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Sheet-like structure of calcium silicate hydrates

E. HENDERSON, J. E. BAILEY
Department of Ceramics, Glasses and Polymers, University of Sheffield, Sheffield, UK

Transmission electron microscopy has been used to characterize the molecular structure of various synthetic calcium silicate hydrates. Using a model two-phase interfacial hydrolysis reaction, a range of hydrates with various compositions and degrees of order were prepared. The basic molecular core structure was found to be a 1 nm thick sheet, consisting of a protonated CaO_x polyhedral layer sandwiched between short-chain silicate groups.

1. Introduction

A typical Portland cement contains $3CaO \cdot SiO_2$ (60%), β-$2CaO \cdot SiO_2$ (20%), $3CaO \cdot Al_2O_3$ (10%), the ferrite phase ($4CaO \cdot Al_2O_3 \cdot Fe_2O_3$) (5%) and gypsum (5%). The calcium silicates on hydration produce an amorphous calcium silicate hydrate, of approximate composition $1.6CaO \cdot SiO_2 \cdot 1.4H_2O$ after drying to a vapour pressure of 8×10^{-3} mm Hg [1] and crystalline $Ca(OH)_2$. The mature cement paste contains roughly 70% calcium silicate hydrate, 20% $Ca(OH)_2$ and 10% aluminate and sulpho-aluminate hydrates [2]. The major component is, therefore, the calcium silicate hydrate, and is consequently of great importance in relation to the overall mechanical properties and durability characteristics of concrete, mortars, etc., containing Portland cements. In spite of this, its micro and molecular structure remains uncertain.

Most microstructural and indirect surface-area studies indicate a two-dimensional layer-like structure [3], and various models have been proposed to demonstrate how this situation might arise [4]. From physicochemical studies of calcium silicate hydrates, Bailey and Stuart [5] have also proposed a layer-like structure. To elucidate more detailed molecular and microstructural characteristics various synthetic hydrates have been prepared and studied with particular reference to possible structural relationships between these and the hydrates in Portland cement pastes [6, 7]. The majority of synthetic preparations are generally regarded from X-ray diffraction evidence to have an overall two-dimensional layer-like structure, reminiscent of the crystal structure of the mineral tobermorite [2, 8]. The basic structure of which is based on a CaO_x polyhedral layer sandwiched between long chain silicate ($Si_2(O/OH)_9$) groups [9]. Structural differences that do exist between synthetic hydrates and tobermorite are thought to be mainly related to the difference in silicate chain length [6, 10]. Most synthetic preparations produce hydrates containing dimer pyrosilicate (Si_2O_7) groups, and other low molecular weight species, plus longer chain silicates depending on preparation conditions [6, 10]; whilst tobermorite contains only long-chain silicate groups [9]. Many of these synthetic preparations contain distributions of low and medium molecular weight silicate chains, close to those found by trimethylsilylation [11] and ^{29}Si NMR [12] to exist in paste-hydrated $3CaO \cdot SiO_2$ and Portland cement. Similar increases in overall silicate chain lengths occur in both synthetic hydrates and hydrated $3CaO \cdot SiO_2$ with rise in preparation temperature [6, 11], indicating, at least in relation to the silicate portion of the structure, the overall structural similarity between these various hydrates.

Other non-layered structures have been proposed for both synthetic calcium silicate hydrates and the hydrates in Portland cement pastes [13, 14]. Gimlett *et al.* [13] have proposed a non-layer structure for calcium silicate hydrates formed by hydrolysing sodium silicate solutions with calcium hydroxide. Their structure is based on a three-dimensional silicate framework, whose intrinsic negative charge is balanced by ancillary calcium counterions. Another structural type not based on tobermorite has been proposed by Grudemo [14] for the hydrate in paste-hydrated Portland cement. More recently a complex microheterogeneous structure for the hydrate present in Portland cement pastes has been proposed by Taylor [15]. In this model such sub-crystalline order as exists may only be confined to the neighbourhood of small fragments of Ca–O layers, perhaps a few nanometres long, and only rarely parallel, with attached low molecular weight silicate groups. These regions are dispersed in a completely amorphous matrix, containing Ca^{2+}, H_2O and polysilicate anions, some 50 nm in size [15].

In view of the above uncertainties concerning the basic structure of the calcium silicate hydrate present in Portland cement pastes, and the relationships between this, and the synthetic hydrates of various compositions and crystallinities, we have studied calcium silicate hydrates formed in a model two-phase system. By using this approach it has been possible to distinguish micro and molecular detail within these hydrates using transmission electron microscopy.

2. Experimental details

Various calcium silicate hydrates were prepared using a novel two-phase system. This consists of a $Ca(OH)_2$ solution as the aqueous layer and hexane containing $(C_2H_5O)_4Si$ as the second phase. To minimize instability at the interface during the addition of the $(C_2H_5O)_4Si$ solution and to ensure early homogeneity,

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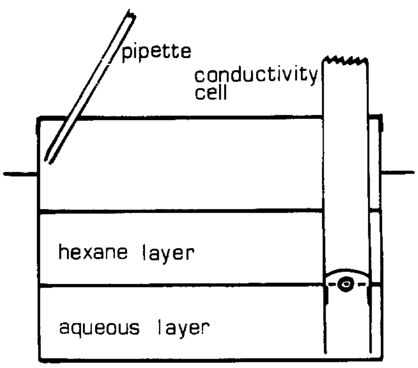

Figure 1 Schematic diagram of apparatus used to investigate the interfacial hydrolysis reaction.

the model system was first partially set up, with initially only 75% of the total hexane run on to the aqueous layer. The $(C_2H_5O)_4Si$ dissolved in the remaining 25% hexane was carefully run down the wall of the partially sealed glass container, in a water bath at 23 ± 0.01° C, using a pipette. The hydrolysis process was followed by determining concentration changes in the aqueous phase using a standard conductivity cell and Wayne Kerr a.c. autobalancing bridge (B642), see Fig. 1. At suitable hydrolysis times, approximately 90% of the organic layer was removed by vacuum suction through a glass capillary. Under an atmosphere of nitrogen, either a "formvar" or carbon-coated copper microscope grid was carefully passed through the interfacial layer. The grids were immediately placed in a vacuum desiccator over SiO_2 gel and pumped for 10 min to approximately 0.1 torr. In the case of the formvar-coated grids, a very thin film of carbon was deposited using an Edwards coating unit. The interfacial material was then examined in axial bright field at 100 kV using a Philips 400T transmission electron microscope (TEM). It is important to realize that as a consequence of the drying process used and high vacuum conditions within the electron microscope, the interfacial hydrates may be disoriented by crumpling and distortion of the film that is deposited on the electron microscope grid. The orientations observed in the image cannot, therefore, be spatially related to the conditions of formation of the hydrates at the interface. The film material was analysed either by a Link System X-ray Analyser 860 Series II (University of Surrey) or EDAX Analyser System (University of Sheffield). Quantitative analysis was undertaken using a "Thin Film" program, using in the instance of the Link System, natural $CaO \cdot SiO_2$ for the elemental *k*-factors and predetermined *k*-factors with the EDAX.

Other non-interfacial calcium silicate hydrates were prepared by mixing $Ca(OH)_2$ and BDH Ltd precipitated SiO_2 with distilled water (H_2O/solid = 5). The specimen examined by TEM was left for 32 days at 100° C in a digestion bomb, Parr 4745. The paste recovered was first washed in an excess of acetone, then vacuum dried in a desiccator over SiO_2 gel. A specimen, with an overall CaO/SiO_2 molar ratio of 1.7, was prepared for examination in the TEM, by making a dilute suspension of the hydrate in propan-2-ol. A drop of this was run on to a carbon-coated copper grid, which was then vacuum dried over SiO_2 gel.

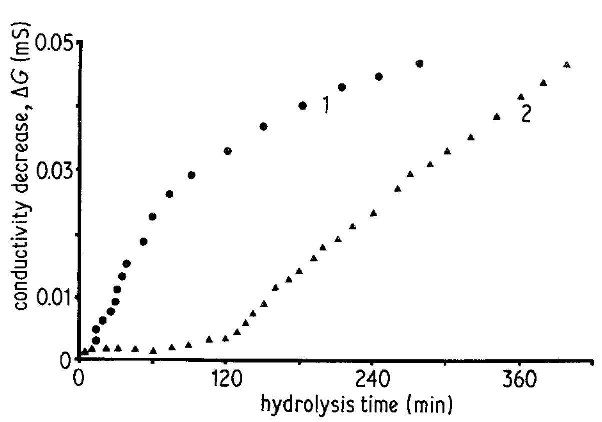

Figure 2 Decrease in conductivity of aqueous phase as a function of hydrolysis time at 23° C. Initial conditions: interfacial molar ratio CaO/SiO_2 of 20 for curve 1, and 2 for curve 2.

3. Results and discussion

The model two-phase system was used to prepare various types of interfacial material for our TEM studies of the micro and molecular structure of calcium silicate hydrate. The system chosen was the one found to be capable of not only providing hydrate material in a format most suitable for detailed TEM, but also of providing a reasonably controlled reaction interface for investigating the hydrolysis reaction

$$(C_2H_5O)_4Si + Ca(OH)_2$$
$$\rightarrow xCaO \cdot SiO_2 \cdot yH_2O + C_2H_5OH$$

The overall reaction was studied by following the decrease in electrical conductivity of the aqueous phase as $Ca(OH)_2$ is consumed. The conductivity scale was calibrated using known concentrations of $Ca(OH)_2$; estimates of the average thickness of the interfacial film can then be made, when used in combination with

1. compositional analysis of the interfacial layer,
2. the surface area of the interfacial layer.

If the above data are combined, a decrease in conductivity of 0.002 mS has been estimated to represent the formation of a ~4 nm thick layer of CH, or ~8 nm thick layer of hydrate with a composition of $1.5CaO \cdot SiO_2 \cdot 2H_2O$. Typical conductivity curves for the hydrolysis reaction at two $(C_2H_5O)_4Si$ concentrations are presented in Fig. 2.

The results for a range of low $(C_2H_5O)_4Si$ concentrations equivalent to initial interfacial CaO/SiO_2 molar ratio of 5 and above are summarized in Table I. Within this range of experimental variables, the following hydrolysis sequence has been defined.

1. Formation of a coherent ~4 nm thick layer of $Ca(OH)_2$, which inhibits the more rapid hydrolysis process for up to 2 h, see Fig. 2. A typical micrograph of the rather featureless layer is presented in Fig. 3. At higher magnification the layer was observed to have a mottled character at the 2 to 4 nm level characteristic of many amorphous materials [16]. Conventional selected-area electron diffraction produced two strong, but diffuse rings centred at 0.33 and 0.28 nm confirming the general amorphous character of the

TABLE I Effect of experimental variables on the character of the interfacial film

Concentration of $Ca(OH)_2$ (factor of saturated)*	Hydrolysis time (h)	TEM analysis: as CaO/SiO_2 molar ratio	Crystallinity: amorphous (a) microcrystalline (mc)
Initial interfacial CaO/SiO_2 molar ratio of 20†			
1.5	1	4	a
1.0	0.16	90	a
1.0	0.50	50	a
1.0	1	40	a
1.0	4	1.91	mc‡
1.0	8	1.77	mc
Initial interfacial CaO/SiO_2 molar ratio of 5			
1.5	0.33	4^4	a
1.5	1	3^4	a
1.2	0.33	4^4	a
1.0	0.16	> 90	a
1.0	0.33	15	a
1.0	0.5	1.5–3	a
1.0	1	4§	a
1.0	4	1.75	a
1.0	8	1.70	a
0.5	2	1.94	mc
0.2	2	1.65	mc

*Concentration $Ca(OH)_2$ given as factor of solubility at 23° C.
†Initial CaO/SiO_2 ratio, defined as molar ratio of equivalent CaO/SiO_2 species at interface ($t = 0$ sec).
‡Unstable in electron beam.
§Layer of variable composition.

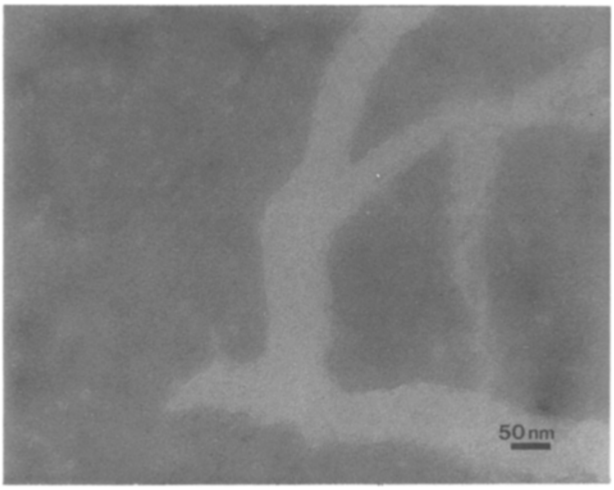

Figure 3 Micrograph of initial amorphous $Ca(OH)_2$ layer on the support film (lighter areas) at initial CaO/SiO_2 ratio of 20.

$Ca(OH)_2$, see Table II. Although basically $Ca(OH)_2$, the layer usually contains up to 5% equivalent SiO_2. This layer is possibly formed as a result of formation of C_2H_5OH at the interface during the initial hydrolysis of $(C_2H_5O)_4Si$ as defined in Equation 1. The resulting C_2H_5OH produced reduces the solubility of $Ca(OH)_2$ which rapidly precipitates at the interface, thereby inhibiting further reaction for periods of up to 2 h, see Fig. 2. The effect of low concentrations of C_2H_5OH on reducing the interfacial solubility of $Ca(OH)_2$ was confirmed in a model experiment. This involved running a dilute C_2H_5OH solution in hexane on to the two-phase system. The interfacial material was collected on a microscope grid and then examined in the TEM. Analysis and selected-area diffraction was used to identify the film as an extremely thin layer of amorphous $Ca(OH)_2$. No equivalent layer was formed over the same time period at the interface between hexane and the aqueous $Ca(OH)_2$ solution. However, the $Ca(OH)_2$ could also be formed due to the presence of hydrolysed silicate species at the interface. Barnes *et al.* [17] have found the surface of siliceous glass to be a good nucleant for $Ca(OH)_2$, and

TABLE II Selected-area electron diffraction of interfacial material

(a) Calcium-rich films

Interfacial $Ca(OH)_2$ film		Crystalline $Ca(OH)_2$: X-ray diffraction data [19], d_{hkl} (nm)
Band range, d_{hkl} (nm)	Band centre, d_{hkl} (nm)	
0.332–0.318(s)	0.325	0.311 (m)
0.281–0.273(s)	0.277	0.263 (vvs)
0.201 (w)	0.201	0.193 (ms)
0.187 (w)	0.187	0.179 (ms)

(b) Calcium silicate hydrate ($xCaO \cdot SiO_2 \cdot yH_2O$) films

Interfacial hydrate films with CaO/SiO_2 ratio of x				Synthetic hydrate: X-ray diffraction data [19], d_{hkl} (nm)
$x = 0.8$, d_{hkl} (nm)	$x = 1.5$, d_{hkl} (nm)	$x = 0.9$, d_{hkl} (nm)	$x = 1.6$, d_{hkl} (nm)	
				1.25(vs)
0.330–0.278(s)	0.327–0.275(s)	0.315(s)	0.312(s)	0.307(vs)
		0.285(s)	0.280(w)	0.280(s)
				0.24(w/d)
0.242–0.180(w)	0.235–0.175(w)			0.21(w/d)
		0.183(m)	0.185(m)	0.183(s)
		0.171(w)	0.170(w)	0.167(mw)
		0.140(vw)	0.141(vm)	0.140(w)
		0.120(vvw)	0.121(vvw)	0.123(vw)
		0.113(vww)	0.115(vvw)	0.117(vw)
		0.105(vvw)	0.103(vvw)	0.111(w)
				0.107(vw)

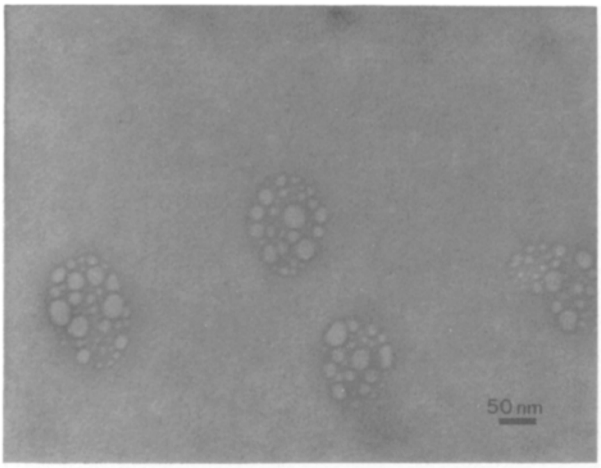

Figure 4 Micrograph of islands of calcium silicate hydrate formed within the amorphous $Ca(OH)_2$ layer.

this is possibly another mechanism by which the 4 nm thick interfacial film is formed.

2. Close to the end of the above period of inhibition of the hydrolysis reaction, islands $\sim 100\,nm^2$ in area and close to 10 to 10^2 nm thick were observed within the basic $Ca(OH)_2$ layer, see Fig. 4. These islands have a honeycomb-like microstructure, and typically analyse as xCaO · SiO_2 · $y H_2O$ with values of x ranging from ~ 0.8 to > 2.

TABLE III Effect of experimental variables on character of the interfacial film

Concentration of $Ca(OH)_2$ (factor of saturated)[*]	Hydrolysis time (h)	TEM analysis: as CaO/SiO_2 molar ratio	Crystallinity: amorphous (a) microcrystalline (mc)
Initial interfacial CaO/SiO_2 molar ratio of 2[†]			
1.5	0.33	1.55	a
1.2	1	1.65	a
1.0	0.16	0.05[‡]	a
1.0	0.33	3[‡]	a
1.0	0.5	1.77	a
1.0	1	1.54	mc/a
0.5	2	1.94	mc
Initial interfacial CaO/SiO_2 molar ratio of 1			
1.0	0.16	2[‡]	a
1.0	0.5	2[‡]	a
1.0	1	1.35	a
1.0	3	0.90	a
0.5	3	1.25	mc
Initial interfacial CaO/SiO_2 molar ratio of 0.4			
1.0	0.16	0.1[‡]	a
1.0	0.5	1.77	a
1.0	1	1.05	a
1.0	4	1.30	a
0.8	4	1.13	a
0.6	4	0.90	mc/a
0.5	4	1.05	mc
0.4	4	0.98	mc
0.2	4	1.05	mc
0.05	4	< 0.05[§]	a
Initial interfacial CaO/SiO_2 molar ratio of 0.1			
1.0	4	0.51[§]	a

[*] Concentration $Ca(OH)_2$ given as factor of solubility at 23° C.

[†] Initial CaO/SiO_2 ratio, defined as molar ratio of equivalent CaO/SiO_2 species at interface ($t = 0$ sec).

[‡] Variable composition.

[§] Non-foil-like in character.

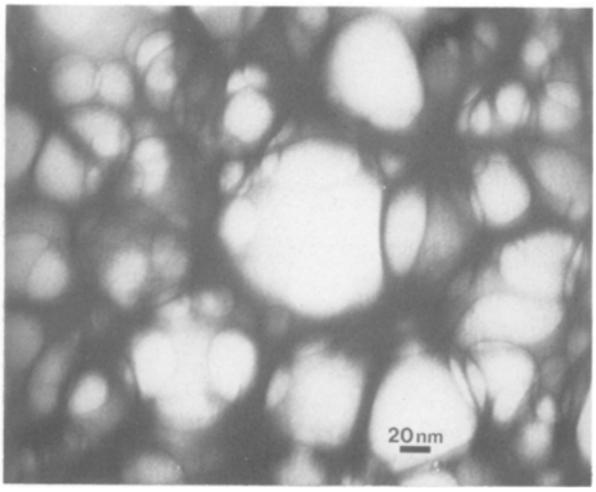

Figure 5 Micrograph of overall microstructure of a typical calcium silicate hydrate interfacial film.

3. Following the end of the inhibition period, the islands of calcium silicate hydrate were found to grow steadily until they covered the available interfacial space, see Fig. 5. During this stage the conductivity curve exhibits a slight oscillatory nature, see Fig. 2. This is thought to be due to formation and subsequent reaction of the transitional layer of $Ca(OH)_2$, estimated from the variations in conductivity to be some 5 nm thick.

4. At later ages the interfacial hydrates are formed at an ever decreasing rate, as indicated in the curvature of the conductivity curves, see Fig. 2. This decrease is no doubt controlled by the diffusion of reactive species through the developing hydrate layers.

At higher $(C_2H_5O)_4Si$ concentrations, when the initial CaO/SiO_2 molar ratio at the interface is less than 5, more complex behaviour was observed. In these conditions the initial $Ca(OH)_2$ interfacial barrier is no longer capable of delaying the rapid hydrolysis reaction, see Fig. 2. TEM examination has revealed the formation of a range of interfacial material depending on experimental conditions. These include typical hydrates, silica-rich material, as well as amorphous material with CaO/SiO_2 ratios in the 2 to 5 range. The results obtained within these experimental conditions are summarized in Table III. The experimental variables controlling the formation of interfacial material of such complexity have not been fully characterized.

The presence of silica-rich species at the interface during the early stages of the hydrolysis reaction at higher $(C_2H_5O)_4Si$ concentrations, could be significant in relation to the mechanism of 3CaO · SiO_2 hydration. Previous studies by Barnes *et al.* [17] have found the siliceous surface of glass to be good nucleant for $Ca(OH)_2$. Birchall and Thomas [18] therefore suggested that the silica-rich surface of hydrating 3CaO · SiO_2 would be a suitable site for the deposition of $Ca(OH)_2$ layers. The formation of calcium silicate hydrate would then occur by deposition of silicate anions on the surface of the preformed $Ca(OH)_2$ lattice acting as a nucleant. The physico-chemical conditions existing in our model system therefore appear to be somewhat similar to those occurring in hydrating

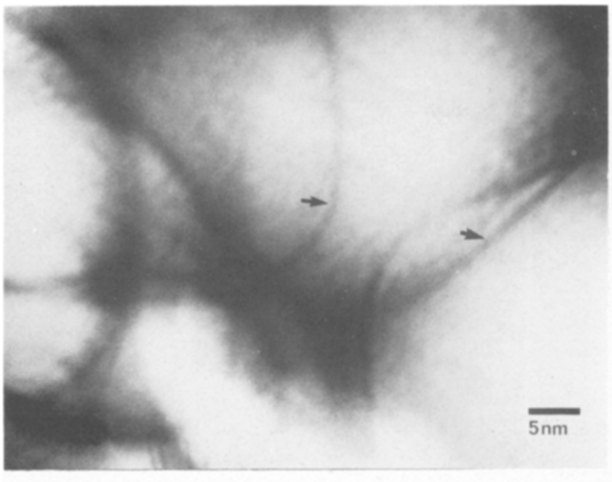

Figure 6 Micrograph of amorphous calcium silicate hydrate, with a CaO/SiO_2 molar ratio of 0.9.

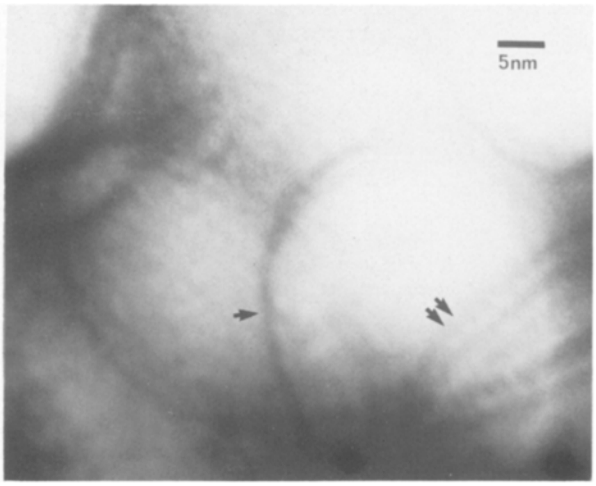

Figure 7 Micrograph of a microcrystalline calcium silicate hydrate, with a CaO/SiO_2 molar ratio of 1.65.

Portland cement. The basic molecular structural character of the hydrates, formed from $3CaO \cdot SiO_2$ or in our model system, would therefore be expected to be similar. Interestingly, at lower equivalent interfacial silica concentrations our TEM studies have directly observed the presence of a generally transient extremely thin ~4 nm thick layer of amorphous $Ca(OH)_2$.

The overall effects of changing the experimental conditions on the composition and crystallinity of the various calcium silicate hydrates are:

1. decreasing the initial CaO/SiO_2 ratio results in earlier formation of an interfacial film of $xCaO \cdot SiO_2 \cdot yH_2O$ with a typical foil-like microstructure;

2. the average CaO/SiO_2 ratio is ~1.8 for the hydrate formed when the initial interfacial CaO/SiO_2 ratio is 20. At the lower initial interfacial CaO/SiO_2 ratio of 0.4 the CaO/SiO_2 ratio in the hydrate decreases to around 1. At the lowest initial ratio studied of 0.1, non-foil-like calcium silicate hydrate with a CaO/SiO_2 ratio of 0.51 was formed;

3. at the high initial CaO/SiO_2 of 20 an unstable microcrystalline hydrate was formed, using saturated $Ca(OH)_2$ solution. However, at all lower initial interfacial CaO/SiO_2 ratios, using saturated or supersaturated $Ca(OH)_2$, amorphous hydrates were formed. These typically contained two diffuse rings in electron diffraction centred at 0.31 and 0.21 nm, see Table II. At lower $Ca(OH)_2$ concentrations, below 50% saturated, various microcrystalline varieties of calcium silicate hydrate with CaO/SiO_2 ratios ranging from 0.98 to 1.91 are formed, see Table III. These usually contain up to 12 well-defined diffraction rings.

The amorphous $Ca(OH)_2$ film has *d*-spacings somewhat greater than those in crystalline $Ca(OH)_2$, indicating overall expansion of the lattice, no doubt due to the disorder present. The microcrystalline hydrates have *d*-spacings close to those obtained by X-ray diffraction for calcium silicate hydrate, type I [19]. The one major difference is the absence of any detectable basal reflection at ~1.2 nm, presumably due to the mode of formation of our interfacial hydrates.

The interfacial material collected during stages 2 and 3 of the hydrolysis reaction has been examined in more detail in the TEM using axial bright-field illumination. A variety of amorphous and microcrystalline hydrates have been examined and within the resolution achieved of close to 0.4 nm, no difference in molecular character was detected. There were, however, certain differences in microstructural detail, such as density of pores and curvature of the foils. With regard to the molecular level features, we have observed within thin regions of the interfacial hydrate films, sheets ~ 1 nm thick extending some 10^4 to 10^6 nm^2, see arrowed regions in Figs. 6 and 7. In certain regions double foils, also ~ 1 nm thick, but ~2 nm and less apart were also observed, see double arrows in Fig. 7. This represents the first direct observation of the molecular character of any synthetic calcium silicate hydrate preparation. The presence of these ~1 nm thick sheets, extending over several hundred nanometres, provides, for the first time, direct experimental evidence at the micro and molecular level of a highly orientated two-dimensional layered structure. No evidence was obtained for a three-dimensional silicate framework-like structure as proposed by Gimlett *et al.* [13] for calcium synthetic silicate hydrate. Although our hydrate films are synthetic preparations, no evidence has been obtained in support of a microheterogeneous structure similar to that proposed by Taylor [15] for the hydrates in Portland cement. No evidence for microheterogeneous regions on the few nanometres scale, was obtained when the sheet itself was examined at high magnification. Instead the film is generally featureless, with only substructure on the 0.5 to 1 nm scale, related to the phase contrast image [16], being observed. A sheet-like structure of the type directly observed in our present studies is shown schematically in Fig. 8. This is derived from that proposed by Ramachandran *et al.* [3], and Birchall and Thomas [18]. These highly orientated structures contain a core layer of protonated CaO_x polyhedra, sandwiched between silicate groups, reminiscent of the layers in crystalline tobermorite [9]. The attached silicate groups are not, however, of infinite length as found in tobermorite, but of considerably shorter length. Typically Si_2O_7, Si_5O_{16}, Si_8O_{25}, etc chains have been found in both paste-hydrated $3CaO \cdot SiO_2$ [11] and Portland

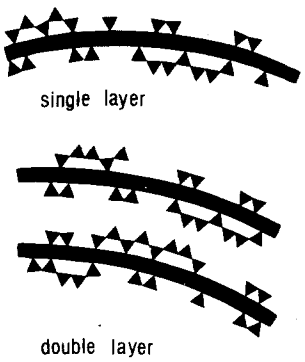

Figure 8 Schematic representation of the layer-like structure of calcium silicate hydrate. Triangles are silicate tetrahedra and the core sheet consists of protonated CaO_x polyhedra.

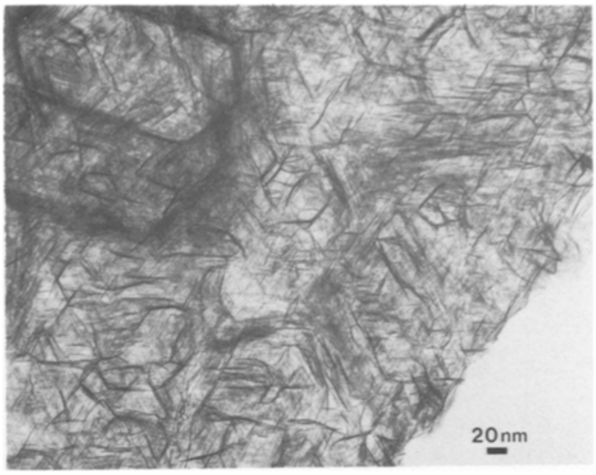

Figure 9 Micrograph of amorphous calcium silicate hydrate (CaO/SiO_2 = 1.7), prepared from $Ca(OH)_2/SiO_2$ paste left for 32 d at 100° C.

cement [20], as well as in various synthetic calcium silicate hydrates [6, 10]. The thickness of the layer shown in Fig. 8, containing CaO_x polyhedra and short-chain silicate groups, can be calculated from the known bond lengths of 0.235 nm for Ca–O and 0.27 nm for Si–O [21]. A layer of this type was estimated to be 1.1 nm thick, very close to the ~ 1 nm directly observed for the foil thickness in our investigations. The estimate is very similar to that found for an equivalent single layer in the crystal lattice of tobermorite [9].

The double foils ~ 2 nm and less apart observed in the high magnification micrograph are also shown schematically in Fig. 8. These are probably due to incipient short-range ordering in a direction at right angles to the sheet, i.e. in the "*c*-cell direction". Such foils represent only a very small percentage of the overall field of view, and are not parallel even over the scale of a few tens of nanometres. The degree of ordering in this direction, therefore, appears to be extremely low. The absence of any significant ordering in this direction is confirmed by the absence of a basal reflection, in any of the electron diffraction patterns obtained of our interfacial preparations, see Table III. The absence of such ordering in these interfacial hydrates is probably related to the physico-chemical character of the interfaces during their formation. Intermolecular forces appear to be operating in such a way as to inhibit ordering in a direction at right angles to the sheet even for microcrystalline hydrates. The weaker long-range Van der Waals forces, operating over 2 nm or more between neighbouring sheets, appear to be incapable, in general, of overcoming the intermolecular hydrogen bonds between the H_2O and C_2H_5OH molecules in the inter-foil region at the interface. As a consequence, only a statistically insignificant number of foils are less than ~ 2 nm apart.

A non-interfacial calcium silicate hydrate preparation with a CaO/SiO_2 ratio of 1.7 has also been examined in the TEM and significant microstructural and molecular detail has again been observed. A low-magnification micrograph clearly reveals a pseudo-hexagonal microstructure, formed by what, at this level of magnification, appears to be material of a fibre-like character, see Fig. 9. Although the general microstructure appears to be highly directionally orientated, conventional selected-area diffraction, was consistent with a generally amorphous hydrate, with two broad rings centred at 0.31 and 0.19 nm. At higher magnification the apparent fibre-like microstructure is now observed to be foil-like, reminiscent of the interfacial hydrates, except in being much straighter, see Fig. 10. High magnification TEM has again revealed foils ~ 1 nm thick, extending over 10^2 to 10^3 nm, see arrowed regions in Fig. 10. In addition, these foils are multilayered in character, some 2 to 4 nm apart, with up to at least six layers, see Fig. 10. This multilayered microstructure is probably the reason why various synthetic calcium silicate hydrates with this high CaO/SiO_2 ratio are thought to be fibre-like in character [22].

The ~ 1 nm thick foils present in the non-interfacial hydrate, are multilayered and much straighter in character, compared in the doublets and highly curved ~ 1 nm foils present in the interfacial hydrates of the same composition. These differences in microstructure are probably related to the difference in microenvironment between the two preparation routes. However, in spite of these, calcium silicate hydrates with the same basic molecular character are formed, retaining the ~ 1 nm foil thickness, typical of a protonated CaO_x polyhedral layer sandwiched between silicate

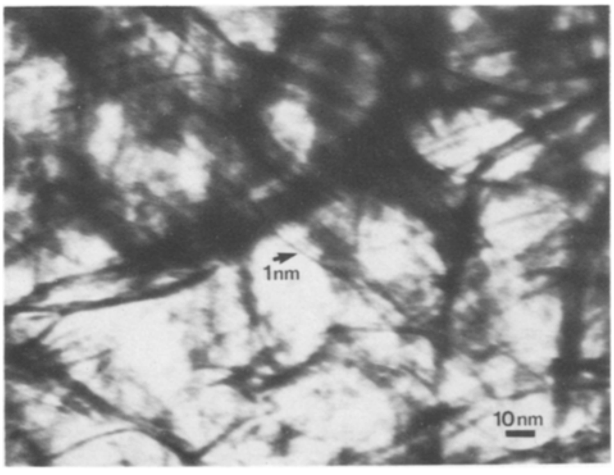

Figure 10 Micrograph of amorphous calcium silicate hydrate (CaO/SiO_2 = 1.7), prepared from $Ca(OH)_2/SiO_2$ paste left for 32 d at 100° C.

chains, as shown in Fig. 8. These basic sheet-like molecular features are therefore retained independently of composition, degree of order, or mode of formation. This strongly suggests, that the calcium silicate hydrate in paste-hydrated Portland cement, has at least a very similar basic molecular structure to that directly observed in the TEM for the synthetic hydrates prepared in this investigation.

4. Conclusions

By using a model two-phase system it has been found possible to not only prepare a wide variety of calcium silicate hydrates, but also to produce the interfacial hydrates in an appropriate format to characterize their microstructural and molecular detail in the transmission electron microscope.

Various amorphous and microcrystalline calcium silicate hydrates with compositions ranging from $CaO/SiO_2 = 0.8$ to 1.9 have been prepared. The composition and degree of order were found to depend on the experimental conditions used. High initial CaO/SiO_2 ratios at the interface were found to produce hydrates with a greater CaO content. Saturated $Ca(OH)_2$ solutions usually produced typically amorphous hydrates, whilst less concentrated solutions, at 50% saturated or less, produced a more ordered type of hydrate exhibiting up to 12 electron diffraction rings.

The majority of these calcium silicate hydrates were found by TEM to have a typical crumpled foil microstructure. In particular hydrate preparations, more detailed TEM has revealed their micro and molecular structural character. The presence of ~ 1 nm thick curved sheets some 10^2 to 10^6 nm^2 in extent have been directly observed, in both amorphous and microcrystalline hydrates, with compositions in the range $CaO/SiO_2 = 0.9$ to 1.75. The ~ 1 nm thick layer appears to represent the basic core structure of these hydrates, consisting of a protonated CaO_x polyhedral sheet sandwiched between short-chain silicate groups. The limited presence of double ~ 1 nm sheets approximately 2 nm and less apart, is indicative of incipient short-range ordering at right angles to the sheet. The absence of reflections, due to such ordering in conventional electron diffraction, provides evidence for the extremely low overall extent of such structural ordering.

The non-interfacial calcium silicate hydrate with a CaO/SiO_2 of 1.7 was thought to have a fibre-like microstructure when examined at low magnification in the TEM. However, more detailed microscopy revealed the actual character of this hydrate at a micro and molecular level. Highly directionally orientated foils ~ 1 nm thick extending some 10^2 to 10^3 nm were observed. Instead of doublets, multilayered hydrate foils between ~ 2 and 4 nm apart, consisting of up to six layers, were observed. In spite of the overall highly directionally orientated character of these foils, conventional electron diffraction contained only two diffuse rings, typical of amorphous materials. The thickness of the ~ 1 nm foils, like similar but more highly curved foils of the interfacial hydrates is again consistent with a basic structural core, consisting of a protonated CaO_x polyhedral sheet sandwiched between silicate groups. The difference in microstructural detail between the interfacial hydrates, which are curved and the linear multilayered non-interfacial hydrate foils, is possibly related to the great difference in preparative conditions, rather than to any basic change in their overall sheet-like molecular character.

Studies of the interfacial reactions producing calcium silicate hydrates in the model two-phase system, suggests a formation mechanism reminiscent of that existing on the surface of hydrating $3CaO \cdot SiO_2$. In addition, the sheet-like molecular level structure of the above synthetic hydrates was found to be retained independently of their composition, degree of structural order, or mode of formation. It is therefore suggested that the calcium silicate hydrates in hydrated Portland cement, could well also contain a similar basically highly orientated ~ 1 nm thick layer-like molecular structure consisting of a protonated CaO_x polyhedral layer sandwiched between silicate groups.

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