



THE CRYSTAL STRUCTURES OF CEMENT HYDRATION  
- A REVIEW AND A NEW GEL STRUCTURE MODEL

Åke Grudemo, MSc(Eng), Consultant,  
Swedish Cement and Concrete Research Institute

SYNOPSIS

The chemical reactions taking place in the course of hydration of an ordinary Portland cement are considered in a general and approximate way. The crystal structures of various hydrated components of cement paste are reviewed, as analysed and described in cement research during the last few decades. Hypothetical alternative structures are discussed briefly. Different theories on the structure of the C-S-H gel in cement paste are especially considered. Data from a recent study by X-ray diffractometry has given some evidence that the structure element of the gel is closely related to the simple double-layer OH element of CH-portlandite, but without any long-range order in the coordination and stacking of the elements.

1. CEMENT PASTE REACTIONS

Cement of the OPC type is composed of mainly five mineral crystal ingredients, four produced by burning of a raw material mixture, and the fifth (gypsum) added in grinding to particle sizes between about 1 and 100 microns, with a characteristic size of 5 microns (corresponding to a specific surface area of about 0.4 square meters per gram). The five components are (M=molecular weight per formula unit, w=typical percentage by weight):

1. Alite (tricalcium silicate with cationic substitutions of chiefly Al and Mg)  
M=228, w=60.
2. Belite ( $\beta$ -dicalcium silicate with substitutions of possibly Al and K) M=172, w=15.
3. Tricalcium aluminate (possibly with small additions of Na and K ions) M=270, w=10.
4. Dicalcium aluminoferrite (so-called ferrite solid solution of composition Ca:Al:Fe varying between 3:1:2 and 3:2:1) M(aver)=243, w=10.
5. Gypsum (calcium sulfate dihydrate, sometimes partly dehydrated to hemihydrate)  
M=172, w=5.

The percentage composition given above can vary considerably between different makes of standard Portland cement. Low-heat cements or construction cements are characterised by a very low content of tricalcium aluminate, and white cements by the absence of ferrite ingredients, with a corresponding increase in alite content. On the other hand, rapid-hardening cements are mostly manufactured by increasing the fineness of grinding. In most cements, small amounts of free CaO and inert MgO (periclase) are also present.

Upon contact with water in a well-mixed paste of normal consistency, the following reactions take place, in about the order indicated. The relative rate of reaction is rapid at first, but slows down considerably with time, due to the blocking and lengthening of the diffusion paths inwards and outwards from the cement crystal surfaces.

Hydration reactions, due to exchange of hydrogen ions vs. other cations:

1. Tricalcium aluminate + gypsum + water ----> ettringite
1. Tricalcium aluminate + alite + gypsum (+ carbon dioxide) + water ----> ettringite - thaumasite solid solution (Si ions replacing Al ions, hydroxyl ions and possibly carbonate ions replacing sulfate)
2. Alite + water ----> portlandite + C-S-H cement gel (reaction initially rapid, but slowing down considerably after some time)
3. Dicalcium aluminoferrite (approximately brownmillerite) + water ----> dicalcium aluminoferrite hydrate (?), or tetracalcium aluminoferrite hydrate + gibbsite or ferric hydroxide (?) (probably slow reaction, hydration product of uncertain identity)
4. Belite + water ----> portlandite (in comparatively small quantities) + C-S-H gel (very slow reaction, may not be complete after several years)

Recrystallisation reactions, due to different causes:

5. Ettringite + tricalcium aluminate + water ----> tetracalcium aluminate mono-sulfate hydrate (secondary reaction, possibly appearing in cements rich in tricalcium aluminate, when the gypsum available has been exhausted)
6. Portlandite + carbon dioxide in water ----> calcium carbonate + water (carbonation reaction)
7. C-S-H gel + carbon dioxide in water ----> calcium carbonate + silica (carbonation reaction)
8. Portlandite + C-S-H gel + carbon dioxide in water ----> thaumasite or similar (carbonation reaction, possibly the cause of some damages reported)
9. Tetracalcium sulfoaluminate hydrate + carbon dioxide in water ----> tetracalcium carbosulfoaluminate hydrate (carbonate ions incorporated in structure, or replacing sulfate or hydroxyl)
10. C-S-H gel (thermodynamically unstable) + portlandite ----> C-S-H crystal variety of some kind (thermodynamically more stable, well-crystallised) (autogeneous reaction, which has been anticipated to occur after very long times, but which has not been observed in ordinary cement paste or concrete of high age, however probably induced by belated autoclaving or in conditions of fire)

## 2. MECHANISMS OF CEMENT HYDRATION

The most recent comprehensive treatments of different aspects of cement hydration, on early hydration and rheology, on the formation of crystal structures and mechanical rigidity, and on the properties of hardened paste, have been given by the principal reporters of the 7th International Congress on the Chemistry of Cement, Paris 1980, by Skalny and Young of USA, by Taylor and Roy of Scotland and USA, by Helmuth of USA, by Sereda, Feldman and Ramachandran of Canada, and by Wittmann of Netherland (former West-Germany, now Switzerland). The list of references given by these authors include about 800 references. The present author finds it convenient to refer to these lists, and to add a couple of later references in the text.

The process of hydration of cement consists essentially in an exchange of cations. Hydrogen ions from the mixing water penetrate the surfaces of anhydrous crystals, and migrate further inwards, replacing part of the cations in the anhydrous crystals, and causing rearrangements of oxygens and the remaining cations. The cations replaced migrate outwards into the water phase, gradually building up lattice elements and complete hydrate crystals of some kind.

It can be noted that the oxygen ions are more or less stationary, both in the interiors of the cement particles and in the water-filled pore space. This can be made evident by calculating the oxygen densities in various compounds, i.e. the density remaining after an imagined removal of all the cations from the lattices. This is for liquid  $H_2O$  0.89, for  $CH$  0.97, for  $C_3A$  1.08, for  $C_3S$  varieties 1.09 to 1.14, for  $BC_2S$  1.22, for  $C_4AF$  1.23, and for  $CSH_2$  1.29. The oxygen densities calculated for some crystalline hydrates are remarkably stable, for tobermorite 1.18, for xonotlite 1.15, for  $C_4AH_{13}$  1.15, and for ettringite 1.13.

The reactivity of the various cement compounds is to some extent reflected in these figures. Tricalcium aluminate and silicate are relatively open structures and give off their cations easily, whereas dicalcium silicate and ferrite phase are more closed, and resist decomposition by intruding hydrogen ions. Gypsum seems to dissolve easily, due to the presence of water molecules in the lattice itself.

In the structure of water, the hydrogen ions are oscillating with a frequency of about  $10^{14}$  Hz between the two  $1/3$  positions on the line connecting the centers of two oxygen ions. From there they can be transported by rotating the oxygen ion through an approximately tetrahedral angle ( $109^\circ 5'$ ) to an oscillating position with another oxygen. If this is a surface oxygen of an anhydrous compound, it becomes hydroxylated, and further one-directional relay movements involving rotations and jumps can proceed, as long as there are other cations available to move in the opposite direction.

Water is a liquid of highly crystalline character, and the structure elements appearing in it are similar to those making up the ice I structure, although collapsed and mobile. When water freezes, the density decreases from 1.00 to 0.92. Both structures are very open, when compared to close-packed water molecules, of hypothetical density 2.01. Freezing stabilises the intermolecular distances and the hydrogen bonds, the oscillation frequency decreasing about ten decades, and the water molecule rotation frequency correspondingly. In the hexagonal-symmetry ice structure, each molecule is tetrahedrally surrounded by four others, in a hexagonal-symmetry structure with  $a=4.51 \text{ \AA}$ ,  $c=7.36 \text{ \AA}$ , where the stacking sequence along the  $c$  axis is AABBAABB.

The unit cell of ice contains four molecules, and between them two cavities large enough to accommodate extra water molecules, and separated by holes about 2.4 Å wide. When this structure is liquefied, about 1/6 of the cavities becomes temporarily filled with water molecules. However, between the molecules there are still holes large enough to allow for the easy diffusion of different types of cations through the water.

It may be of some interest to compare the minimum sizes of spaces between spherical water molecules of 2.76 Å diameter in different regular polyhedra, and the sizes of the cations liberated from the surfaces of the cement crystals, as expressed by their ionic diameters, according to the well-known Pauling values.

The spaces considered are: tetrahedral, octahedral, dekahedral (two close-packed square groups), and cubic, with diameters 0.62, 1.14, 1.78, and 2.02 Å, respectively. The cations considered are: Si, S (sulfuric ion), Al, Mg, Ca, Na, and K, with Pauling diameters 0.82, 0.84, 1.00, 1.30, 1.98, 1.90, and 2.66 Å, respectively. It should be emphasized that these figures are only theoretical and approximate, and certain differences can occur in diameters calculated from the interionic distances observed in various oxide structures involving these cations.

These figures seem to indicate that Si, S, and Al ions are too small to fill out octahedral spaces, whereas the Ca ion is far too big to be squeezed into an oxygen octahedron. This is true for Si and S in a great majority of real oxygen structures, but Al can occur in tetrahedral as well as octahedral coordination, depending on the nature of other cations present, and Ca can occupy octahedral spaces in many cases, especially in simple structures such as CaO (cubic face-centered, regular octahedron, 3.40 Å O-O distance) and Ca(OH)<sub>2</sub> (hexagonal layer-lattice, somewhat distorted octahedron, 3.59 Å O-O distance). In other structures, the Ca ion appears in less expanded oxygen polyhedra, such as distorted dekahedra (ettringite, thaumasite), and in more irregular polyhedra of different types (calcium silicate hydrates occurring as minerals or produced hydrothermally at elevated temperatures).

The first stage of hydration of cement is a complex process, and there are different opinions on many points, as reviewed by Skalny and Young in their report at the Paris congress. It seems that the capillary pore space is rapidly saturated with Ca, Al, and S ions. The Si ions are, however, fixed in their initial group of four oxygens. This group must be transported as a whole through the water lattice, probably by some kind of wiggling movement, and this takes time. Supersaturation with respect to the other ions is reached already at about 0.2 per cent hydration, and the material required for this comes from a surface layer of about 10 Å thickness.

It would appear that the further reaction is temporarily retarded at this stage, due to the formation of thin surface layers of nucleating ettringite on the aluminate surfaces, and of silica or perhaps an unstable variety of thaumasite (C<sub>6</sub>S<sub>2</sub>S<sub>3</sub>-hydrate) on the silicate surfaces. These layers must be broken up and reorganized by the cations working their way out from the lower layers of the anhydrous crystals.

After some time, perhaps a couple of hours, CH crystals nucleate and start to grow at some places in the capillary pores. This is a comparatively rapid process, as shown by Greening by means of time-lapse TEM films, and tends to fill the whole pore with a stack of CH lamellae, at the same time emptying temporarily a large number of near-by pores from Ca ions. Later on, when the paths of diffusion between pores have been closed, due to the progressing formation of silicate gel, such large crystals of CH are prevented from forming.

### 3. THE STRUCTURES OF THE C-A-S-H AND C-S-S-H COMPOUNDS

The structures of ettringite and thaumasite have been thoroughly studied by single-crystal X-ray diffraction intensity measurements and refinements of electron density syntheses, ettringite by Moore and Taylor (Acta Cryst. 1970), and thaumasite by Edge and Taylor (Acta Cryst. 1971), using comparatively large-sized crystals from natural sources. The hexagonal-columnar structure is now well-established, with  $a=11.26 \text{ \AA}$ ,  $\frac{1}{2}c=10.74 \text{ \AA}$  in ettringite, and 2.0 to 3.3 per cent smaller, 11.04 and 10.39  $\text{\AA}$  in thaumasite, with essentially isostructural contents of the unit cells.

The Al ions in ettringite, and the Si ions in thaumasite, are built into OH octahedra lined up along the trigonal axis, around which trigonally arranged Ca ions are coordinated to the square group formed by adjacent octahedral edges, and to four other oxygens in water molecules in interstitial positions of the cell. The O configuration around the Ca ions is said to be "a trigonal prism having two additional apices". It can also be described as a distorted dekahedron. The structure is further filled out with interstitial sulfate, carbonate in thaumasite, and water groups.

These analyses are obviously very elaborate, accurate, and reliable, the reliability index being about 0.10 for a total of several hundred structure factors measured. It would therefore seem unreasonable to speculate on the possibility of some other structure within the same unit cell, that could give a similar agreement. However, it is tempting, if only for the sake of argument, to raise the question, if the configuration of ions must necessarily be the same in the nearly-colloidal crystals of ettringite and mixed ettringite-thaumasite, with lateral dimensions about 0.2 microns, and rapidly formed in the first stages of cement hydration, as in the large crystals, of sizes 0.1 mm and more, which are slowly stabilised under favourable conditions in nature

The only way of studying microcrystalline materials is by means of powder diffraction diagrams from reasonably pure substances. A sample labeled ettringite from Ettringen, Germany, turned out to be a mixture. A sample of thaumasite from Långban, Sweden, was probably pure, but the distribution of indexable intensities (about 50 peaks in the normal  $2\theta$  range) was obviously distorted, due to crystal orientation effects (reinforcements of intensities with  $l=0$ ). A sample of synthetic ettringite ( $C_3A+3CSH_2$ , more than 90 per cent reacted in excess water) gave a diagram with excellent agreement in the peak positions (apart from the slight displacement of peaks caused by the larger dimensions of the unit cell), but there are great discrepancies in the distribution of peak intensities. However, this is hardly surprising, considering the differences in unit cell contents, even if the structures are broadly isostructural.

Evidently, the comparison should be made between synthetic ettringite and pure mineral samples of natural ettringite, properly prepared to avoid orientation effects. However, this remains for future work.

Speculating on the possible arrangement of ions in alternative ettringite structures, it would seem natural to return to a modified version of the thaumasite structure proposed by Welin (Arkiv Min. Geol. 1956). The Si ions (or Al ions in ettringite) are located on the trigonal  $c$  axis, tetrahedrally surrounded by four OH ions, with their apices perhaps alternately pointing in the + or - direction in adjacent columns. About halfway between are trigonal groups of Ca ions, located in nearly regular OH or water octahedra, sharing one corner with a tetrahedral apex oxygen, and one edge with the basal OH of the next tetrahedron. These units are arranged in parallel in hexagonal fashion, and in the interstices are the remaining constituents of the molecule, trigonally arranged  $SO_4$  groups and water molecules.

When the number of reactive Al ions exceeds the number of sulfate groups available, the ettringite structures can no longer be stable, but convert to tetracalcium sulfoaluminate hydrate of the so-called monosulfate variety, of the hexagonal-plate type first indicated by Buttler, Dent Glasser, and Taylor (J Amer Ceramic Soc 1959), and later confirmed in several ways, according to Taylor and Roy (Paris Congress 1980). The central unit of this structure is a close-packed double-layer of OH ions, with two Ca and one Al ion in three octahedral sites, with a hexagonal unit of about 5.7 Å. These layers are not directly superimposed, as in ordinary CH-portlandite, but interstratified with water layers containing sulfate groups, one sulfate per two Al ions. The basal spacing of this layer-lattice is about 8.9 Å.

Upon moderate heating, the Al ions are expelled from their octahedral sites, forming a glass-phase, and are replaced by Ca ions from near-by layers, so that regular CH layers are formed.

An alternative structure was suggested by the present author (Washington Symp 1960, Trans Royal Inst Techn 1965). In this structure, the central unit was a CH double-layer with 1/3 of the octahedra empty, the Al ions being instead accommodated in tetrahedra unilaterally attached to the CH layer, and S ions in other tetrahedral groups, in a layer-lattice unit resembling that of kaolinite clay. Heating single-crystals in the beam of an electron microscope induced changes in the SED diagrams which were interpreted as a movement of Al ions from tetrahedral positions to the empty octahedral sites in the CH layer. However, this type of structure is obviously rather hypothetical, and its existence is now considered very unlikely.

#### 4. THE STRUCTURE OF CH - PORTLANDITE

The simple structure of calcium hydroxide was examined by several investigators already in the early years of X-ray crystallography. The structure element is a hexagonal-symmetry double-layer of OH ions with Ca ions in octahedral positions. FIG 1 shows eight units of this layer element. The layers are stacked in hexagonal fashion, forming a hexagonal unit cell with  $a = 3.593\text{Å}$ ,  $c = 4.909\text{Å}$ . Assuming spherical-symmetry ions with Ca at the origin, the z/c coordinates of the OH ions is  $\pm 0.30$ , and the ionic diameters are: for Ca 2.22Å, and for OH 2.86Å. Thus, the structure seems expanded, and the density is not very high, 2.24.

The X-ray diffractogram of an ordinary cement paste, fully hydrated, is dominated by a CH pattern, with 6 peaks below  $2\theta = 60^\circ$ , as shown in FIG 2. The average relative intensity of these peaks, as compared to 100 per cent pure CH, indicates a maximum CH content of about 30 per cent at water/cement ratios between about 0.4 and 0.6, decreasing towards lower w/c (due to the presence of unhydrated cement), and towards higher w/c (due to the formation of C-S-H gel of higher C/S ratio, and to the initial addition of colloidal silica, necessary in order to prevent separation of water).

The hexagonal symmetry of the CH lattice seems to indicate a regular and well-built structure. However, the large and variable B values ( $B = \text{X-ray peak width at half-intensity}$ ), as observed by the author (Cem Concr Res 1984), between 0.23 and 0.32  $^\circ 2\theta$ , point to a relatively-small size of undisturbed lattice units, between about 500 and 800Å. In other samples, B values as small as 0.13  $^\circ 2\theta$  have been measured (for the 18 $^\circ$  basal reflection), corresponding to a lattice unit of about 2000Å. However, the generally enlarged peak widths, as well as the large spread in peak areas even in unoriented samples, can be associated with lattice disturbances of an unknown type, such as stacking faults, or curved lattice layers.

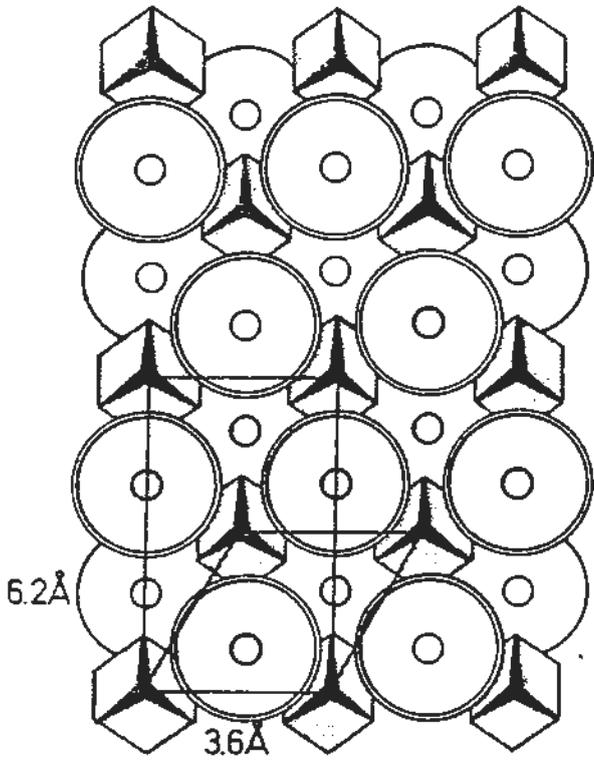


FIG 1 CH crystal structure, layer lattice element with Ca ions (cubes) in octahedral positions between OH ions, situated 1.47Å above and below the Ca plane. More exact cell size 3.593Å. Next layer stacked directly on top, at a distance of 4.909Å.

CH structure

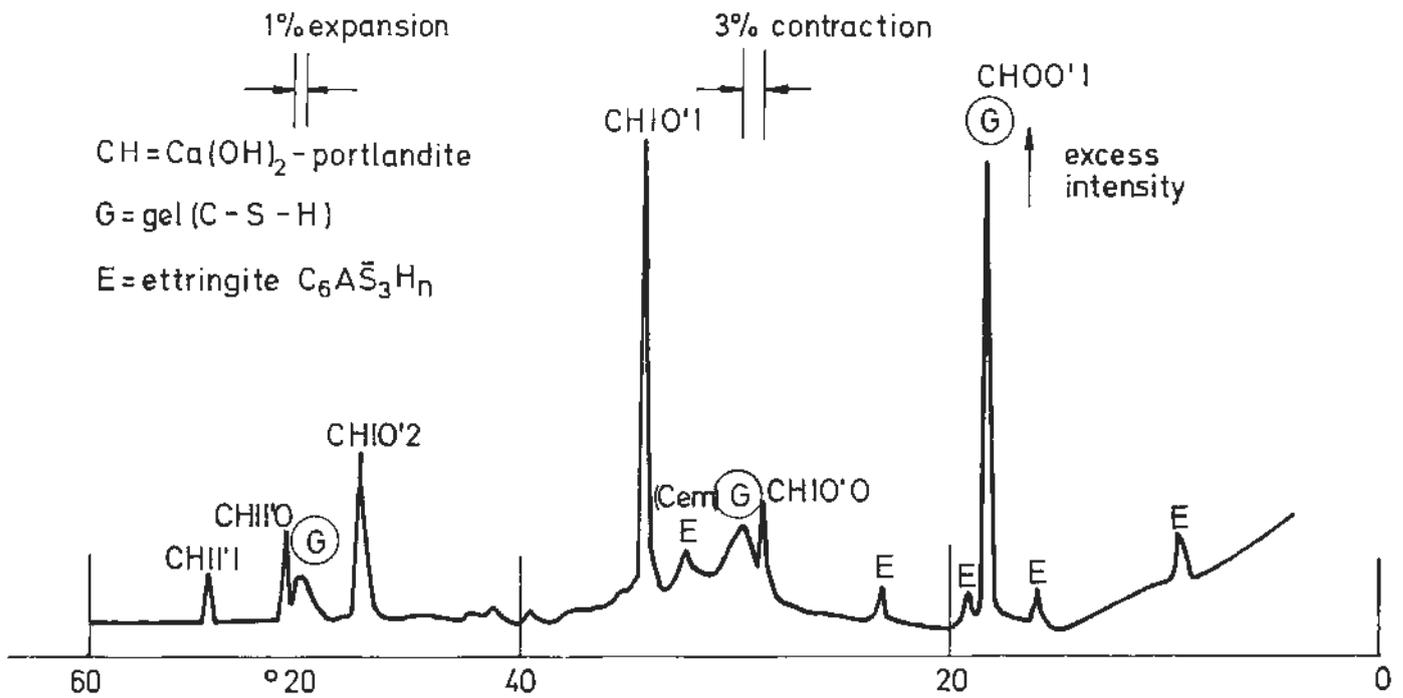


FIG 2 X-ray diffractogram of ordinary cement paste, fully hydrated (solid-plate sample)

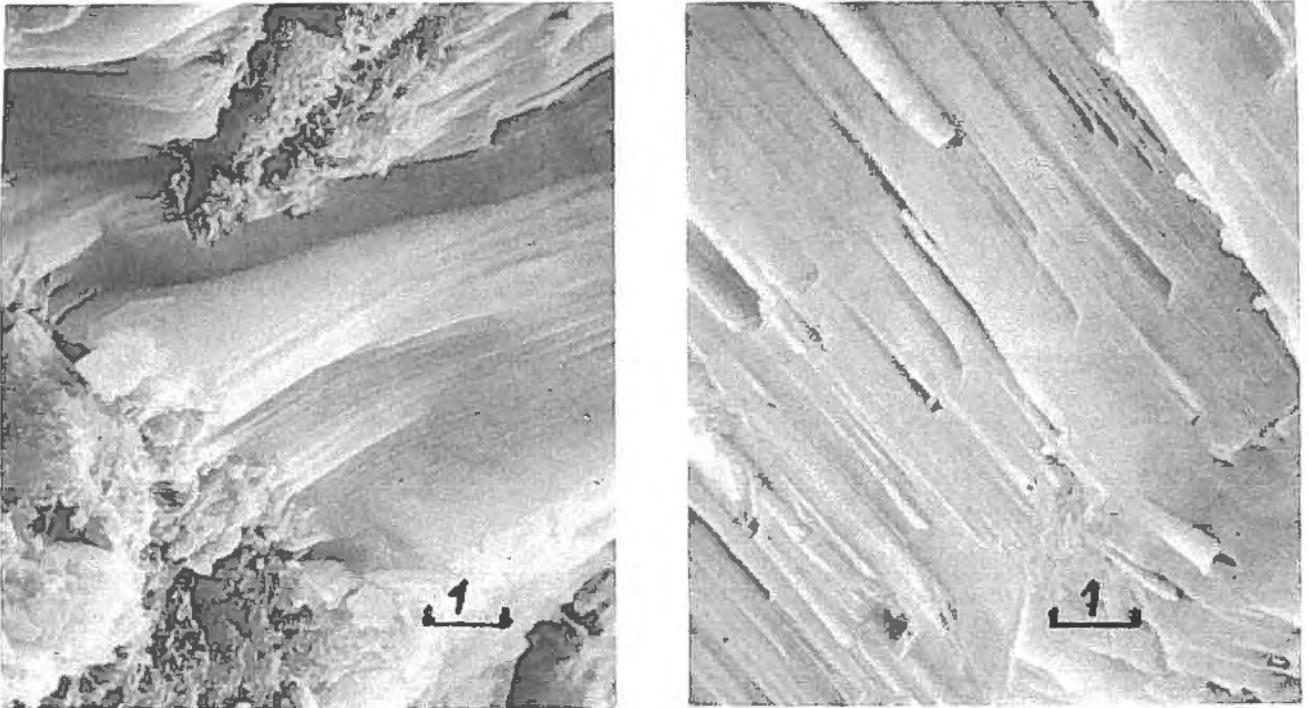


FIG 3 SEM micrographs of the lamellar CH phase in cement pastes: white cement (about 85 per cent alite, no ferrite phase, C/S nearly 3), w/c 0.5, 5 days hydrated (left), and 80/20 mixture white cement/silica (Siogel, reactive, high-surface area), w/solid 0.5, 5 days hydrated (right). There is no obvious difference in morphology of the CH phases, nor in morphology of the gel phases (cf. below).

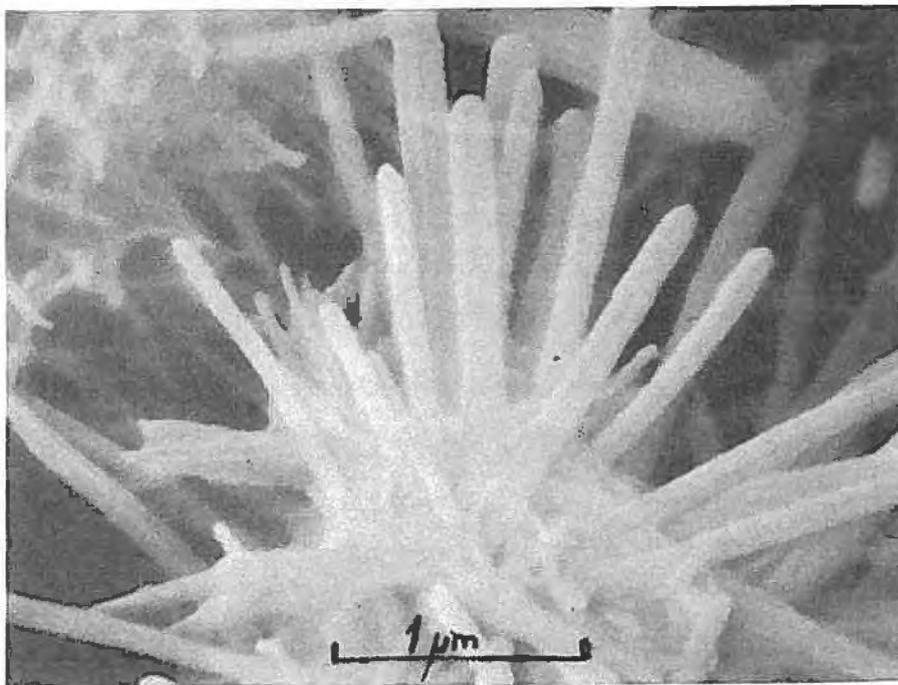


FIG 4 Ettringite-type structures in the mixed white cement/colloidal silica paste. The particles are 0.1 to 0.2 microns in diameter, and two to three microns long.

5. THE STRUCTURE OF THE C-S-H GEL PHASE IN CEMENT PASTES

It is shown in FIG 2 that the X-ray diffraction effects given by the C-S-H gel consist of only two weak and diffuse peaks, one in the 3.2 to 2.9Å range, and one in the 1.86 to 1.79Å range. There is, in particular, no sign of any long-distance basal spacing. The selected-area electron diffraction effects observed by the author (Trans Royal Inst Techn 1965) are similarly uncertain. Several other investigators have arrived at the same conclusions. Thus, it would seem almost impossible to use these effects as evidence for any structural identity with, or even similarity to, some better-crystallised C-S-H mineral.

The C-S-H phase diagram is a complex one, as shown in Table 1, which is a rearrangement, in phase diagram form, of the table given by Taylor and Roy (Paris Congress 1980) as a compilation of all the crystalline C-S-H compounds found in geological samples, and in autoclaved products, in numerous investigations during especially the last 30 years.

TABLE 1 SCHEMATIC C-S-H PHASE DIAGRAM

°C				
<u>1000</u>	CS-WOLLASTONITE	C <sub>1.5</sub> S-KILCHOANITE	C <sub>2</sub> S (ALFA BETA GAMMA)	C <sub>3</sub> S-ALITE
<u>500</u>	C <sub>0.83</sub> SH <sub>0.17</sub> -TOBERMORITE 9Å		C <sub>2</sub> SH <sub>0.2</sub> (CI)-RUSTUMITE	
			C <sub>1.6</sub> SH <sub>0.4</sub> -KILLALAIT	
	CSH <sub>0.17</sub> -XONOTLITE		C <sub>2</sub> SH <sub>0.33</sub> -DELLAITE	
	C <sub>0.58</sub> SH <sub>0.25</sub> -TRUSCOTTITE	C <sub>1.33</sub> SH <sub>0.33</sub> -FOSHAGITE		C <sub>2.5</sub> SH <sub>0.5</sub> - CALCIO-CHONDRODITE
	CSH <sub>0.33</sub> -ROSENHAHNITE		C <sub>2</sub> SH <sub>0.5</sub> (C̄)-FUKALITE	
<u>200</u>	C <sub>0.7</sub> (ANK)SH <sub>0.36</sub> -REYERITE	C <sub>1.17</sub> SH <sub>0.33</sub> (C̄)-SCAWTITE	C <sub>2</sub> SH-ALFA-HYDRATE	
	C <sub>0.67</sub> SH <sub>0.67</sub> -GYROLITE	C <sub>1.25</sub> SH <sub>1.25</sub> -TOBERMORITE 10Å		
	C <sub>0.83</sub> SH <sub>0.83</sub> -TOBERMORITE 11Å		C <sub>2</sub> SH-HILLEBRANDITE	
	C <sub>0.5</sub> SH-OKENITE	C <sub>1.5</sub> SH <sub>1.17</sub> -METAJENNITE		C <sub>3</sub> SH <sub>1.5</sub>
	Z-PHASE CSH-SUOLUNITE			
	C <sub>0.67</sub> A <sub>0.11</sub> SH-TACHARANITE	C <sub>1.5</sub> SH <sub>1.5</sub> -AFWILLITE		
<u>100</u>	C <sub>0.5</sub> SH <sub>1.33</sub> -NEKOITE			
	C <sub>0.83</sub> SH <sub>1.5</sub> -TOBERMORITE 14Å	C <sub>1.5</sub> SH <sub>1.83</sub> -JENNITE		
	C <sub>0.83-1.25</sub> SH <sub>x</sub> -C-S-H(I)	C <sub>1.5-2.25</sub> SH <sub>x</sub> -C-S-H(II)		
	CEMENT HYDRATION PRODUCTS: C <sub>1.5-2(or more?)</sub> SH <sub>2+x</sub> + CH-PORTLANDITE			
<u>0</u>				
	C/S ratio---->0.5	1.0	1.5	2.0
				3

The X-ray diagrams of tobermorite 11Å, comparatively well-crystallised (from Siporex, autoclaved cement-quartz mixture), and C-S-H(I) of various C/S ratios 0.8 to 1.5 (colloidal silica in lime solution, shaken for several weeks) show a certain resemblance with respect to the regions of strongest peaks (although the tobermorite peaks are much sharper), and these regions also agree broadly with those of the two much weaker peaks of the cement gel (except for the basal reflections, which are missing in the cement paste diagram), cf. Grudemo (Studies Concr. Techn. 1979). On the basis of these similarities, it was generally assumed, for many years before about 1970, that tobermorite of some variety was the model crystal for the possible formation of structure elements in cement paste.

The crystal structures of most of the minerals of Table 1 have been more or less successfully determined in later years, and the tobermorite structure was one of the first to be solved, by Megaw and Kelsey (Nature 1956). Its molecular unit is a layer composed of two sheets of polymerised  $(\text{SiO}_2)_n$  chains kinked in a special way suitable for accommodating a double layer of Ca ions in the oxygen polyhedra between them. The complex nature of this structure, as well as its C/S ratio, which is far too low, makes it unsuitable as a model for cement gel.

This fact was pointed out by Taylor and his associates (Tokyo Symp. 1968, Moscow Congress 1974), who suggested the mineral jennite as a more suitable model structure. According to Gard and Taylor (Cem Concr Res 1976), the jennite structure, as well as that of the related low-temperature compound C-S-H(II), contains mainly dimeric  $\text{Si}_2\text{O}_7$ , possibly broken-down chains, with the missing silica replaced by Ca ions, increasing the C/S ratio to 1.5, thus more in agreement with that of C-S-H gel in cement paste. However, the layer-lattice character still remains, with long-distance basal spacings: 11.4Å in tobermorite, variable 14.6 to 9.7Å in C-S-H(I), 10.5Å in jennite, and about 10Å in C-S-H(II). The total absence of indications of an X-ray peak in this  $2\theta$  region in cement paste seems to rule out any of these compounds as model substances.

The present author made an attempt at showing that plausible C-S-H structures could be conceived, at least hypothetically, without introducing polymerised silica chains and layer lattices with basal spacings in the 6 to 12°  $2\theta$  range (RILEM-d'INSA symp Toulouse 1972). The structure suggested had hydrogen-bonded chains of silica tetrahedra arranged in a 6.2 x 6.2Å square fashion, and between them Ca ions and water molecules. It remains to show that the long-range order of such a regular lattice could be so totally destroyed that only the 200 or 002, and 020 reflections remain to be seen in the X-ray pattern.

The present general opinion in this matter is expressed by Taylor and Roy (Paris Congress 1980): "As Diamond (Sheffield Conference 1976) has emphasized, the structure possesses only short-range order, and the absence of any powder spacing in the 9-15Å region shows that there is no close approximation to a set of regularly spaced layers. The structure must differ markedly from those of such crystalline or quasi-crystalline phases as tobermorite, jennite, C-S-H(I) or C-S-H(II), and the use of any of these as models is likely to be misleading." ... "The most obvious interpretation of the weak x-ray peaks or bands at 1.8 and about 3Å is that they are hk reflections from layers similar to those in  $\text{Ca}(\text{OH})_2$ , but possessing only short-range order and distorted because many of their oxygen atoms are shared with silicate tetrahedra in a particular way."

## 6. TESTS FOR A C-S-H GEL STRUCTURE BASED ON THE CH LATTICE

It would seem possible to test the idea put forth by Taylor and Roy, on the structural similarity between the C-S-H gel and the CH crystal structures, by examining the CH basal reflection region near  $2\theta = 18^\circ$ , in order to study if there is any extra peak, or increase in intensity, in this range, possible to be interpreted as a contribution given by the C-S-H gel.

In order to test the possible existence of such effects, the author made a series of X-ray intensity measurements on different paste materials, as reported recently (Cem Concr Res, Jan 1984).

The materials studied were pastes of white cement and standard portland cement, of w/c ratios between 0.32 and 1.32, and fully hydrated (6 years in moist conditions). Separation of water was prevented by addition of colloidal silica (Aerosil) in increasing amounts, up to 5 per cent per weight cement. This did not change the overall C/S ratio very much. However, the large variation in w/c ratio obviously caused great changes in the gel structure with respect to morphology: aggregates of small, structureless particles in the 0.32 white cement paste, entangled heaps of extremely fibrous particles in the 1.32 paste, in both cases mixed with lamellar stacks of CH crystals of the ordinary appearance (cf Fig 3).

The integrated intensities of the X-ray peaks of CH and gel were counted both for the pastes (solid-plate samples, freshly cut and dried in alcohol) and comparison samples of pure CH and gel. The intensity ratios gave the contents of the two components, in per cent by volume, which are reproduced in Fig 5 from the report referred to above.

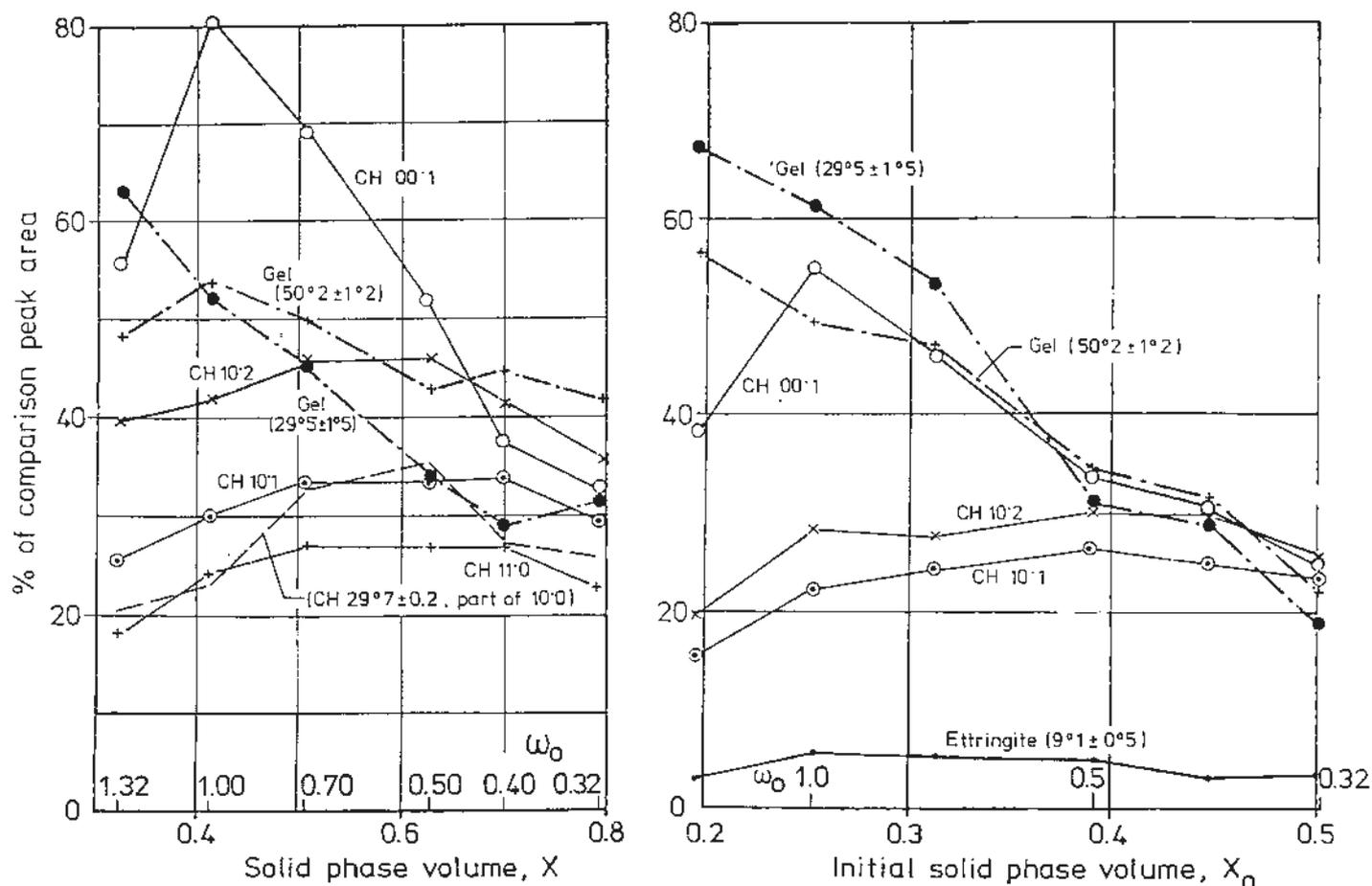


FIG 5 Contents of CH and C-S-H gel in pastes of white cement (left) and standard portland cement (right), from ratios of counts for X-ray diffraction peaks

Nearly all the curves for the CH content show the same trend: a low maximum at intermediate w/c, falling off especially towards high w/c values. The most reliable absolute value for the maximum is given by the strong 10°1 peak: about 34 % for white cement pastes, about 27 % for the standard cement pastes. The differences in level for other peaks are not considered important, since they are probably caused by intensity shifts due to different modes of crystallisation of the CH crystals in the pastes and in the comparison material.

The gel content, on the other hand, seems to decrease more or less steadily from the expected value, about 60 %, at the lowest solid phase volume (highest w/c) down to an apparent value of between about 20 and 40 % in the densest pastes. This decrease could be due to several causes: a real decrease in gel content, a successive lowering of the C/S ratio of the gel, and to the development of more ill-crystallised gel elements in the denser pastes, as is indicated by the SEM pictures shown in the report in Cement and Concrete Research.

It is interesting to note that the curve for the CH basal reflection follows the same trend as those of the gel content, apart from a steep rise between w/c 1.32 and 1.00. This phenomenon can hardly be interpreted in more than one way, since with solid-plate samples crystal orientation effects are out of the question: that the 18° peak is in reality a superposition of two peaks, one CH peak of normally varying intensity, and a gel peak with an unknown comparison (100 %) value, and varying as the other gel peaks.

Thus, it seems that the "mystery of the missing basal spacing" of cement gel could be solved by stating that it has been concealed behind the basal spacing of CH. It was suggested in earlier reports that the general symmetry of the CH unit cell could be maintained in the sub-crystalline arrangements of ions in the C-S-H gel structures. Assuming a slightly distorted orthohexagonal CH cell,  $6.10 \times 3.65 \times 4.91 \text{ \AA}$ , and in the absence of any long-range order, the only gel peaks to be seen would be the 29°2 (20) and the 50°0 (02), diffuse but resolved from the corresponding CH peaks at 28°7 and 50°7, whereas the basal reflection would coincide with the CH basal reflection, if present. In the pastes of high w/c, a shift of the maximum intensity towards 18°02 (18°06 in pure CH) has been observed, indicating the appearance of a second peak.

## 7. TENTATIVE STRUCTURE OF THE CH-TYPE GEL

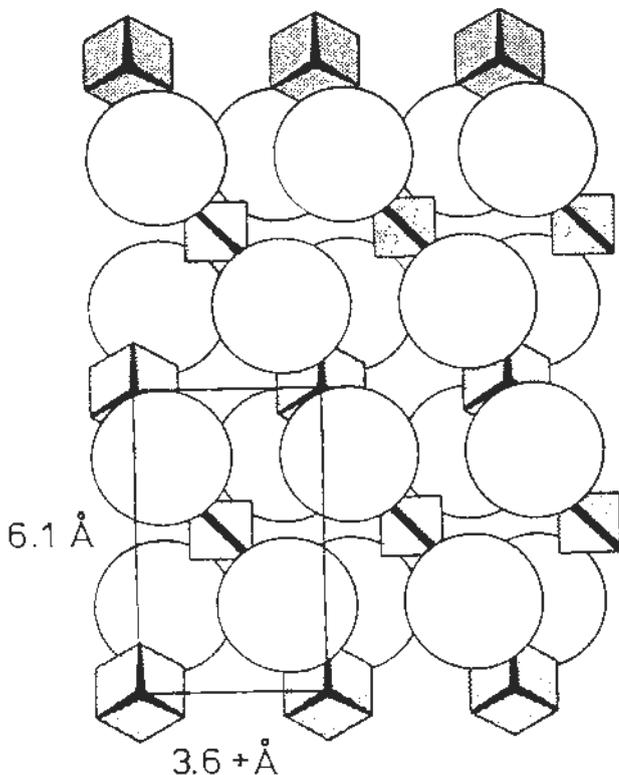
It might seem surprising, considering the multitude of more or less well-crystallised compounds of varying composition displayed in Table 1, that none of these can be formed from the calcium silicates in cement paste. However, these compounds have been formed in thermodynamic conditions energetic enough to permit a complete liberation of the ionic groups involved, and their reorganisation into crystalline structures in a state at least approaching true equilibrium. The low-temperature products of a fairly crystalline nature do not appear ordinarily in cement pastes, but are produced by bringing together the reaction ingredients separately in aqueous solution (C-S-H(I)) or, according to Taylor and Roy (Paris Congress 1980), by aging dilute suspensions of the calcium silicates present in cement (C-S-H(II)).

Most of the gel mass observed quantitatively by its diffuse peaks in X-ray diffractograms from solid cement paste, fully hydrated, has been formed under much more cramped conditions, and at temperatures too low to permit the attainment of true thermodynamic equilibrium. The reaction ingredients are mixed intimately on the ionic scale already by the cement burning process, and the reaction energy provided by the hydroxylation of oxygens by hydrogen ions advancing through the internal structure of the calcium silicate crystals, is only sufficient for a

brief and incomplete loosening-up of the crystal lattice. The Ca ions and the  $\text{SiO}_4$  tetrahedra are temporarily liberated and transported over mostly very small distances, before being again fixed and frozen in some configuration far from crystalline equilibrium.

However, some kind of ordering principle is likely to prevail. The ordering mechanism might be provided by the arrangement of Ca ions in layers containing trigonal or orthohexagonal CH cells, reorganised to accommodate Si ions. A possible configuration is shown in Fig 6, which can be derived directly from Fig 1 by removing every second Ca ion and distorting the corresponding hydroxyl octahedron to two tetrahedra of slightly irregular shape, with an Si ion accommodated in one of them. The octahedral group surrounding the Ca ion is of course also distorted by this displacement of oxygens, but this distortion is not considered impossible, since Ca ions are known to appear in many types of irregular polyhedra in different crystal lattices. The orthohexagonal cell is supposed to contract from 6.22 to 6.10Å in one direction, and to expand from 3.59 to 3.64Å in the other direction, whereas the distance between superimposed layers remains about the same, 4.91Å.

An extension of the structure in Fig 6 would lead to a fibrous structure, with rows of free  $\text{SiO}_4$  groups, perhaps hydrogen-bonded, and of composition CSH. To bring the C/S ratio up to observed values, 1.5 to 2.0, it seems necessary to introduce regular  $\text{C}_2\text{H}_2$  cells, or void  $\text{CH}_3$  cells, at certain intervals, perhaps in the sequence CSH-CSH-CSH- $\text{C}_2\text{H}_2$ , of C/S ratio 1.67. For reasons of isotropy, these chain elements would tend to run in different hexagonal directions, thus forming a mosaic of distorted crystal elements. Such a mosaic, of course more regular than could be conceived to occur in real structures, is shown in Fig 7. In more open and spacious systems, such as pastes of high w/c ratio, one chain direction could be expected to predominate in the nucleation of gel structures, which would lead to the formation of fibrous particles.



C-S-H gel structure

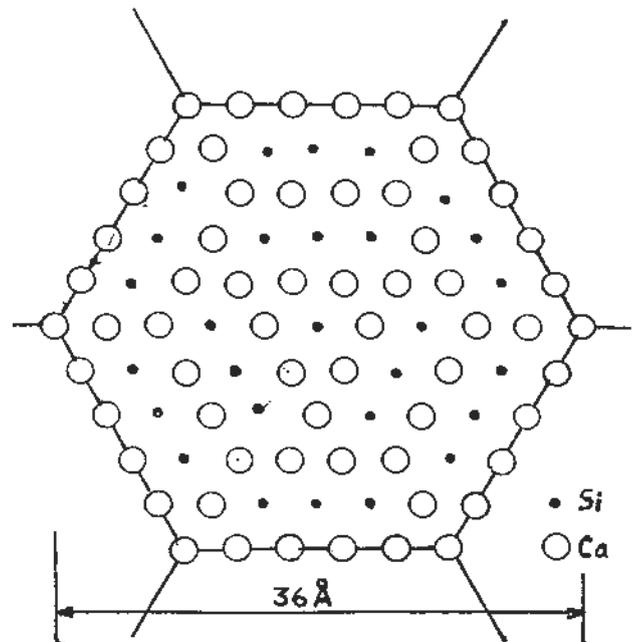


FIG 7 Mosaic of CH-type cells in C-S-H layer, C/S = 1.68

FIG 6 C-S-H gel layer, based on the CH cell  
Cubes = Ca, tetrahedra = Si, circles = O or OH

It seems justified to raise the question, if it is not the addition of reactive silica that causes the formation of a so-called CH-type gel structure, and consequently the increase with w/c of the apparent gel content. Since it has not been possible to prepare a stable and otherwise undisturbed cement paste without the addition of some kind of thickening agent, preferably high-surface silica gel, with a capacity of taking up water to reach paste consistence amounting to 10 to 15 times its own weight, no information is available in this matter for the materials now studied. However, the matter can be illustrated by comparing the electron-optical micrographs of gel structures in ordinary cement paste and in an 80/20 mixture of cement/colloidal silica paste, water/solid 0.50, 5 days hydrated, viz. the same materials as shown in Fig 3 with respect to their CH structures. The corresponding gel structures are shown in Fig 8. There is no apparent difference in morphologic features between the pastes, in spite of the fact that one of them has an overall initial C/S ratio of less than 1.5, instead of nearly 3, as in the ordinary paste.

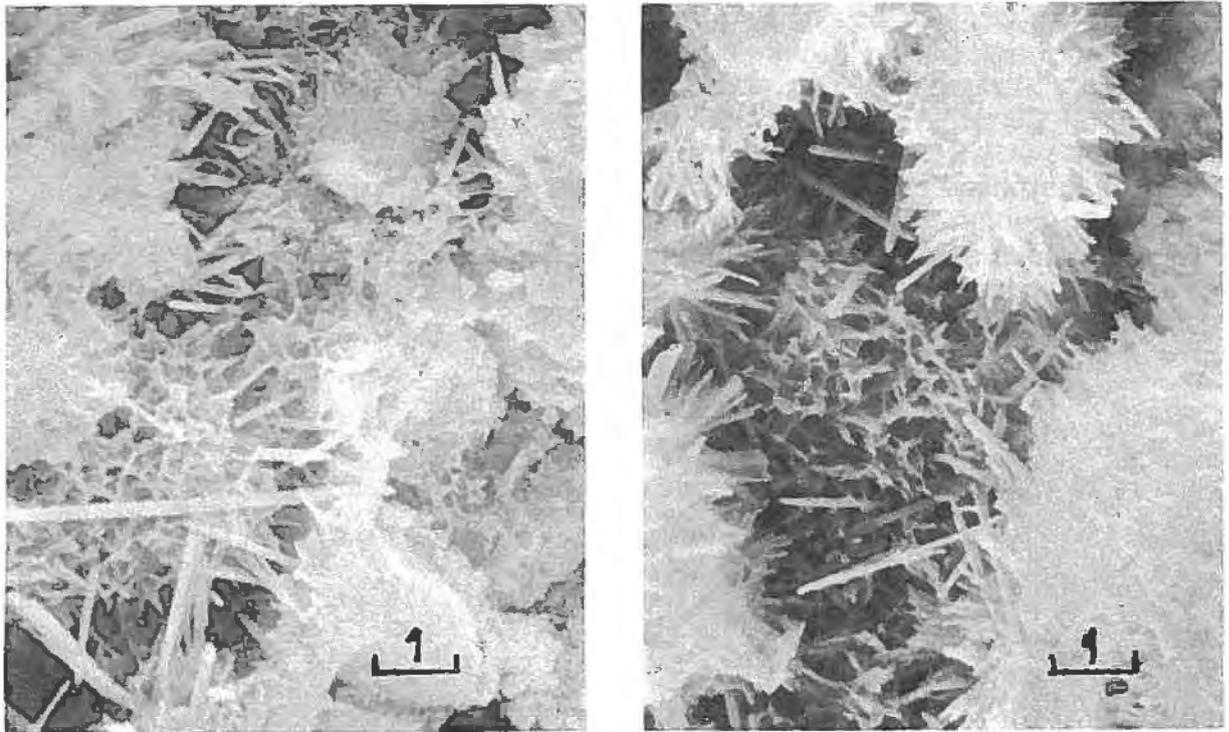


FIG 8 Morphology of two pastes, one made with white cement (left), the other with a white cement/reactive silica mixture, in proportion 80/20, both with a water/solid ratio of 0.5, and hydrated 5 days