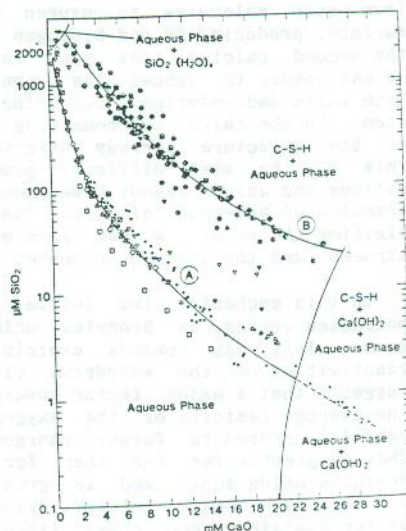


Fig. 6. Concentration data for C-S-H from various investigations; phase fields are only roughly delineated (Jennings, 193).

Barret et al. (209) discussed equilibria in the $\text{CaO-Al}_2\text{O}_3\text{-CO}_2\text{-H}_2\text{O}$ system with reference to the formation of $\text{C}_4\text{AC}_0.5\text{H}_{12}$ in cement systems.

8.3 PORE SOLUTIONS IN CEMENT PASTES

Since the Paris Congress, the compositions of cement pore solutions have been studied either by filtration or centrifugation at early ages and relatively high w:c ratios or by using "squeezers" to cause outflow of liquid under pressure (207,208,210-215). The results confirm and extend those of earlier workers, beginning with Lawrence (216) and Longuet et al. (217). For typical cements and normal w:c ratios, the concentrations of Na^+ , K^+ , Ca^{2+} , SO_4^{2-} and OH^- reach levels above 0.01 M within 1 h. Those of Ca and SO_4 subsequently fall, and are typically below 5 mM by 1 d, but those of Na, K and OH remain high, so that the solutions become ones essentially of alkali hydroxides. The concentrations change relatively little after a few days. Typical concentrations for pastes more than a few days old are Na, 0.05-0.2 M; K, 0.2-0.5 M; pH, 13.4-13.8. Other concentrations, including those of silica and alumina, are extremely low, even during the first few minutes (210).

Diamond (212) reported on pastes of a moderate alkali cement (0.32 % Na_2O , 0.60 % K_2O) at w:c = 0.4. The Na and K concentrations were compared with those that would have existed had all the alkalis in the cement dissolved and stayed in solution. Corrections were applied for the water bound in the products, which was assumed to be that retained at 105° (211), corresponding to 0.21 g/g cement for complete hydration. On this basis, about 80 % of the K and 60 % of the Na were found to remain in solution indefinitely.

The above correction for bound water appears too small, as much interlayer water in C-S-H and AFm phases, and water in AFT phases, is lost below 105°C. Recalculation assuming a more realistic bound water content of 0.32 g/g for complete hydration indicates that only about 55 % of the K and 45 % of the Na remain in solution indefinitely. Glasser and Marr (213,214), using a correction similar to the above, studied two cements, one high and the other low in alkalis. They found that about one third of the Na was in solution at 14 months, and their results indicate that about 60 % of the K is also in the solution. They stressed the difference in behaviour between Na and K, and the desirability of considering them separately; Na was much more readily accommodated in the solid products than was K.

Electron optical analyses do not distinguish material present in the pore solution from that in the hydration products, because the pore solution evaporates on drying and the dissolved material is deposited. Recent SEM analyses on pure portland cement pastes (9) show Na and K contents in the products agreeing to within experimental error with those not accounted for by unreacted clinker phases.

Concentrations during the first hour were studied by Thomas and Double (210), using a cement containing 0.19 % Na_2O and 0.42 % K_2O at w:s = 2. The Ca and SO_4 concentrations increased rapidly in the first 2 m to peak values around 60 mM and then dropped in 20 m to 30 mM. The authors attributed this to dissolution of gypsum and precipitation of ettringite or a sulphoaluminate gel; as noted earlier, Bailey and Hampson (206) attributed it to dissolution of a more soluble form of calcium sulphate and precipitation of secondary gypsum. The Na, K and OH concentrations also rose rapidly in the first few minutes, Na and K

becoming constant at 5 mM and 20 mM, respectively, after 10 m. Studies from 1 h onwards were reported by Luke and Glasser (215), using a squeezer with pastes of high and low alkali cements at w:c = 0.6. For a cement similar in composition to that studied by Thomas and Double (210), Ca was relatively constant at 22-24 mM and SO_4 at 35 mM during the period from 1 to 6 h, both falling sharply during the acceleratory period that followed. Comparison with the results of Thomas and Double is difficult because of the difference in w:c ratios, but there are suggestions that both Ca and SO_4 concentrations may pass through more than one maximum during the first 6 h. Early hydration has also been followed by electrical conductivity (218).

All the concentrations result from balance between dissolution and precipitation effects. During the early period, Na and K are supplied mainly by alkali sulphates and C_3A , SO_4 by gypsum, hemihydrate, and alkali sulphates, OH by C_3A and alite, and Ca by alite, C_3A and the calcium sulphate phases. The phases most likely to be precipitated are secondary gypsum and other sulphates, C-S-H, AFT phase, and probably amorphous initial products. A full explanation of the changes in concentrations requires knowledge of the phases present at each stage, and of the appropriate solubility products, activity coefficients and stability constants of complex species. The approach described by Bailey and Hampson (206) is appropriate. The distribution of alkalis between individual phases in the unreacted cement, and especially between alkali sulphates and major clinker phases, should be taken into account.

9 ADMIXTURES

9.1 INORGANIC ADMIXTURES

Many inorganic salts accelerate the hydration, both of cement and of C_3S ; a smaller number retard it. Previous investigations giving systematic information on the basic chemistry were summarized by Double (219) and by Wilding et al. (220), who also reported new data for cement. They noted that, in general, both the length of the induction period and the rate of the subsequent reaction were affected, a plot of the height of the main heat peak against the time after mixing at which it occurred giving a linear relationship with high positive correlation.

Unless added in very high concentrations, relatively few inorganic salts retard hydration. With most of those that do, precipitates are formed, and in some such cases, it has been shown that protective coatings are formed around the cement grains (207, 221,222); this may apply to the others also. The formation of a precipitate does not necessarily cause retardation, however; MgCl_2 , for instance, is an accelerator.

For C_3S and cement alike, accelerating effects are approximately additive properties to which both anion and cation contribute. They are so widespread as to suggest that some generic property of electrolytes is involved, which may however be augmented or counteracted by specific effects (185). Compared with such organic retarders as sucrose, relatively high concentrations are needed. Very broadly, the effectiveness of an ion increases with its charge and decreases with its size, though a rank order is more clearly established for cations than for anions (220), and Ca is apparently more effective than would be expected from its charge and size. The situation is complicated by the fact that many ions are present partly as complexes, such as CaOH^+ (220). As was noted in a paper by Double (219), the ranking of ions shows

similarities to the Hofmeister series, which relates to the coagulation of hydrophilic colloids. The basis of this series is that particles of such colloids are kept apart by water molecules, for which the added ions compete. Wilding et al. (220) considered that the rate of hydration was controlled by diffusion of water and solutes through protective layers of C-S-H formed at a very early age around the cement grains, and that flocculation rendered these more porous. It is very probable that flocculation or coagulation of the C-S-H is the major effect, though, as was noted in Section 6.2.2, the rate of hydration in the induction and acceleratory periods, both for cement and for C_3S , is probably controlled more by nucleation and growth of the product than by its ability to act as a diffusion barrier. Jennings (198) suggested that the C-S-H particles grow by aggregation or accretion of smaller particles, possibly under 10 nm in size. This is precisely the type of process to which flocculation processes of the kind discussed above apply.

NMR evidence and CH determinations (Sections 2.2.3 and 4.2.1) show that the addition of $CaCl_2$ does not alter the Ca/Si ratio or silicate anion structure of the C-S-H formed from C_3S . Differences in late strengths are probably due to ones at the microstructural level, which have been observed on fracture surfaces (120,157), and which, in turn, can probably be attributed to ones in the rate and other conditions under which the C-S-H is formed.

The study by Wu and Young (189) on Ca and OH concentrations in C_3S suspensions containing various admixtures was mentioned in Section 6.2.2. The authors found that the times at which maximum supersaturation in CH was attained were in all cases shorter than for C_3S mixed with water; with the salts, the rates at which the C_3S supplied ions to the solution were nearly always greater, but the level of maximum supersaturation was essentially unaffected. In a similar study by aqueous solution analyses and calorimetry, Brown et al. (223) found that, in presence of $CaCl_2$ or $CaSO_4$ (≈ 0.02 M), acceleration began only after CH precipitation had started. They reasoned that acceleration by Ca salts was partly due to depression of the OH concentration through the common ion effect; however, this did not account for the fact that the accelerating effect depended on the nature of the anion, and some other effect, possibly flocculation of a colloid or alteration in the product microstructure, was probably also operative.

From calorimetry, combined water determinations and SEM studies, Odler and Wonnemann (224) concluded that addition of alkali sulphates to cement does not affect the progress of C_3S or C_3A hydration. The setting time is shortened, especially with K_2SO_4 due to formation of syngenite, $K_2Ca(SO_4)_2 \cdot 2H_2O$.

9.2 ORGANIC ADMIXTURES

In contrast to inorganic admixtures, many organic substances retard the hydration of both cement and pure C_3S , and are often effective at very low concentrations. Double (219) and Wilding et al. (220) included a number of organic admixtures in the plots of calorimetric data mentioned in the previous section. As with inorganic admixtures, both the maximum rate of heat evolution and the time taken to reach it are in general affected, and approximately the same relationship between these two quantities was found to apply in the two cases. They noted that sucrose and raffinose are especially good retarders.

Thomas and Double (225) studied the hydration of cement, C_3S and β - C_2S in the presence of the disodium salt of ethylene diamine tetraacetic acid (EDTA) at w:s ratios of 2-10. In contrast to what happened in the absence of the admixture, for which Si concentrations in the solution were $< 50 \mu M$ even by 20 s, an initial flush of Si into the solution occurred, but the concentrations decreased in 10 m to approximately the levels found for the controls. This effect was attributed to complexing of Ca by EDTA, making it unable to precipitate the silicate. This situation could only continue until all the EDTA had been used up; one EDTA anion is required to complex one Ca ion. Separate experiments confirmed that EDTA could prevent precipitation of C-S-H. EDTA is only moderately effective as a retarder. Its action was attributed to increase in the amount of C-S-H formed after the EDTA had been used up, and decrease in its Ca/Si ratio, which affected its morphology; both factors made it more effective as a protective coating.

Thomas and Birchall (226) and Birchall and Thomas (227) examined the mechanism of retardation by sugars. They determined concentrations during the first few hours of hydration in cement slurries with w:s = 2 and usually 50 mM in sucrose. As with EDTA, Si concentrations reached much higher values than in the absence of admixtures, though more slowly. In contrast to what occurred with EDTA, they did not decrease again, but remained high for at least 5 h, the longest time studied. The analytical concentrations of other elements were also high; at 1 h, at a sucrose concentration of 50 mM, they were, approximately, Ca, 125; Si, 21; Fe, 7; Al, 5; OH, 250, all in mM/l. Hydroxide was determined by titration to phenolphthalein, and includes the sucrose anion. Studies using ^{13}C NMR and ^{29}Si NMR gave no evidence that Si-sucrose complexes were formed in solution, and it was concluded that the high concentrations existed in solution because sucrose was adsorbed on nuclei of hydration products, which it thus poisoned and prevented from growing. This hypothesis was previously suggested, in relation to CH, by Young (228).

Birchall and Thomas (227) supported this conclusion with further evidence. Experiments using sucrose and either CaO or CH confirmed that sucrose inhibited nucleation of CH and showed that the solutions contained a 1:1 Ca-sucrose complex of formula $R-O^- \cdots Ca^+ \cdots OH$, where $R-O^-$ is the sucrose anion. The important difference in behaviour from EDTA (226) was that the latter complexed Ca in the solution, but the Ca-sucrose complex was also adsorbed on the surface of the CH. The non-precipitation of C-S-H might be explained (226) by assuming that formation of a layer of C-S-H began with its CH-like central part, to which the silicate ions were later added, thus making it possible for poisoning by the Ca-sucrose complex to occur. One may add a further argument for supposing that the Ca-O part of the structure in any local region is formed before the Si-O part: a CH layer can exist without being condensed with silicate anions, but the manner in which the silicate ions condense is peculiar to the Ca compounds, and is entirely different from that found, e.g., with Mg. It is however, not necessary for an entire layer of a metal hydroxide structure to be pre-formed before the silicate anions are added to it.

In reply to a comment by Chatterji, Thomas and Birchall (229) considered that the Al and Fe were present in the strongly alkaline, sucrose-containing solutions as hydroxo complexes. They also (226) related the retarding properties of a number of other sugars to their structures and chemical behaviour

with cement. Sucrose and raffinose were especially good retarders because they were non-reducing sugars and contained 5-membered rings. These characteristics favoured the formation of complexes having pendant $-CaOH$ groups, which were the actual retarding species. Sucrose and raffinose acted as monodentate ligands; some other compounds, e.g., reducing sugars and hydroxycarboxylic acids, were probably bidentate. Like the sexadentate EDTA anion, they tended to complex the Ca in solution, but were not readily adsorbed on a growing CH or C-S-H surface.

Other important classes of organic admixtures include air entraining agents and superplasticizers. Apart from incidental retarding effects, no major effects on the chemistry of the hydration process, as opposed to the rheology, seem to have been reported, and these classes of admixture will not be considered here. There is, however, evidence that superplasticizers may be adsorbed preferentially on particular clinker phases, and this may be expected to affect the early hydration reactions; also, the different dispersion of the cement grains in the mixing water may affect the microstructure of the mature product. There is as yet little systematic information on the pastes of low w:c ratio that can be prepared with their use; Groves's (10) study of CH in such pastes has already been mentioned.

10 KINETICS AND MODELLING

The modelling of hydration kinetics has recently been reviewed (230), and only a few aspects and investigations will be discussed. Parrott and Killoh (231) outlined a method for modelling the degree of hydration, heat evolution and bound water content in cement pastes. They began by summarizing data from the literature, and adding some new data (232), for the percentages of individual clinker phases consumed as a function of time. For alite, the ranges of observed values were, approximately, < 10, 40-60, 70-80 and 85-95 % at 0.1, 1, 10 and 100 d, respectively. The corresponding ranges for belite were < 5, 10-20, 30-50 and 60-95 %. For the aluminate phase, they were 5-20, 25-40, 75 and 90 %, and for the ferrite phase, zero, 20, 60 and 90 %. The data for the aluminate and ferrite phases, and also for alite and belite at low degrees of reaction, were scanty. The large spread of values for alite and belite is probably as much a result of the low precision of the available experimental methods (Section 4.1.1) as of real differences between cements.

Parrott and Killoh constructed a fitted curve for each phase from these data on a semi empirical basis. It was then assumed that the phases could be treated as hydrating independently and that the behaviour of each did not change during the course of hydration. Values were assumed for the bound water content of the products formed from each, and for the heat evolved from each, on complete hydration. It was thus possible to calculate the cumulative heat evolution, bound water content and degree of reaction for the cement as a whole, which was defined as the weight mean for the four phases. In these calculations, which gave satisfactory agreement with a range of data from the literature, account was taken of the specific surface area of the cement, w:c ratio and relative humidity (rh). New calorimetric data suggested that in the early stages of reaction, hydration rates for all four phases were proportional to the specific surface area, and that later, this variable had little effect. An equation was given relating hydration rate to rh, and a correction was introduced that lowered the assumed hydration rates if the degree of hydration exceeded $1.333 \times (w:c)$.

The effect of particle size distribution has received attention. Knudsen (233,234) described what he termed the "dispersion model" of cement hydration. He assumed that the degree of hydration, α , could be obtained by integrating the contributions from particles of different sizes, each of which was represented by an equivalent radius, r , and that for a given time, t , an equation could be written in which some function of $\alpha(r,t)$ was equal to either kt/r or kt/r^2 , where k was a constant. These two types of equation represented linear and parabolic kinetics, respectively. Knudsen showed that, after the integration had been carried out for realistic particle size distributions, a wide range of functions of α could be used with little effect on the results; it was, however, possible to distinguish whether the underlying kinetic law was linear or parabolic. He concluded that the effects of particle size distribution swamped most of the other factors affecting the kinetics, and that the possibility of establishing any detailed kinetic law from the experimental data were accordingly limited. The results did not support the widely held view that a change to diffusion control occurs after the acceleratory period; depending on the cement, and possibly on the conditions of hydration, either a linear or a parabolic law appeared to be followed throughout. The pre induction and induction periods were excluded from the analysis.

The assumptions underlying this approach require careful investigation. The importance of particle size distribution, especially at low degrees of hydration, is not in doubt, but it is difficult to reconcile the conclusions noted at the end of the previous paragraph with the experimental data on microstructural development described in Section 5.

Bezjak (235) adopted a different approach to the problem of particle size distribution. He allowed that the kinetic law governing hydration for each particle changed as hydration proceeded, but considered that the times at which these changes took place depended on the size of the particle; as a result, different kinetic laws operated simultaneously, for particles of different sizes. The assumptions in this approach, too, require careful scrutiny in the light of the microstructural evidence.

As noted by Brown et al. (230), a number of workers have represented the kinetics of C_3S or cement hydration by the Avrami-Erofeyev equation, $-\ln(1 - \alpha) = kt^m$, where k and m are constants. As these reviewers noted, the justification for its use in this context is questionable. The derivation of the left hand side of the equation assumes that nucleation of the product occurs at random within the volume initially occupied by the starting material to which α relates, and that the product also forms within this volume; this is not what happens on hydration of cement. The significance of the right hand side of the equation, which relates to nucleation and growth, is less questionable, and the values of m obtained by applying the equation may be meaningful. It must nevertheless be noted that this approach can take no account of particle size distribution, and that it is all too easy to obtain a linear relationship in the double logarithmic plots that are used in applying the equation.

The hydration of cement is a complex process, and the factors governing its kinetics are very imperfectly understood. For these reasons, the most practical attempts to model it have been those with

a high proportion of empirical content. To exploit to the maximum the high degree of predictive capacity that such approaches can provide, a broad base of experimental data is needed. This does not appear to exist at present, and its acquisition is probably the most important prerequisite for advances in the modelling of hydration kinetics. Kinetic data are needed for (a), otherwise identical cements differing in particle size distribution hydrated under identical conditions; (b), different cements of as nearly as possible the same particle size distribution hydrated under the same conditions; and (c), the same cements hydrated at different temperatures, w:c ratios and relative humidities, and under realistic conditions in which temperature and relative humidity are not constant. These data need to include determinations of the fractions of each of the individual clinker phases reacted, obtained, e.g., from QXDA; overall estimates of the degree of hydration, obtained, e.g., from "bound water" determinations, are not sufficient. The particle size distributions of the cements, bulk chemical compositions, and quantitative phase compositions, determined, e.g., by QXDA, as opposed to Bogue compositions, need to be known. Given a basis of data of this type, an approach along the lines followed by Parrott and Killoh (231) probably offers the greatest possibility of further development. It may be possible to combine it with that of Knudsen (233,234) to take greater account of the effects of particle size distribution.

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