A new model for the C-S-H phase formed during the hydration of Portland cements.

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Abstract

A model is developed to explain why the C-S-H phase that grows during the hydration of Portland Cements initially requires a high water content, much of which is lost by gentle drying. It is proposed that the rapid growth of C-S-H during the hydration of alite (C₃S) in Portland cements initially occurs by adsorption of fully hydrated aqueous calcium cations onto anhydrous anionic basal sheets of a silicate-deficient (dimeric) tobermorite-like composition. Both divalent (Ca²⁺) and univalent (CaOH⁺) solvated cations are incorporated to balance the negative charge of the basal sheet, leading to significant structural disorder, explaining the poorly-crystalline nature of the C-S-H formed. Some of the solvation water is lost irreversibly on first drying due to the formation of Si-O-Ca-O-Si bridges, explaining irreversible shrinkage. The initially-formed C-S-H is metastable relative to a form with longer silicate chains, towards which it may slowly evolve with separation of water and CH.

Keywords: C-S-H, cement hydration, drying shrinkage, physical properties

1. Introduction

Portland cement is currently the most important manufactured material on Earth, at around 4 billion tonnes per year. It is the major chemically-active ingredient in concrete, and is thus essential for construction worldwide. But, even though Portland cements have been used for almost two centuries, and chemically-similar calcium silicate-based cements had been used for millennia before that, some aspects of their behaviour remain surprisingly poorly understood. It is well known that such cements harden principally by “hydration” - reaction with water to form hydrated mineral phases that bind together the other (usually less expensive) ingredients of concrete, i.e. mineral fillers and mineral “aggregates” of varying sizes, ranging from powders tens of microns in diameter up to large stones, which fill most of the volume. It is also well known that the key hydrated phase formed by reaction of Portland cement and water is a poorly-crystalline solid of somewhat variable composition, known simply as “C-S-H” to signify that its main chemical components are CaO, SiO₂ and H₂O (C, S and H, respectively, in conventional cement chemist’s oxide notation.) Understanding the fundamental nature of C-S-H is critical to understanding most aspects of the performance of concrete, since C-S-H plays such a dominant role in determining the mechanical, physical and chemical properties of concrete. But both the mechanism of formation and the structure of this C-S-H remain rather poorly understood at the atomic-to meso-scale. In this paper, we propose a simple chemical model to resolve some of these issues. Many aspects of this new model are still very speculative, but we present a significant amount of circumstantial evidence which appears to support it, and we hope that this will encourage other investigators to examine in more detail whether the new model provides the basis of a better understanding of their own experimental data, and whether it might also serve as the basis of an improved atomistic model for C-S-H.
2. Background

Taylor first proposed that the C-S-H formed during cement hydration could be considered to be a kind of silica-deficient solid solution between the crystalline calcium silicate hydrate phases tobermorite and jennite.[1] Richardson[2] provides a thorough review of the established structures of crystalline calcium silicate hydrates and provides a more generic model for C-S-H which is based on the full range of possible solid solutions between tobermorite, jennite and portlandite (calcium hydroxide, CH). But even the simple terms tobermorite and jennite do not refer to single phases: each terms covers two or more closely related phases with slightly different structures and water contents. It is now widely believed that the C-S-H that forms during Portland cement hydration can in many respects be considered to be a kind of “defective” tobermorite,[3] but the nature of the defects is still not well understood. What is observed is that the amorphous C-S-H that forms when Portland cements or the analogous pure basic calcium silicates, C$_3$S and C$_2$S, are hydrated under water-saturated conditions at temperatures in the normal concrete use range (0-60°C) has an average composition close to C$_{1.7}$SH$_4$; but the H/S ratio, n, is extremely difficult to determine precisely due to its sensitivity to preparation conditions. The C/S ratio of C-S-H is in general also influenced by the composition of the surrounding aqueous phase, which is usually close to saturation with respect to portlandite during cement hydration, giving a C/S close to 1.7, but which decreases as the system becomes more undersaturated relative to portlandite.[4]

Precipitated C-S-H (known as C-S-H (I)) can be produced in the laboratory by various simple chemical means, such as reaction of portlandite and reactive silica in stirred slurries, or double decomposition of solutions of sodium silicate and soluble calcium salts; but excess water is always needed. However, the way in which C-S-H is produced during cement hydration is by reaction of either of the two anhydrous calcium silicate phases found in all Portland cements, i.e. “alite” (impure tricalcium silicate, C$_3$S) and “belite” (impure dicalcium silicate, C$_2$S). The terms alite and belite are used to describe the actual phases found in commercial cements, which contain significant levels of impurities; but the equivalent pure calcium silicate phases can be synthesized in the laboratory and they both react in essentially the same way with water, regardless of the presence or absence of common impurities:

\[
\begin{align*}
\text{C}_3\text{S} & + 5.3 \text{H} \rightarrow \text{C}_{1.7}\text{SH}_4 + 1.3 \text{CH} \\
\text{C}_2\text{S} & + 4.3 \text{H} \rightarrow \text{C}_{1.7}\text{SH}_4 + 0.3 \text{CH}
\end{align*}
\]

It is observed that pure C$_3$S will not hydrate fully unless sufficient water is available to form portlandite plus a C-S-H of composition close to C$_{1.7}$SH$_4$, as shown above.[5] But C-S-H readily loses water on even gentle drying, so the observed H/S ratio in solid C-S-H preparations is always significantly lower than 4, and is very sensitive to the precise details of the drying procedure used.

The water content of C-S-H preparations is usually divided into two classes: “bound water”, i.e. water which is considered to be “chemically” bound and thus requires significant heating to remove it; and “evaporable water”, or water that is only weakly (“physically”) bound. The amount of bound water in the C-S-H usually formed in Portland cement hydration is equivalent to H/S values of 1.3-1.5 according to Jennings,[6] but the methods used to determine bound water in practice vary between different authors and thus give slightly different results. This problem is endemic to all forms of C-S-H. Richardson[7] summarizes published data on the H/S ratios of many different C-S-H(I) preparations in a graph which is repeated here for convenience as Fig. 1. Despite the large scatter in the data, probably mainly due to differences in the drying procedures used, it can clearly be seen that there is a large difference between the trend lines representing the minimum H/S values for samples dried gently and samples dried harshly. For the C/S ratio of 1.7 which we consider typical of the C-S-H formed during the hydration of pure di- and tri-calcium silicates, or of ordinary Portland cements, the lower trend line gives a H/S value of about 1.4 (i.e. for bound water,) and the higher trend line gives a value of about 2.4 for “total” water. However, many points lie well above the upper trend line, so total H/S values as high as 3 or even greater are clearly possible with very gentle drying.
Many investigators consider the “true” water content of C-S-H to be only the bound water content, and assume that the additional more weakly-bound water found in wet C-S-H is simply either superficially adsorbed or else trapped in very small pores, first called “gel pores” by Powers. [8] Powers noted that such gel pores were an inherent part of the C-S-H formed during cement hydration, but ascribed their formation to poorly-defined “random growth processes.” It is generally agreed that C-S-H is a nano- and meso-structured amorphous phase with a very high internal specific surface area. This is shown by classical gas adsorption or porosimetry techniques, which require strong pre-drying, but also by techniques such as SANS, SAXS and NMR proton relaxation spectrometry that do not require any pre-drying. However, the actual specific surface area determined depends strongly on the method used. Because of this, a full description of the hydration states of C-S-H, and the estimation of its specific surface area, pore size distribution, and density, is a very complex subject about which much has been written, the most recent detailed summary being that of Jennings. [9]

It is well-established that reactions (1) and (2) occur via dissolution-precipitation processes which, for much of the reaction, appear to be kinetically controlled by the growth of the product phases, primarily the C-S-H. [10][11] Since crystalline portlandite is the only other hydration product, and since portlandite growth is not usually strongly hindered in these pure systems, the aqueous phase from which the C-S-H grows is usually only slightly above saturation with respect to portlandite. Thus, the C-S-H that forms in both of the above reactions is chemically very similar, although its microstructure may appear subtly different from one case to another. The equilibrium CaO-SiO₂ phase diagram for the C-S-H system at ambient temperatures and pressures is reasonably well established under water-saturated conditions. But it suffers from a great deal of complexity which appears to be due to the existence of many subtly different forms of C-S-H, implying that C-S-H stability must be influenced by its nano- or meso-structure, which in turn depends on the way it is produced. [12] However, there is no model which clearly explains why so much “gel water” consistently gets incorporated into the C-S-H nanostructure during cement hydration.

Currently, the most widely accepted model for the structure of C-S-H, intended to explain its density, specific surface area, porosity and water content, is that of Jennings. [9] This model is based on a colloidal microstructure composed of nanometric particles of a tobermorite-like material arranged into structured agglomerates with various different meso-structures which can, according to Jennings, account for the different densities, porosities and specific surface areas observed in practice. However, while this model can explain many of the physical properties of hardened C-S-H, it appears to be inconsistent with the growth mechanism of C-S-H during cement hydration. Gartner [13] pointed out that any theory purporting to explain the structure of the C-S-H produced in cement hydration must also be compatible with the observed growth kinetics of the phase; and most current evidence points towards the growth of C-S-H being, at least at early ages, the rate-limiting step in the hydration of C₃S, and also of Portland cements. But the type of agglomerated nano-particulate meso-structure proposed in the Jennings model seems incompatible with a normal steady growth process. It seems much closer to the type of structure that one would expect for a precipitate formed from a highly supersaturated solution, e.g. as in well-known processes for the precipitation of amorphous silicas by acidification of alkali silicate solutions. But the C-S-H formed in cement hydration grows steadily from a solution that is apparently not extremely supersaturated, and its growth rate initially appears to be roughly proportional to either the volume or the surface area of the C-S-H produced, which accounts well for the observed acceleratory period in alite hydration. [10][11] The growth of C-S-H in cement hydration thus seems to behave more like a normal crystal growth process rather than a rapid precipitation, but nevertheless the C-S-H that forms appears to be very poorly crystalline. It was to reconcile these opposing factors that Gartner [13] concluded that C-S-H grows essentially as two-dimensional crystalline elements (e.g. sheets or ribbons) but with inherent stacking defects that cause it to appear poorly-crystalline by X-ray diffraction, despite the high degree of 2-D order within the planes of the calcium oxide layers. This suggests a final meso-structure similar to that originally proposed by Feldman and Sereda. [14] However, the nature of the C-S-H defects that give rise to this type of meso-structure remains unclear. Gartner hypothesized that the poor crystallinity might be caused by local sheet curvature due to missing silicate
groups, since the conditions under which C-S-H forms in cement hydration typically involve very low aqueous silica concentrations; but this hypothesis has never been verified experimentally. More recently it has been shown by mathematical modelling\[15\] that the type of defective C-S-H growth mechanism with a branching step proposed by Gartner is compatible with both the kinetics of C\textsubscript{3}S (and Portland cement) hydration and the resulting full three-dimensional paste meso-structure as determined by non-destructive scattering techniques.

Despite some recent progress in understanding the mechanism of cement hydration,\[11\] and also in understanding the structure of the C-S-H formed,\[3\] the origin and nature of the gel water in C-S-H still remains something of a mystery. The Jennings model treats it as water present in the pores between agglomerated nanoparticles, whereas the older Feldman-Sereda model,\[14\] which is closer to the models envisaged by Gartner\[13\] and Etzold,\[15\] treats it as water in very small pores trapped between layers of tobermorite-like sheets. Both of these very different sets of models consider that a certain minimal amount of non-evaporable water is present as strongly bound "interlayer water" between the basic tobermorite-like sheets, and that this interlayer water is distinct from the water which is apparently less strongly bound in the gel pores. Moreover, recent attempts at atomistic modelling of C-S-H by molecular dynamics approaches,\[16\][17], predict H/S ratios in the range 1.4-2.3, so such models also do not yet seem capable of explaining the origins of "gel water."

Recent studies of hydrated cement and alite pastes by sophisticated proton magnetization relaxation spectrometry techniques appear to show two distinct types of water at the nanoscale in well-hydrated saturated pastes, tentatively identified as "gel water" and "interlayer water," the former having relaxation times about three times longer than the latter, suggesting that it is present in larger (but still nanometric) pores \[18\]. These observations appear compatible with both the Jennings and Feldman-Sereda models. However, using this technique, the ratio between the amounts of "gel water" and "interlayer water" in hydrated cement pastes appears to decrease significantly with the degree of hydration, ranging from a factor of about 2 at early ages down to a factor of closer to 1 at high degrees of hydration.\[18\] This observation is specific to the proton relaxometry method because no other method purports to be capable of measuring gel water as a function of degree of hydration.

Thus, a fundamental problem in cement chemistry is to find an explanation for why formation of high C/S C-S-H during cement hydration always seems to require a very high water content, while much of this water is apparently only very weakly bound to the structure, either by surface adsorption or else "trapped" in very small "gel" pores that are nevertheless an inherent structural feature. And why does the amount of this weakly-bound water appear to increase roughly linearly with increasing C/S ratio - is there some very specific structural relationship between the C/S and H/S ratios in C-S-H? In the rest of this paper a new model is proposed and developed to try and resolve these questions. This leads to an explanation of how the water behaves when the C-S-H is subject to drying or aging, which in turn can give us a better understanding of many of the physical and mechanical phenomena critical to the performance of concrete.

3. Proposed Model

We propose that most of the above observations can be explained by the following set of hypotheses:

(i) High C/S C-S-H grows most rapidly (in a metastable form) with basal sheets of tobermorite-like structure but with the silicate ions initially mainly present as dimers, as first proposed by Taylor\[1\] and shown diagrammatically in Fig. 9. of Ref. [2], reproduced here as Fig. 2.

(ii) The basal tobermorite sheet of this C-S-H is essentially anhydrous, with a net negative charge localized on its silicate groups which must be balanced either by protons or by metal cations, either in the interlayer space (in the case of multiple layers) or else simply adsorbed on the external surfaces. These cations may be more or less hydrated and more or less covalently
bound to the silicate groups on the sheets. Protons are generally thought of in this context as being fully covalently bound (i.e. as silanol groups,) but with increasing pH these groups ionize and the protons are then replaced by the available dissolved metal cations, which, in the pure C-S-H system, can only be calcium ions. Such ions can form bonds of intermediate electrostatic/covalent character with the -SiO\(^2-\) groups.

(iii) The net negative charge per repeating basal unit (in the simplest case, equivalent to one silicate dimer) of the main layer increases with the ionization of the silanol protons as shown in Fig. 2. Due to the high pH of hydrating alite or belite, the relevant case here is that of complete ionization, giving two anionic groups per silicate dimer, as shown in Fig. 2(a).

(iv) As a starting point, given that C-S-H is usually grown from aqueous solutions of low-to-moderate ionic strength, we assume that the calcium cations that balance the net negative basal charge are initially incorporated into the growing solid in a state that is fully hydrated. The actual number, \(m\), of water oxygens in the inner hydration shell of aqueous calcium ions, \((\text{Ca}(	ext{H}_2\text{O})_m)^{2+}\), ranges from as high as 10 to as low as 6, depending on the activity of water and presence of other ions, etc.[19][20] In crystalline calcium silicate hydrates, the oxygen-coordination number of calcium atoms can range from 6 to 8, although most cases it falls in the range 6-7.[7] In this work we make the simplistic assumptions that: (a) the lowest energy state for the charge-balancing calcium ions will have \(m = 6\), i.e. the most stable inner ligand shell contains only six oxygens closely packed around calcium ion; and (b) the charge-balancing calcium ions are initially incorporated with a higher coordination number, i.e. with at least six water or OH ligands, plus one \(\equiv\text{Si}-\text{O}\) ligand attaching the ion to the basal sheet.

(v) In the pH range typical of saturated and supersaturated portlandite solutions a significant fraction of the calcium cations in solution are present as CaOH\(^+\) ion pairs,[20] which we will represent as \([\text{Ca}(\text{OH})(\text{H}_2\text{O})_3]^{2+}\) ions. We also assume that the CaOH\(^+\)/Ca\(^{2+}\) ratio of the cations incorporated into the growing hydrate is determined by that in the aqueous phase, which increases with increasing pH, (see Fig. 3), although the two ratios need not be identical – i.e. there may be some selectivity in the incorporation of these ions into the hydrates.

Combining the above set of assumptions and starting with the simplest basic repeating unit of C-S-H as one side of the basic calcium oxide sheet with a single bonded silicate dimer (see Fig. 2) gives the chemical formula \([\text{Ca}_2\text{Si}_2\text{O}_7]^2-\) if one treats it as being fully ionized. In the pure system at the high pH typical of alite hydration these negative charges can only be balanced by \([\text{Ca}_(\text{H}_2\text{O})_3]^{2+}\) or \([\text{Ca}(\text{OH})(\text{H}_2\text{O})_3]^{2+}\) ions. (Note: In a subsequent paper we will treat the more general case including low C/S C-S-H, in which case silanol groups must also be considered.)[21] We assume that the low C/S end composition of this series, \((\text{Ca}_2\text{Si}_2\text{O}_7)^2+\text{[Ca}(\text{H}_2\text{O})_3]^{2+}\) (i.e. \(\text{C}_3\text{S}-\text{H}_6\)) is at least stable enough to be capable of forming solid solutions. We then further assume that, as the aqueous CaOH\(^+\)/Ca\(^{2+}\) ratio increases even further, single \([\text{Ca}(\text{H}_2\text{O})_3]^{2+}\) ions can be replaced by pairs of \([\text{Ca}(	ext{OH})(\text{H}_2\text{O})_3]^+\) ions. We can thus write the hypothetical high-Ca end member of this solid solution range as \((\text{Ca}_2\text{Si}_2\text{O}_7)^2-\cdot2(\text{Ca}(\text{OH})(\text{H}_2\text{O})_3]^+)\), or \(\text{C}_3\text{S}_2\text{H}_11\). The composition of the “high C/S, high H/S solid solution” can thus be written as: \((1-\gamma)(\text{C}_3\text{S}_2\text{H}_6) + \gamma(\text{C}_3\text{S}_2\text{H}_{11})\). If, for example, we choose \(\gamma = 0.4\), this simplifies to \(\text{C}_3\text{S}_2\text{H}_8\), i.e. \(\text{C}_3\text{H}_7\text{SH}_4\), the formula often used in above to describe the saturated C-S-H formed during C3S or C2S hydration. It thus appears that our high C/S, high H/S solid solution formula with \(\gamma = 0.4\) comes very close to representing “normal” cement C-S-H, which forms at the pH of slightly supersaturated portlandite solutions. A simple 2D representation of on basal sheet of the composition with \(\gamma = 0.33\), which has equal numbers of \([\text{Ca}(	ext{H}_2\text{O})_3]^{2+}\) and \([\text{Ca}(\text{OH})(\text{H}_2\text{O})_3]^+\) ions, is shown in Fig. 4 as an illustration of the concept.

Our solid solution formula is initially restricted to C-S-H with C/S ratios between 1.5 and 2. But the mean chain length (MCL) of the silicate ions in hydrated C3S pastes is usually found to be greater than 2, even
at quite early ages.[3] Increasing MCL decreases the C/S ratio[1] of the C-S-H, which could allow the model to be extended to lower C/S ratios without changing its basic principles.

The aqueous phase composition that is most pertinent to cement hydration is the invariant point at which C-S-H coexists with portlandite. Now, it is well established that the Si content of this aqueous phase is about three orders of magnitude lower than its Ca content,[12] so, for the purpose of establishing the aqueous CaOH+/Ca²⁺ ratio, we can ignore Si and simply use a solution in equilibrium with portlandite as a model. The compositions of portlandite saturated solutions at various levels of dissolved alkali (NaOH) were calculated from the data given in[22] and are summarized here in Fig. 3. The ratio is very sensitive to pH, increasing from 0.2 in the pure alkali-free system up to above 1 at alkali metal concentrations above about 0.2M, conditions which can often be found in concretes made from cements with high soluble alkali contents. But in the alkali-free system the only way in which the pH can be increased is by increasing the degree of portlandite supersaturation.

Now, the CaOH+/Ca²⁺ ratio in C-S-H growing from such a liquid phase will not necessarily be identical to the ratio in the solution; it will presumably also depend on the relative chemical affinity of both of these aqueous calcium ions for the growing phase. The CaOH+/Ca²⁺ ratio in our high C/S C-S-H solid solution formula is given by the expression \(2\gamma/(1-\gamma)\), which, for \(\gamma=0.4\), has the value 4/3, which is almost seven times the ratio expected in pure saturated limewater at 20°C. If C-S-H with \(\gamma<0.4\) does represent the typical product formed during the hydration of pure C₃S in the absence of any soluble alkalis, this implies that the growing C-S-H has a considerably greater tendency for the incorporation of \([\text{Ca(OH)}(\text{H}_2\text{O})\gamma]^+\) ions than for the incorporation of \([\text{Ca(H}_2\text{O})_5]^+\) ions. This in turn implies that the bonds initially formed to such ions are not simply electrostatic but instead have significant “covalent” character. For comparison, it is reported that C-S-H grown from NaOH-rich portlandite-saturated solutions does not appear to retain much sodium - any trapped sodium ions are readily leached from it.[3] Since fully hydrated sodium ions would be expected to have similar dimensions and charge to \([\text{Ca(OH)}(\text{H}_2\text{O})\gamma]^+\) ions,[23] they would, on purely electrostatic considerations, be expected to be taken up to a similar extent. So the preferential bonding of calcium ions in growing C-S-H is either due to their divalent charge, in which case our assumption of CaOH⁺ uptake must be wrong; or else due to stronger inner-shell ligand bonding to aqueous CaOH⁺ ions than is possible with aqueous Na⁺ ions. The latter interpretation is supported by other observations that suggest that aqueous calcium ions can take up to 10 water oxygens in their inner solvation shell, whereas sodium usually can take only 6.[24] The coordination number and solvation behaviour of hydrated ions is not easy to model with current computationally-feasible approaches such as molecular dynamics. We hope that improved atomistic models and greater computational power will soon allow modellers explain both the variable C/S ratio and the initially very high water-content of C-S-H when it forms under saturated conditions.

Our new model of C-S-H growth can explain why cement hydration requires more water than is traditionally assumed to be part of the chemical structure of C-S-H. Our model implies that C-S-H can grow very rapidly by the incorporation of highly-hydrated calcium cations from the solution, although this initial product is clearly metastable and may rearrange quite quickly into a more stable form. Thus, no complicated explanations of the type given by Powers[8] are required to explain the incorporation of gel water. In our model the C-S-H formed in cement hydration initially grows as a solid hydrate phase of composition close to C₁.₇SH₄. At initial water/cement ratios below that required for complete hydration using that formula, hydration of cement pastes stops even when stored under excess water as soon as all internal water-filled space is filled with hydrates, even though extra water is available from outside, because C₃S or C₂S hydration is an inherently non-expansive process under usual hydration conditions. As for why C₃S or C₂S hydration is inherently non-expansive, we suggest, following Gartner’s explanation of expansive hydration processes,[25] that this is because the hydrates formed bond directly both to each other and to the anhydrous precursor phases (C₃S or C₂S) in water and thus present no repulsive interfaces where significant expansive growth could occur.
Our new model also explains the nature of at least one class of “defects” that allows C-S-H to have a wide range of C/S ratios. In the case covered here, i.e. C-S-H with C/S ratios ranging from 1.5 to 2, the replacement of one [Ca(H$_2$O)$_3$]$^{2+}$ ion by two [Ca(OH)(H$_2$O)$_3$]$^{+}$ ions can be considered to be such a defect. Note that this explanation is also consistent with the proposal of Nonat and coworkers that the C-S-H in this composition range is a distinct phase, referred to as “γ-C-S-H.”[26] If this ionic replacement occurs in a somewhat random way, it can also explain why the C-S-H that grows in these lime-rich hydrating systems is so poorly crystalline. The replacement of one [Ca(H$_2$O)$_3$]$^{2+}$ ion by two [Ca(OH)(H$_2$O)$_3$]$^{+}$ ions clearly implies significant structural changes, because the two [Ca(OH)(H$_2$O)$_3$]$^{+}$ ions will occupy much more space than a single [Ca(H$_2$O)$_3$]$^{2+}$ ion. This will tend to push apart the basal sheets and presumably reduce the strength of the bond between them, increasing the likelihood that the C-S-H will tend to grow mainly as single sheets and making a high degree of stacking order in the c-direction (perpendicular to the basal sheet) initially less likely, resulting in loss of crystalline order in that direction. For that reason, many of the charge-balancing calcium ions may, at least initially, be bonded to the outsides of isolated sheets, rather than between sheets. We thus have a model in which the C-S-H initially grows mainly as single sheets with “adsorbed” cations, which can later form primary agglomerates, presumably mainly by stacking in the c-direction without much crystalline order.

The model also has implications in terms of the presence of CaOH bonds in the structure. The extreme high C/S member of our proposed high C/S C-S-H solid solution series, C$_8$S$_2$H$_{11}$, contains 50% of its total calcium as CaOH$^+$ ions, so, for C/S = 1.7 (i.e. γ=0.4) we would expect a (CaOH+)//(total Ca) ratio of 0.4*50%, i.e. 20%. This is reasonably close to the value of 23% of Ca in CaOH groups determined by Thomas et al. by inelastic neutron scattering.[27] To explain such a high CaOH content, Thomas et al. assumed that the C-S-H either contained some portlandite in solid solution, or else had a partially jennite-like structure, whereas we have deliberately avoided either of these assumptions here so as to keep our model very simple. But we must allow for the possibility that the initial structure given by our model may be very short-lived. If one does assume a jennite-like structure, it is far easier to obtain C/S ratios >> 1.5 even with MCL values well above 2, and even without any CaOH$^+$ interlayer cations. But one then must also assume a significantly higher degree of inner shell water coordination than 6 for the Ca$^{2+}$ ions incorporated into the C-S-H to explain the observed high initial H/S ratios. However, the basic concepts of our new model could otherwise remain very similar under a jennite-like structural assumption. These alternative possibilities will be treated in a subsequent paper dealing with the full range of possible C-S-H compositions.[21]


The methods which have commonly been used to try and understand the nature of the water in C-S-H include water desorption, mercury intrusion porosimetry (MIP) and gas adsorption (e.g. BET), all of which require strong drying, which unfortunately destroys the original structure of the C-S-H. Water desorption can be done gently over a range of temperatures by controlling the relative humidity; or more strongly by heating (e.g. thermogravimetry). The traditional definitions of gel water and interlayer water are somewhat arbitrary but relate to the concept that gel water is trapped in nanometric pores, while interlayer water is more strongly bonded between the basal sheets. However, in our new model, essentially all of the structural water in freshly-precipitated wet C-S-H is actually present in the inner hydration shell of the charge-balancing calcium ions, which may be either in interlayer (“internal”) positions or else in equivalent “external” positions on the outside of sheets. When the C-S-H is dried, however, these hydrated calcium ions will almost certainly tend to lose their water ligand molecules in discrete steps. For example, we might assume that, during C-S-H growth, an aqueous [Ca(OH)(H$_2$O)$_3$]$^+$ ion may initially bond to the C-S-H basal sheet via a single ≡SiO-Ca ligand bond, increasing its inner shell oxide coordination number by 1 unit (e.g. from 6 to 7). This type of inner coordination shell ion-pair bonding might suffice to explain the initial rapid precipitation of C-S-H with a high H/S ratio. But as soon as we start to dry this C-S-H, there will be a tendency for the calcium ions to lose some of their coordinating water molecules. Perhaps the first step might be the loss of only one water molecule, which
would then put the calcium ion into an (octahedral) six-coordinated state, a state found in many common hydrated calcium salts. Beyond that, one can imagine that stronger drying will result in the loss of more water, forcing the calcium ions into more coordination with the oxygens on nearby ≡Si-O⁻ or ≡Si-O-Si⁻ groups. In this case, the symmetry of the coordination shell around each calcium will tend to decrease, while the strength of the bonding of the remaining water ligands will presumably increase.

We can thus look at the initial desorption path of water from wet C-S-H as a being series of successive reorganizations of the local hydration shells around the charge-balancing calcium cations, rather than loss of water from nanometric gel pores. Such nanometric pores may well form as a consequence of the initial dehydration process, but need not necessarily have been present in the fresh wet C-S-H. This can explain why the specific surface area of C-S-H measured by gas sorption (via the BET equation) appears to be so much higher when water vapour is used than when an inert non-polar gas (e.g. N₂) is used.[28] According to our model, the water vapour sorption process cannot be described by the BET theory, since it depends mainly on changes in the hydration states of the charge-balancing calcium cations which are situated either on the outside or in the inside of poorly-stacked C-S-H sheets. Clearly, the surface area accessible to non-polar molecules such as N₂ is unlikely to extend to the inner hydration shell of calcium cations, especially if they are in interlayer positions.

Maruyama et al.[29] carefully measured the relative-humidity (RH) dependence of the mass and length changes of well-hydrated cement pastes (HCP) made from a white cement with a relatively high calcium silicate content, for which the mass and length changes can mainly be ascribed to changes in the C-S-H. Their data show that the well-known irreversible shrinkage which occurs during the first drying of water-saturated HCP, and which is probably responsible for most of the physical damage to real concretes caused by drying under realistic exposure conditions, is restricted to the RH range above about 50%. Low-temperature DSC data for the same specimens after long term storage at various relative humidities followed by rapid rewetting just prior to the measurement are shown in Fig. 5. There is a major change in behaviour somewhere between conditioning at 60% RH and conditioning at 70%RH. Somewhere in this RH range lies the point below which some of the non-freezable water is permanently lost, i.e. is not readily regained on rewetting – so one can say that it appears to be lost irreversibly. But even above 70% RH there are apparently irreversible changes in the relative ease of freezing the rest of the water. For example, samples always kept water-saturated contain considerably more water that is difficult to freeze (i.e. freezes below -18°C) than samples stored at 80% RH or below.

The observation of irreversible drying shrinkage at high RH has always been rather hard to explain. Conventional wisdom assumes that it is caused by “capillary forces,” which could explain the agglomeration of small particles; but this explanation does not explain its irreversibility. However, our new model explains it in terms of the oxygen bonding in the inner coordination shell of the charge-balancing calcium ions. We assume that the C-S-H which grows during cement hydration under water-saturated conditions initially contains “fully-hydrated” calcium cations bound to the growing C-S-H sheets by a combination of electrostatic forces and weak coordination bonding in such a way that the adsorbed calcium cation initially has more than 6 inner-shell oxygen ligands. This initial state has a relatively high water content but also has the possibility of stabilization by reduction of the number of inner shell oxygen ligands. The most stable coordination number is probably six, which represents the type of octahedral coordination of the interlayer calcium cations of the type observed in the crystal structure of 14Å tobermorite.[30] Now, in the crystalline 14Å tobermorite structure each interlayer Ca²⁺ ion is coordinated to four water oxygens and two silicate oxygens. But it is not necessary to go this far in a single step. We suggest that the calcium cations will probably dehydrate in a series of steps. So, a [Ca(H₂O)₆]²⁺ ion bound to a bridging site between two silicate dimers on the basal sheet might go from an initial 8-coordinated state down to 7-coordinated state and then to a 6-coordinated state by successive loss of two water molecules:

\[
\text{≡SiO}^- + [\text{Ca(H}_2\text{O)}_6]^{2+} \rightarrow [\text{≡SiO-Ca(H}_2\text{O)}_5]^{+} + \text{H}_2\text{O} \quad (3a)
\]

\[
[\text{≡SiO-Ca(H}_2\text{O)}_5]^{+} + \text{OSi≡} \rightarrow \text{≡SiO-Ca(H}_2\text{O)}_4\text{OSi≡} + \text{H}_2\text{O} \quad (3b)
\]
The result of these two successive steps is the formation of what is likely to be a more stable arrangement of the divalent calcium ion, coordinated to four water ligands and two ≡SiO\(^2\)-groups, just as it is in 14Å tobermorite. But, unlike in tobermorite, the two most likely ≡SiO\(^2\)-groups for coordinating a charge-balancing Ca\(^{2+}\) ion in our initially dimeric high C/S C-S-H are probably the ≡SiO\(^2\)-groups on adjacent dimers, with the Ca\(^{2+}\) ion thereby filling the position left vacant by the absence of a bridging silicate ion, as is shown in Fig. 2a. Due to the strong coordination of such a “bridging” calcium ion, it seems likely that such a two-step dehydration process should be effectively irreversible, leading to an equivalent irreversible shrinkage via a reduction in the spacing between closely stacked C-S-H basal sheets, even if the sheets are not stacked in any very specific crystalline orientation.

For a [Ca(OH)(H\(_2\)O)\(_3\)]\(^+\) ion coordinated with an anionic ≡SiO\(^2\)-group on a basal sheet the first dehydration might be from an initial 7-coordinated state down to 6-coordination as follows:

\[≡SiO^- + [Ca(OH)(H_2O)_3]^+ \rightarrow ≡SiO-Ca(OH)(H_2O)_4 + H_2O \] (4)

After reaction (4), per our model, for C-S-H with C/S > 1.5 there should be no free anionic silicate groups remaining to further react with this attached hydroxylated calcium ion because they are all already occupied by other calcium ions. Thus, the only way that it can undergo further stabilization, if it happens to lie between two basal sheets juxtaposed closely enough, is by coordinating with a non-anionic ≡Si-O-Si≡ oxygen on another other basal sheet close enough to it, thus forming a bridge between the two sheets. We can write this reaction as follows:

\[≡SiO-Ca(OH)(H_2O)_4 + ≡Si-O-Si≡ \rightarrow ≡SiO-Ca(OH)(H_2O)_3-O(Si≡)_2 + H_2O \] (5)

Thus, if we assume that the most stable first dehydration state of all charge-balancing calcium cations is six, with two of the bonds being to silicate oxygens, then first stable dehydration states of these calcium ions will be those shown on the right hand sides of equations (3b) and (5). We can then insert these values into the equation for the γ-C-S-H solid solution range, giving the “first stable dehydrated solid solution state” of this γ-C-S-H as \{(1-γ)(C\(_S\)S\(_H\)) + γ(C\(_S\)S\(_H\))\}. The H/S ratio of this hypothetical dehydration state of C-S-H goes from H/S = 2 for γ = 0 (C/S = 1.5) up to H/S = 3.5 for γ = 1, with a value of 2.6 at γ = 0.4 (for which C/S = 1.7). This falls within the range of experimental data for gently-dried C-S-H summarized by Richardson[7] and shown in Fig. 1., where the relevant points and trend line for our “first stable dehydrated solid solution state” model have been added to the graph. Once this “first stable dehydrated solid solution state” has been attained, it seems unlikely that further dehydration can lead to the creation of more Si-O-Ca bonds of equivalent strength to those formed in the first set of dehydration reactions, because of geometric constraints. Thus, further dehydration is likely to result simply in loss of further calcium ion ligand water while the calcium ions themselves are constrained within a rigid cage determined by the crosslinks formed in the first stable dehydrated solid solution state.

Subsequent loss of one more water molecule per calcium ion will give the following “second dehydrated solid solution state”: \{(1-γ)(C\(_S\)S\(_H\)) + γ(C\(_S\)S\(_H\))\}, for which the water content ranges from H/S = 1.5 for γ = 0 up to H/S = 2.5 for γ = 1, with a value of 1.9 at γ = 0.4 (C/S = 1.7). Loss of yet another water molecule per calcium ion produces a “third dehydrated solid solution state”: \{(1-γ)(C\(_S\)S\(_H\)) + γ(C\(_S\)S\(_H\))\}, for which the water content ranges from H/S = 1 for γ = 0 up to H/S = 1.5 for γ = 1, with a value of 1.2 at γ = 0.4 (C/S = 1.7). This latter state lies reasonably close to the trend line for the “bound water content” typically observed after strong drying, (Fig. 1,) and gives the same slope. The calcium ions in these strongly dehydrated states would be expected to be present in more highly asymmetric coordination shell environments than those in the more highly hydrated states. The four proposed principal hydration states of the high C/S solid solution are summarized in Table 1.

This type of calcium ion bridging between silicate oxygens ligand binding provides a very plausible mechanism for effectively irreversible cross-linking between nearby basal sheets as they are forced into close proximity, e.g. by surface forces during the first drying process. It does not require that the two sheets which become cross-linked be in a perfect crystalline orientation with respect to each other. They must simply be close enough at the point where a bridging calcium ion is available. Lack of perfect
orientation will also limit the number of sites where such calcium bridges can form, and will give the 
resulting calcium-cross-linked structure the observed low degree of crystallinity. This bridging process 
does not necessarily require drying – it might occur spontaneously as sheets approach closely because 
of space-filling due to only hydration. But is that case it seems likely that the water released by reactions 
3-5 would not be able to escape easily and might well remained trapped in nanometric pores between 
layered sheets. This provides a possible explanation of why the “gel water” appears to be present in 
such trapped pores by proton NMR relaxation measurements (see later).

This model seems to fit the observations of Maruyama et al.[28][29] regarding the way that C-S-H 
behaves during first drying. Once the initial cross-linked meso-structure has formed, apparently at RH 
values well above 50%, the structure is effectively “locked in.” This produces “packets” of individual 
basal sheets which define a relatively permanent 3-D nanostructure which is retained in all further drying 
and wetting cycles. The irreversible shrinkage associated with this process occurs mainly by the 
permanent reduction of the interlayer distances within the assembled packet of basal sheets, but this 
also creates larger spaces, e.g. “interhydrate” pores, between the assembled packets of sheets in the 
boundary zones where they do not line up in parallel. Thus, interhydrate pores are, to a large extent, 
created during the irreversible first drying. The packets of sheets are also presumably bonded to each 
other by the same type of calcium-mediated bonds that hold the sheets together inside the packets, but 
the number of such external bonds per packet is relatively small compared to the number within the 
packets. This picture is essentially very similar to that shown in Fig. 15 of Ref.[29]. The model also fits 
the observation of Setzer [31] that the length-change isotherms of the first desorption and the 
subsequent re-wetting and re-drying processes lie on the same curve when the strain data are plotted 
as a function of evaporable water content. This is essentially because all the bulk volume changes, both 
reversible and irreversible parts, are directly related to changes in the amount of water around the 
hydrated charge-balancing calcium cations. The only difference is that the irreversible part occurs when 
two water ligands out of 6 total ligands around a calcium ion are replaced by ≡Si-O ligands, a step that 
is presumably thermodynamically favoured even under wet conditions but can occur more rapidly with 
the help of capillary forces during first drying. The number of new ≡Si-O-Ca-O-Si≡ bridges created 
during first drying is not necessarily very large, as many may have already been formed prior to drying, 
with the water left over from their formation remaining trapped in nanometric gel pores.

After the irreversible shrinkage, further drying (see Table 1) simply removes more hydrate from water 
around the charge-balancing calcium ions, with significant deformation of the structure in the form of 
further reductions in interlayer spacing. But most of this further drying and the associated deformation 
is essentially reversible on rewetting, because it is simply a loss of coordination water from calcium ions 
held in position in a “cage” already formed by oxygen atoms attached to silicate ions on the basal sheets. 
Once this cage-like meso-structure has been locked in by the formation of calcium bridges during the 
first drying, it is not easily changed simply by further cycles of wetting and drying unless the drying is so 
severe that other major structural changes ensue.

Another related issue is the large reversible hysteresis that is also observed during the re-wetting and 
re-drying of C-S-H after the first drying. This hysteresis is especially noticeable in water adsorption 
isotherms carried out rapidly (e.g. by means of a water vapour sorption analyser).[29] To explain this 
effect we assume that the water bonded to interlayer calcium ions cannot escape rapidly during drying, 
nor re-enter rapidly during rewetting, because it has to diffuse out of the space between two stacked 
basal sheets within a “packet.” This sets a kinetic limitation to reaching equilibrium if the experiment is 
done rapidly. It can also explain why the hysteresis appears to increase with the rate of drying. During 
the HCP drying branch there is a noticeable “kink” or “step-down” from about 40% RH down to about 
33%RH which appears to signify the lower RH end of the zone in which the kinetics of loss of water from 
between sheets dominates the drying process. The same type of kink is also observed for C-S-H 
preparations of lower C/S ratios, but not for C/S below 1.1, further implying that it is related to charge-
balancing calcium ions.[29] Below this kink the isotherm seems to show far less hysteresis. The kink is 
not observed (or at least, not in the same place) in the adsorption branch, but in this regard it is worth
noting that the sorption isotherm experiments of Maruyama et al. were always conducted with the adsorption branch first, after a short period of strong dehydation of the fully hydrated and carefully RH-conditioned HCP at 105°C under a significant vacuum, which one would have thought, should have served to stabilize all of the possible interlayer and inter-agglomerate bridging sites with essentially irreversible cross links. The near complete loss of hydrate water from calcium ions both inside and outside the agglomerated C-S-H sheets due to this strong dehydrated will leave all the remaining calcium ions (either external or internal) in a very water-deficient state without any suitable (=Si-O-) groups nearby that can stabilize them against rehydration. They will thus be able to pick up water very quickly; and, at the lower RH end of the isotherm, water should be able to re-enter the spaces between sheets and diffuse towards the most strongly hydrophilic calcium ions before the edges of the sheets tend to seal themselves off at higher RH values. This should effectively displace the “kink” in the re-adsorption isotherm to much higher RH values, which is what is observed.

However, our model cannot yet explain all of the other long-term moisture-history-sensitive changes that have been observed, such as the fact that the width of the drying hysteresis loop is smallest for samples dried for long periods at intermediate RH values (40-50%) but larger for samples dried for long periods either at higher or at lower RH.[28] Maruyama suggests that the main difference between long-term drying and short-term drying is that long-term drying allows sufficient time for additional chemical rearrangements to occur in the C-S-H. This is certainly a strong possibility. We have already suggested that silicate polymerization and loss of CaOH⁺ groups are likely to be thermodynamically favourable processes, both of which should lead to further loss of charge-balancing calcium ions and their associated water. Maruyama et al.[28] also observed that silicate mean chain length (and also the Al/Si ratio) of C-S-H in low-Al HCP samples increased more after drying for longer periods at lower RH values. This does at least give a potential explanation for why HCP samples stored for long periods at low RH do seem to be different from those stored at higher RH. Cong and Kirkpatrick[32] also showed that MCL increased and OH groups decreased more when C-S-H was heated than just dried, which can perhaps be taken as being equivalent to the effects of long term strong drying.

5. Silicate chain length

We have so far assumed that the C-S-H initially grows with only dimeric silicate groups attached to a tobermorite-like anionic basal sheet charge-balanced by fully hydrated Ca²⁺ or CaOH⁺ ions. However, this is clearly an over-simplification. It is well known that the mean silicate chain length (MCL) increases with age and with increasing curing temperature in real hydrated cement paste (HCP) specimens.[32][33][34] In laboratory-prepared C-S-H(I), MCL values of about 3 are typically observed for samples with C/S ratios above about 1.2 (note: a MCL value of 3 implies that one in four silicate bridging sites is occupied.)[7] But it is also clear that the MCL should decrease with increasing C/S ratio,[3] so it is actually quite surprising that values very close to 2 are rarely observed in laboratory-prepared C-S-H preparations. This may simply be due to difficulties in preparing pure C-S-H samples with C/S ratios of 1.5 or above in this way. But, either way, we need to understand by what mechanisms the MCL of the C-S-H in HCP might increase over time in well-hydrated cement systems. Now, we will start by ruling out the simplest explanation, which is incorporation of additional silica into the C-S-H, because this is very unlikely to occur rapidly enough in portlandite-saturated systems due to low silica availability. So we will assume that C-S-H can change its MCL without any net change in C/S ratio.[35]

For C-S-H in equilibrium with portlandite, as in hydrated cement or alite pastes, we therefore assume that the silicate-dimer form of C-S-H is metastable relative to a form of C-S-H with more highly polymerized silicate anions. In order to increase the degree of silicate polymerization without adding any more silica to the C-S-H, we need to invoke some kind of “disproportionation” process of the initially dimeric basal unit. For example, if we assume the initial C-S-H composition to be simply dimeric C₆S₇H₆,(γ=0 in our high C/S solid solution series,) possible disproportionation processes could be written as:

\[5([Ca₂Si₅O₁₀]₂\bullet[Ca(H₂O)₆]²⁻ → [2[Ca₂Si₅O₁₃(OH)]₂\bullet 3[Ca(H₂O)₆]²⁻ + 4Ca(OH)₂ + 7H₂O………………….(6a) \]

or
Note that these reactions are clearly not single step processes but rather imply multi-step processes in which some Si and Ca atoms must migrate over significant distances. The overall reactions shown here convert silicate dimers into pentamers, increasing MCL from 2 up to 5, this range (2 to 5) being that typically observed in hydrated C-S-H pastes covering the range of ages typical of actual concrete in use.[36][37] The relatively poor fit of calcium ions in bridging positions between silicate dimers might then explain why silicate polymerization, in which a silicon atom effectively replaces an interlayer calcium ion in the bridging position, is apparently favoured thermodynamically.

Note also that pentamers are shown in (6a) with a single silanol group on the bridging tetrahedron, as in 14Å-tobermorite Error! Reference source not found..[30] but this group may well ionize further at high pH (or at high aqueous C/S ratios,) as shown in (6b). Either way, this disproportionation process clearly creates a lot of excess calcium hydroxide and also reduces the total water content of the C-S-H, at least if one assumes that the H₂O-coordination number of the charge-balancing calcium ions remains at 6. The Ca(OH)₂ produced by such reaction may initially remain effectively “adsorbed” or “dissolved” in the C-S-H, e.g. as sections of basal sheets of portlandite or jennite-like structure dispersed between the majority of tobermorite-like sheets of the C-S-H. But such regions are probably metastable and may tend to leach out in the long term and precipitate as crystalline portlandite whenever the conditions are favourable, e.g. at high water/cement ratios, where large capillary-pore spaces are available for portlandite growth. This is consistent with recent observations on the aging of C-S-H in HCP.[38]

Another potential instability in the freshly precipitated C-S-H (according to our model) lies in the presence of charge-balancing [Ca(OH)(H₂O)₅]⁺ ions. Since no crystalline calcium silicate hydrates containing CaOH⁻ cations are currently known to exist, they may well be metastable with respect to Ca²⁺ ions; but how exactly could such a conversion occur? One possibility seems to be via strong inner-shell coordination bond formation with the ≡SiO⁻ group to which the CaOH⁺ ion is initially closest, releasing a hydroxide ion into solution:

\[ \equiv\text{SiO}^- + [\text{Ca(OH)(H}_2\text{O})_5]^+ \rightarrow (\equiv\text{SiO-Ca(H}_2\text{O})_3)^+ + \text{OH}^- \]  

This reduces the net negative charge on the basal sheets by one, and it is effectively also the first step in the dehydration process of one of the charge-balancing calcium cations. The hydroxide ion released into solution must evidently be balanced by a cation, and the simplest option is via another CaOH⁺ ion:

\[ \text{OH}^- + [\text{Ca(OH)(H}_2\text{O})_5]^+ \rightarrow \text{Ca(OH)}_2 + 5\text{H}_2\text{O} \]

The net result of these two reactions is replacement of two CaOH⁺ ions by one Ca²⁺ ion and the release of one mole of CH plus five moles of water. It is thus also a dehydration reaction, where the CH produced might, (as discussed above for silicate dimerization,) at least initially, either become incorporated into the C-S-H in the form of portlandite-rich or jennite-rich regions.

It is notable that all of the rearrangements in the structure of C-S-H proposed above involve release of considerable amounts of water, in much the same way as the cross-linking dehydration reactions discussed in the previous section. Given that the gel water content of C-S-H in fully-hydrated cement pastes appears to remain roughly constant with aging, it seems plausible that the released water does not escape, but is retained in nanometric voids trapped between basal sheets, close to its source. Thus, all of the processes in equations 3-8 can be as contributing to water in “gel pores,” but it is not yet clear when the movement of this water from the coordination shells of calcium ions in the interlayer spaces to actual nanometric voids takes place.

6. Comparison with proton NMR relaxation data

The recent study of a white cement paste (sealed-cured at w/c = 0.4) using NMR proton relaxometry techniques by Muller et al.[18] showed three principle relaxation times for the main hydrates, typically about 10, 100 and 340 μs, plus a fourth weaker signal at longer and more variable relaxation times. It was proposed that these four distinct signals come from, respectively, protons in portlandite and other crystalline hydrates, protons in “interlayer water” in C-S-H, protons in “gel water” associated with C-S-H, and protons in small capillary “interhydrate” pores. These assignments appear to make sense in
terms of the general aspects of both the Jennings model and the Feldman-Sereda model of C-S-H, as well as Powers’ concept of gel water. The three principle relaxation times do not appear to change very greatly as a function of initial water/cement ratio, or of the degree of hydration of the HCP, although the longest of these relaxation times, associated with “gel water,” does decrease somewhat with increasing hydration time. The signal ascribed to gel water is about double the intensity of the signal ascribed to interlayer water at early ages but their intensity ratio decreases at later ages, approaching a 1:1 when hydration approaches completion. The proton relaxometry approach is especially useful because of its ability to follow the state of water throughout the hydration process. By comparison, using Powers’ definition and the methodologies available prior to proton relaxometry, gel water could only be measured accurately at the point at which hydration effectively stops.

A more recent proton relaxometry study by Gajewicz et al.[39] examines the effect of drying similar HCP samples to those used in [18]. After “strong” drying at 60°C, the only signals remaining were a relatively strong one for “crystalline hydrate water” (as expected) plus a relatively weak one for “interlayer water.” But on rewetting the previously weak “interhydrate water” signal increased most rapidly, while the “interlayer water” signal came back quite slowly, and finally the “gel water” signal came back even more slowly while at the same time the “interhydrate water” signal decreased. This was taken as indicating that “gel pores” refilled only slowly after strong drying, and the water required to refill the gel pores had to first pass through the interlayer. While this seems very consistent with our concept that gel pores probably form as isolated nanometric water-filled voids sandwiched between sheets of C-S-H, the details of the signal frequencies and intensities, and their behaviour during hydration, do not seem to be completely consistent with our new model.

It is important to determine whether these proton relaxometry data are compatible with the new model for C-S-H formation proposed herein, but we are not competent to do this ourselves. We hope that this paper will provoke a thorough examination of the issue by the appropriate experts. In that regard, it will be important to consider the rates of exchange of protons in the hydration shells of calcium ions bound either weakly or strongly to the basal C-S-H sheets, and positioned either on the outside or sandwiched between sheets. Can they give rise to the different relaxation times consistently observed throughout the hydration process? If not, then another reasonable explanation may be that the initial C-S-H structure rearranges very quickly to one in which much of the calcium ion ligand water is displaced into nanometric voids trapped between basal sheets, as suggested in the previous section.

7. What is the relevance of the new model to paste permeability measurements?

It is well known that the permeability of hardened cement pastes, both to water and to many aqueous solutes, decreases as the initial water/cement ratio is decreased, and can be extremely low for well-cured pastes for which the initial w/c ratio is below that required for complete hydration of the cement. Powers[8] attributes the very low values to “capillary discontinuity” while assuming that the paste still contains gel pores, but in our new model we can simply treat the very low permeability in well-cured low w/c pastes that have never been dried as being due to complete space filling by saturated C-S-H. If there are gel pores in this C-S-H, they are trapped between sheets and thus essentially inaccessible. We would therefore expect saturated paste permeability to increase after the first drying of the paste due to the irreversible first shrinkage mechanism described in the previous sections, and the creation of inter-hydrate pores. This is entirely in accord with the observations of Powers.[8]

8. Is all the C-S-H in any given sample of HCP the same on the micron scale?

Up to this point, we have treated all the C-S-H in any given sample of hydrated cement or C3S paste as being the same, assuming that it has undergone exactly the same thermal and hygral history and is essentially at local equilibrium. However, there are strong arguments in the literature for the coexistence
of at least two distinct forms of C-S-H on the scale of the original anhydrous cement particles. It is
referred to either as “inner product” (IP) or “outer product” (OP) C-S-H by microscopists because it is
observed to occur in areas apparently previously occupied or unoccupied by anhydrous clinker phases,
respectively.[40] But it is referred to as “high density” (HD) or “low density” (LD) C-S-H by physicists,
who do not necessarily equate IP with HD or OP with LD, despite strong circumstantial evidence for
such equivalence.[41] In Powers’ original model,[8] there was never any consideration of differences in
“cement gel” at this scale, nor was this consideration taken into account in Young and Hansen’s estimate
of the global wet C-S-H formula $\text{(C}_{1.7}\text{SH}_{4})$ [5] that we have used throughout this paper as a kind of
average composition. So, if there are differences at the microstructural scale, they could imply
differences in both the C/S and the H/S ratio that simply average out to the respective values of 1.7 and
4.0 that appear to be typical. Thorough electron microscopy work shows clearly that the C/S ratio of C-
S-H in cement pastes can vary widely from point to point. But it also seems to imply that it does, at least
at later ages, tend towards a similar C/S ratio in both the IP and OP C-S-H.[42] However, it is far less
easy to determine whether or not there is any such equilibrium in terms of the local H/S ratio, and this
also appears to be an important subject for further research.

What we might expect, from a purely physico-chemical mechanistic approach, is that the growth of OP
C-S-H dictates the kinetics of C3S hydration, at least during the acceleratory period.[11][13] If so, our
mechanism for the incorporation of water into C-S-H should be particularly pertinent to OP C-S-H, which
grows from a relatively dilute interstitial solution. On the other hand, IP C-S-H appears to form essentially
by leaching of Ca$^{2+}$ ions from the anhydrous calcium silicate phases and their replacement in the
structure by protons (for charge balance) plus some additional water molecules for space filling.[4] Thus,
IP C-S-H forms in locations where one might expect the effective water activity to be somewhat lower
and the effective basicity somewhat higher than for the OP, but where the spatial concentration of Si is
also high. This might tend to lead to the IP C-S-H having a more disorganized structure than the OP,
but also having a lower initial water content due to a higher initial probability of forming -Si-O-Ca- bonds
with charge-balancing calcium cations. Thus, the IP could be effectively partly dehydrated relative to the
OP even from the time of its formation; but in this case we presumably also have to assume that the OP
C-S-H must have an initial H/S even greater than 4.

9. Additional indirect evidence for the new model from C3S hydration experiments

Two of the authors were previously involved in separate studies of the kinetics of C3S hydration which
showed clearly that the addition of freshly-precipitated C-S-H to C3S suspensions or pastes served as
an efficient means of accelerating C3S hydration and effectively removing the “induction period.”[43][44]
Both of us observed that, in order for this type of “C-S-H(I)” to be most effective at accelerating C3S
hydration, it was important never to let it dry out before use. Thus, in both published studies, the reported
results of nucleation experiments are given for C-S-H(I) preparations that were kept wet from the time
of their precipitation until the time of their use, although we apparently neglected to mention this explicitly
in either of our publications. We believe that nucleation of new C-S-H growth occurs either at the edges
or on the outer surfaces of existing packets of sheets, so agglomeration of individual sheets into packets
will decrease the number of nucleation sites as well as their degree of dispersion throughout the paste.
Now, our new model provides a clearer explanation for why it is so important to keep the preparations
wet – it helps avoid the first dehydration step of charge-balancing calcium cations which tends to bind
together the initially-precipitated separate C-S-H sheets. If the sheets had simply agglomerated due to
capillary forces during drying, one would have thought that they might more be easily re-dispersed with
strong agitation after rewetting.

10. New hypothesis for the mechanism of action of “shrinkage reducing agents.”
Our C-S-H model also provides us with a totally new viewpoint from which to explain the rather poorly-understood mechanism of action of organic additives that are used in concrete to reduce the length changes due to drying or autogenous shrinkage, typically referred to as “shrinkage-reducing agents” (or admixtures) – SRAs. Although it is generally assumed in the literature that these agents work simply by the reducing the surface tension of the aqueous phase in HCP,[45] recent work has shown that their mechanism of action is probably more complex than that.[46] Based on our new C-S-H model, we hypothesize that the organic molecules used as SRAs have a tendency to adsorb (probably only weakly) on top of the silicate groups on C-S-H basal surfaces, thus partially covering potential bridging silicate group oxygen atoms and retarding the formation of calcium bridges between juxtaposed C-S-H sheets. This should tend to reduce the rate of irreversible shrinkage during first drying. It makes chemical sense, as the most effective SRA molecules typically comprise low molecular weight glycols and alkylether (poly) oxyalkylene glycols, which would be expected to adsorb (albeit quite weakly) on silicate surfaces. It is reported that the adsorption of DPTB, (a well-known and commercially effective SRA,) on HCP is essentially negligible under water-saturated conditions,[47] but it is also very likely that the adsorption could be enhanced significantly by reducing the relative humidity below 100%. A mechanism of action of the type that we propose affects principally a kinetic phenomenon (the rate of formation of calcium bridges during drying) rather than a thermodynamic phenomenon (the surface tension of the pore solution) and also requires a rather high concentration of the additive in order to have enough to effectively block all the likely sites for cross linking. This seems to be quite in line with actual observations on the performance of SRAs, which typically require very high dosages, of the order of at least 1% by mass of cement, to have a significant effect. The effect of SRAs being primarily seen on irreversible shrinkage, rather than reversible shrinkage, is also consistent with some of our own recent observations.[48]

11. Possible role of the new model in explaining mechanical properties

It seems likely that our new model must also have implications in terms of mechanical properties such as modulus, strength and creep. However, these implications are not immediately obvious and require more thought. Strength is a very complex mechanical phenomenon, and relating it to simple structural concepts at the atomic and nano-scale is fraught with dangers.

As for basic creep, the mechanism of this phenomenon is still very poorly understood for most oxide-based materials.[49] However, our model contains the concept of bond formation between C-S-H sheets and also between agglomerates or “packets” of such sheets. Bonds of the type envisaged here are discrete entities involving calcium ions bridging between oxygens in silicate groups. Such bonds can presumably be broken and reformed due to thermal or mechanical fluctuations. This may provide a new way to think about the movements which occur during creep, which typically involves very small displacements. Moving of a bridging bond from one site to an adjacent site as a result of stress coupled with thermal activation seems likely to be an important component of the creep of concrete and of cement paste, which is known to be mainly due to creep in the C-S-H phase.[49] The fact that, according to our model, formation of exactly the same type of bonds is responsible for irreversible drying shrinkage, may also make it easier to explain the “Pickett Effect” - the observation that the creep of concrete under load is greatly increased if the material is also subject to drying at the same time.[50] More research is clearly needed to develop an atomistic model of the creep of C-S-H.

12. Summary and perspectives for further work

The highly speculative model proposed in this paper is intended to resolve the enigma of the apparently unavoidable inclusion of “gel water” into the hydrates during the hydration of the calcium silicate phases in Portland cement. Rather than treating this water in the conventional way, as being trapped in
nanoscopic pores formed by random growth processes of the C-S-H, we instead hypothesize that it forms due to initial incorporation of charge-balancing calcium cations in the very highly hydrated state found in aqueous solution, with at least 6 water-oxygens in their inner ligand sphere. This can explain why gel water is always incorporated into the growing C-S-H, and it also explains why the hydration of the calcium silicate phases essentially stops if insufficient water is available for incorporation as gel water. Thus, gel water is chemically required to form the C-S-H product, and is not simply water trapped by random chance in very small pores.

A second important hypothesis is the assumption that the charge-balancing calcium ions required for electroneutrality of the C-S-H comprise not only fully hydrated Ca$^{2+}$ ions, but also fully hydrated CaOH$^+$ ion-pairs, which are known to represent a significant fraction of the Ca in the aqueous phase from which C-S-H grows during cement hydration. This hypothesis can also explain the variable C/S ratio of the high-C/S C-S-H that forms during cement hydration, sometimes referred to as γ-C-S-H. It can also explain its poor degree of crystalline order, especially in the c-direction.

By combining these novel hypotheses with the conventional wisdom that this high-C/S C-S-H is built of tobermorite-like anhydrous anionic basal sheets in which all or most of the bridging silicate groups of the “dreierketten” silicate anions are initially missing, we can account for the observed limiting composition of wet C-S-H ($\text{C}_{1.7}\text{SH}_4$) at the point where hydration stops due to lack of space.

The model explains the irreversibility of the first-drying water loss, which mainly occurs at relative humidities above 50%, as being due to the formation of calcium bridges between silicate groups (attached to basal C-S-H sheets) via the loss of some of the initial water ligands and their replacement by oxygen ligands bound to the silicate groups. The driving force for this is a reduction in the coordination energy of the bridging calcium ions. The result is the effectively irreversible formation of Si-O-Ca-O-Si bridges between adjacent C-S-H sheets brought into contact by the drying process. Further water loss is then largely reversible (at ambient temperatures) because it occurs from the remaining water ligands around calcium ions that have become constrained within a cage determined by the structure formed by the initially-formed Si-O-Ca-O-Si bridges.

The model also proposes that the initially-formed C-S-H structure is metastable and evolves over time, (accelerated by drying or heating,) towards more cross-linking via Si-O-Ca-O-Si bridges as well as a more stable tobermorite-like structure that contains more bridging silicate groups, giving a higher mean silicate chain length. But these rearrangements, whether due to aging or drying, imply separation both of water and of a secondary calcium rich phase which is probably portlandite but could also be jennite. Initially, the calcium rich phase probably forms nanometric precipitates, effectively giving a solid solution. It also seems likely that the water released by such rearrangements in the absence of drying remains trapped in nanometric voids sandwiched between adjacent basal sheets. This can explain why “gel water” is always found in nanometric pores and also why it appears (according to recent proton relaxometry data) to have to pass through the interlayer region between adjacent C-S-H sheets in order to escape during drying or re-enter during wetting.

Due to the speculative nature of the proposed model, a considerable amount of further work will be required to test its validity, preferably using a combination of atomistic modelling and non-destructive techniques such as proton relaxometry and neutron or X-ray scattering which can be applied to wet materials. A very important aspect of the model is its emphasis on specific bonds between C-S-H sheets and also between “packets” of sheets, rather than a continuum explanation for inter-particle attractions. In all cases the bonds are mediated by calcium ions lying between anionic silicate groups, but the strength of the bonds will be determined by their (Si-)O-Ca distances, which will tend to decrease as the number of oxygen ligands around the calcium ion decreases. Thus, the bonds become stronger as water is lost. Because the model requires us to consider a wide range of possible coordination environments around the calcium ions in question, very sophisticated atomistic modelling techniques are likely to be needed to obtain realistic models that can explain the whole range of compositions and properties of that very complex defective phase which we simply refer to as “C-S-H.”
13. Dedication

We wish to dedicate this paper to the memory of Hamlin M. Jennings, a good friend, colleague and mentor, discussions with whom encouraged this work, but who sadly passed away in 2015.

14. References


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Table 1: Summary of the main hydration states of our proposed high C/S C-S-H solid solution series, based on the formula \( \{(1-\gamma)(C_3S_2H_6) + \gamma(C_4S_2H_{11})\} \) for the wet state as initially precipitated. Two molecules of water are lost per charge-balancing calcium-ion in the first dehydration step to stabilize these calcium ions irreversibly with two (Si-O) groups replacing the lost water molecules. Beyond this, further dehydration occurs by simple (and reversible) loss of the remaining ligand water. The “third stable dehydration state” appears to be close to the traditional value for “chemically bound water” (see Fig. 1.) Further dehydration beyond this may well produce other irreversible structural changes.
Fig. 1: Plot of H/S against C/S for C-S-H(I) preparations, (Fig. 2 from Ref. [7], reproduced here for convenience). The filled circles represent samples that were lightly dried (e.g. in flowing N\textsubscript{2} at room temperature) and the unfilled circles represent samples that were more strongly dried, i.e. at around 110°C or more. We have added two 5-point stars joined by a dotted line to represent the “first stable dehydration state” of C-S-H according to our new model; two triangles to represent the “second dehydration state” and two four-point stars to represent the “third dehydration state.” (See Table 1. for a full definition of these hydration states).
Fig. 2: Fig 9 from ref.[2], reproduced here for convenience. Pale blue circles are calcium atoms; the pale blue shaded area represents the main Ca-O basal sheet; small red (or black) circles are oxygen atoms, and dark blue triangles represent silicate tetrahedral (with silicon atoms in their centres).
Fig. 3: Calculated CaOH⁺/Ca²⁺ ratio in portlandite-saturated NaOH solutions up to 0.3M
Fig. 4. Schematic of a single basal layer in which the negative charge is balanced by equal numbers of Ca\(^{++}\) and CaOH\(^{+}\) solvated cations, \(\gamma = 0.33\) giving the overall composition \(\text{Ca}_{20}\text{Si}_{12}\text{H}_{46} = \text{C}_{1.67}\text{Si}_{3.83}\).
Fig. 5. Low-temperature DSC measurements on HCP preconditioned at various relative humidities and rewetted just prior to analysis. A Bruker AXS DSC3100 heat-flux type DSC was used, with a cooling rate of 5 degC/min applied directly to small samples (about 10mg) broken from the wet hardened paste specimens. The reference material was corundum, and the calibration was done with purified water and cyclohexane. The C/S ratio of the C-S-H in these pastes was estimated to be about 2 by XRD/Rietveld analysis and mass balance. This is relatively high, but this value was consistent among all the samples dried under different RH conditions. In the legend, the temperature indicates the peak of heat of solidification. Further details of sample preparation are given in refs [28] and [29].