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A PROPOSED MECHANISM FOR THE GROWTH OF C-S-H DURING THE HYDRATION OF TRICALCIUM SILICATE

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ABSTRACT

This paper presents a novel theory that can explain some previously mysterious aspects of the structure of C-S-H gels in cement pastes. The structure is seen as a consequence of the growth mechanism, taking as a model the growth of C-S-H during the hydration of tricalcium silicate. It is postulated that C-S-H grows as wavy or buckled sheets or ribbons. Growth occurs mainly at the edges of the sheets, or ends of the ribbons, except when new sheets nucleate on top of an existing sheet, which can only occur in certain well-ordered flat regions. This can lead to exponentially increasing growth rates at early ages, before steric hindrance of the sheets is significant. The model can also explain other unusual aspects of the structure of the final hydrated product, in particular the possible occurrence of nanocrystalline regions of different composition (tobermorite-like, jennite-like and even portlandite-like), allowing for a wide range of calcium/silica ratios in the product, as a function of the solution composition during the growth process. © *1997 Elsevier Science Ltd*

Background

The mechanism of hydration of the basic calcium silicates found in portland cement, and the structure of the resulting C-S-H gels, have been a subject of much interest to cement chemists, and there are still many unresolved issues. In particular, the rapid acceleration that occurs after a short induction period, especially notable in the hydration of tricalcium silicate (C_3S), has not been completely explained. During the acceleratory period, the rate of hydration appears to increase rapidly with time. Curves of $d\alpha/dt$ vs. a for C_3S hydration in pastes at early ages show an almost linear dependence, (see Fig.1, taken from ref.1), which implies an exponential dependence of α on t. (Note: in this case, α represents the fractional degree of hydration of the anhydrous C_3S, but it has been, with justification, assumed to be directly proportional to the amount of C-S-H formed after the minimum in the curve which occurs at a very low value of α). This implies that some rather unusual kind of "autocatalytic" process is controlling the rate, and it has been proposed that this process is related to the nucleation and growth of one of the product phases, i.e. C-S-H or portlandite. The author has reviewed the literature on this subject, (1), and has concluded that it is unlikely that growth of portlandite is the rate limiting process.

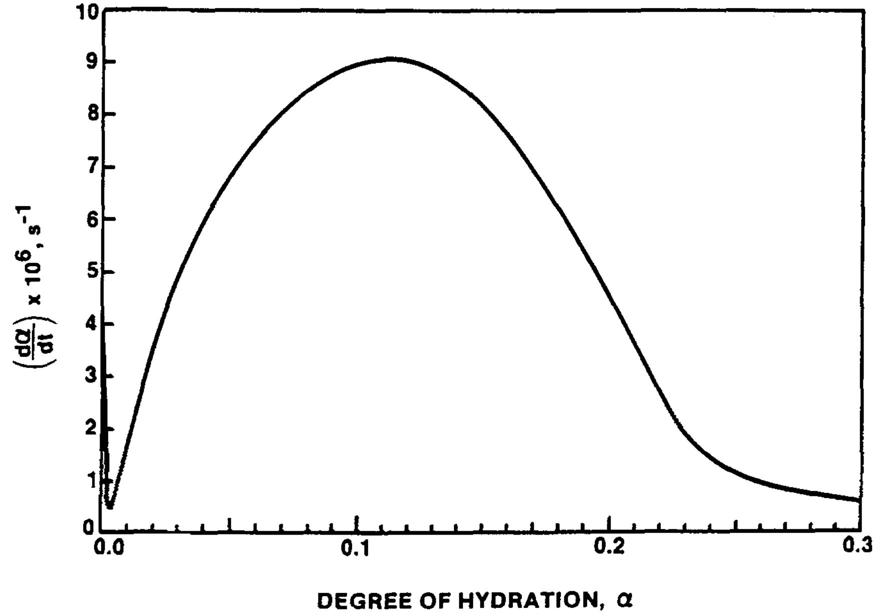

FIG. 1.
Hydration rate vs. degree of hydration for C_3S (from ref. 1).

Addition of portlandite does not generally accelerate the reaction, whereas addition of C-S-H usually does. The evidence points to the growth of C-S-H being rate-controlling during the acceleratory phase.

The present paper is an attempt to develop a theory to explain the puzzling phenomenon of C-S-H growth in cement hydration, and link it to some of the other properties of the hydrate that apparently make it unique. Much of the discussion is speculative, and the author hopes that this will stimulate the readers to test the hypotheses presented here.

Concepts

The precipitation of a crystalline substance from solution can, in simplistic terms, be viewed as a sequence of nucleation and growth processes. The first step, nucleation, is one in which a critical nucleus of the product forms spontaneously from a supersaturated solution, either on an existing surface (heterogeneous nucleation) or in the solution (homogeneous nucleation). The former process is far more likely at low levels of supersaturation. Once the nucleus has reached supercritical size, it can grow at a rate dependent on the number of active growth sites on its surface, and also dependent on the level of supersaturation. If there are only a fixed number of growth sites per crystal, its rate of growth, $d\alpha/dt$ (mass/time), will be roughly constant at constant supersaturation. If each surface of the crystal can spontaneously develop new growth sites (by a process of continuous heterogeneous nucleation), then rate of growth of the crystal should be proportional to its surface area, at constant supersaturation. Assuming that the growing crystals maintain their shape, the surface area is proportional to α raised to the 2/3 power, giving the equation:

$$d\alpha/dt = k(\alpha)^{2/3} \quad (1)$$

Integrating this equation gives a t^3 dependence of α on time. However, the result should be the growth of large blocky crystals, which is not observed in C-S-H in cement. It should be noted that a similar equation can also apply to the growth of an amorphous phase from a supersaturated solution, as has indeed been considered in the case of polymer spherulites (2), where the product phase is essentially spherical. In either case, the only way that the rate can have a higher order than 2/3 in α is if there is also a continuous nucleation process.

It is now well-established that C-S-H has some kind of layered structure, although it clearly has relatively little long range order, especially in the direction perpendicular to the layers (i.e. there is no detectable basal spacing reflection in its X-ray diffraction pattern, but some of the in-plane reflections do appear, albeit weakly).(3) This would tend to suggest that it grows most rapidly in the plane of the sheets, which are based on the same kind of Ca-O layers found in tobermorite, jennite, and portlandite. However, a phase which grows essentially only in two dimensions would be expected to show lower-order growth kinetics, that is, $d\alpha/dt$ should depend on α to the half power if it is assumed that the rate of growth is proportional to the perimeter of the sheet. Clearly, this cannot account for the nearly exponential rate of growth observed in the early stages. The only way to get such a high rate is to assume that some kind of continuous nucleation process occurs in parallel with regular growth.

The observations that C-S-H grows with acceleratory kinetics of a fairly high order in time and yet is an amorphous phase with some kind of underlying laminar structure seem hard to reconcile. The product is generally thought of as truly amorphous, i.e.. consisting of a collection of a very large number of discrete colloidal particles. This type of product might be formed by the precipitation of a material from a highly supersaturated solution (e.g. such as in the manufacture of silica gels). In such a case, however, one would expect the rate of product formation to be essentially just the nucleation rate, because the product consists essentially of a series of nuclei. This type of process can occur when the rate of homogeneous nucleation exceeds the rate of growth on existing nuclei. In the case of C_3S hydration one could imagine that this might be the case very close to the surface of the anhydrous phase. Such a process probably occurs at the very beginning of the C_3S hydration process and leads to the formation of some kind of metastable coating on the anhydrous grains, prior to the onset of the acceleratory growth phase (1). As would be expected, this is observed as a rapid decline in $d\alpha/dt$ with increasing time (or α) at very low levels of α (see Fig. 1). This period of the reaction is also associated with a large increase in the C/S ratio of the solution, and has been discussed thoroughly by Barret and coworkers (e.g. ref 5). However, it cannot account for the acceleratory growth kinetics observed after the "induction period."

In the case of C-S-H, there also seems to be almost no tendency for it to recrystallize at room temperature, from which one might conclude that the free energy difference between amorphous C-S-H and the probably more stable mixture of potential crystalline products must be small under these conditions. It is, therefore, interesting to consider how the growth process might dictate the structure of the product. It is also important to be able to explain the fact that the amorphous C-S-H can have a wide range of compositions (C/S ratios). Recent work appears to show that C-S-H contains many nanocrystalline regions of different composition, i.e. it seems to be a mixture of phases on a nanometer scale, rather than a single phase.(4) How can this type of mixed phase possibly grow in what appears to be a regular manner? The author believes that these observations can be reconciled if we make some additional speculative assumptions.

Hypotheses

The fundamental assumption that we will make is that all of the hydration products of C_3S (and of C_2S) at ambient temperatures are based on calcium-oxygen layers similar to those found in crystalline portlandite. Taylor (3) has already pointed out that tobermorite has such a structure, (consisting of layers of Ca-O sandwiched between polymeric silicate anions,) and that the higher C/S ratio phase, jennite, is probably also based on a (distorted) Ca-O layer sandwiched between silicate anions of some kind. It was also noted that the C-S-H that forms in C_3S hydration at early ages contains mainly dimeric silicate ions. There are very few monomeric or oligomeric silicates in the initial product. However, the liquid phase from which this product precipitates is believed to contain mainly monomeric silicate anions, rather than dimers.(6) This highlights the fact that growth of a complex crystalline phase such as C-S-H from solution involves a series of consecutive chemical reactions, during which aqueous solvated species rearrange and form new covalent and ionic bonds in the solid phase. It is not possible at this time to say which of these steps is likely to be rate-controlling under any given conditions. However, it is certainly possible that formation of silicate dimers could control the rate under certain conditions, especially at low silicate concentrations in the solution phase. It should be noted that the maximum potential rate of formation of dimers will fall as the square of the monomer concentration.

Let us consider how C-S-H might grow from a supersaturated solution containing calcium, hydroxyl, and silicate ions. At the early stages of C_3S hydration, the solution phase is relatively high in silica content and favors a C-S-H of a low C/S ratio, but, with precipitation of C-S-H, the solution evolves to one with a high C/S ratio, favoring a C-S-H of a higher C/S ratio (5). The relationship between the C/S ratio in solution and in the equilibrium product is dictated by thermodynamics(6). Assume that the small nuclei of C-S-H which presumably form at very early ages in the hydration process (when the solution has a low C/S ratio) have a tobermorite-like structure, but frequently consist of only a single layer-in other words, they are essentially two-dimensional. If the relative rate of growth of such a nucleus is high in the plane of the CaO sheet, it will grow as a sheet, giving a two-dimensional product. This makes sense because there is relatively little in the tobermorite structure to bind two such sheets together-this structure has silicate anions on both sides of the Ca-O sheet, and develops a slight negative charge which must be balanced by interlayer calcium ions, so that it is easy to imagine that there is a very low energy of interaction between two such sheets-the situation is similar for many clay minerals, where it is often easy to debond the sheets completely.

As these "tobermorite" sheets grow, we could envisage a situation where, by random chance, one side of the sheet becomes locally depleted in silicate ions (dimers). This will become more probable as the C/S ratio of the solution rises (at which time the absolute silicate ion concentration falls to quite low values). If this can happen, it constitutes a defect in the sheet, and should induce some kind of local stress, which could be relieved by inducing curvature in the sheet. Chemically, the local curvature of the basic tobermorite sheet, coupled with the missing silicate ions, represents a site of different characteristics from the normal flat sheet, with many interesting consequences, e.g. with respect to ion-exchange, properties, etc. It is possible that, once the sheet has grown a certain distance past the defect, it would require a significantly higher activation energy to bind a silicate dimer to the site from which it was initially omitted, since this would require flattening the sheet locally, and mechanical factors may then inhibit such a change.

We must now consider the question of how additional sheets of product can form. If we had regular crystallization of a layer compound, such as tobermorite, we would anticipate that the process might evolve, from the initial growth of a flat sheet, by nucleation of a second sheet on the first sheet. Let us assume that the chance of such an occurrence is only significant in areas of the sheet that are crystallographically "perfect." These should, of course, be flat. Once the second sheet nucleates, it can grow rapidly and thus thicken the first sheet. This process should lead to well ordered multilayers-i.e. crystals of tobermorite. However, as noted above, this does not seem to happen in C-S-H growth at ambient temperatures. Instead, what might happen is the following. Assume that our first growing sheet of tobermorite-like structure is "wavy" due to random silicate ion defects on either side. Occasionally, however, there will be regions that are essentially perfect, and, over these regions, new layers can spontaneously nucleate. The new sheet can follow the sheet on which it nucleated only for as far as it goes without significant curvature. If it encounters an area of high curvature, it can separate and continue growing as an independent sheet.

Thus, heterogeneous nucleation can produce a second sheet which, while attached to the first sheet at one point (its birthplace), may be separated from it at other points. If the site of sheet nucleation remains active, several layers can form at that site, leading to a blocky region that could have significant order in the direction perpendicular to the sheet, i.e. it could behave as a nanocrystalline region of tobermorite-like structure, whereas the buckled sheets growing independently of each other away from this region are essentially amorphous. We might also assume that, as silicate ion concentrations fall in solution, some sections of the growing sheet may become jennite-like, or even, in the extreme case, portlandite like. This might explain a C-S-H gel in which dense nanocrystalline regions of tobermorite-like, jennite-like and portlandite-like structure can coexist, separated by amorphous regions in which the sheets are highly buckled and, presumably, incorporate large amounts of water in the disorganized volumes between the buckled sheets. Such a structure can clearly allow for a very wide range of C/S ratios, the actual composition being a function of the conditions under which the product was formed. The concept of portlandite nuclei being part of the C-S-H seems possible to reconcile with the known facts of high portlandite supersaturation at early ages, coupled with the observation that silicate ions tend to act as "poisons" for the growth of crystalline portlandite(1).

The hydration kinetics of the buckled sheet model are difficult to analyze in three dimensions, but the author has constructed a two-dimensional analogy which shows that it could account for hydration kinetics of a high order. Imagine the sheets as lines in two dimensions. Each line has two ends and the lines can only grow at their exposed ends. Thus, for a single line with two ends, the rate of growth is constant. Further, assume that the lines are wavy (buckled), but that there are occasional locally linear (flat) regions at which new lines can initiate on one or other side of the existing line. The number of such linear regions should, on a random model, be simply proportional to the total existing length of lines. The rate of nucleation of new lines is thus proportional to the total existing length of lines, assuming that the lines remain well-separated. Once a new line is initiated, it also has two growing ends, and we must assume that they can propagate independently of the line which gave birth to them, (although this will depend on the local curvature of each line, i.e. they can also impede one

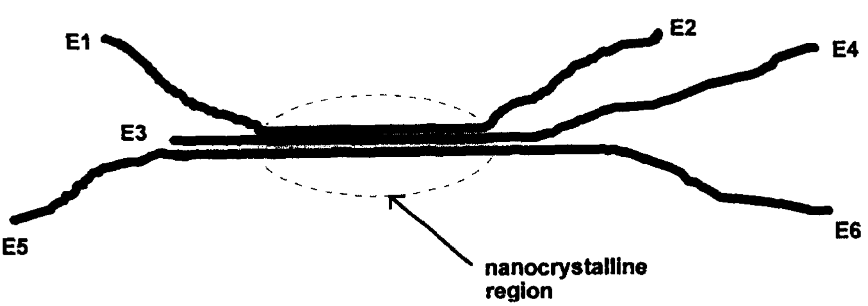

FIG. 2.
Schematic of growth process.

another). Fig. 2. Shows the concept schematically, with three separate sheets of C-S-H emanating from a common nucleation point which can be considered a "nanocrystalline region."

The kinetics of this process, in the absence of entanglements, is simply given by two linked differential equations:

2) $$dL/dt = k_g \cdot E$$ (subscript g for growth)

3) $$dE/dt = k_n \cdot L$$ (subscript n for nucleation)

(where L represents the total length of all lines, equivalent to the total amount of product formed, and E represents the total number of growing ends, equivalent to growth sites, and the appropriate rate constants are as shown). The simplest solution to these coupled equations is an exponential function of the form:

4) $$L = L_0 \cdot \exp(k_a \cdot t) \qquad E = E_0 \cdot \exp(k_a \cdot t)$$

where:

5) $$L/E = L_0/E_0 = (k_g/k_n)^{0.5} \qquad k_a = (k_g \cdot k_n)^{0.5}$$

(a more complex solution is required for different boundary conditions).

Thus, it can be seen that a mechanism such as this can account for an exponential growth rate if there is plenty of free space for the hydrates to grow without entanglement. This seems to be the case in the early stages of C_3S hydration, when most of the C-S-H gel formed is "outer product," growing in the solution space between cement particles. Also, the fraction of nucleation sites to total hydrate depends on the ratio of the two rate constants. We should be able to relate this to the relative proportion of nanocrystalline regions in the product, and also in terms of porosity (the porosity should be greater if there are fewer nucleation points tying the sheets together). This ratio is certainly influenced by temperature and can perhaps also be influenced by dissolved ions, e.g. in the case of classic hydration accelerators.

It is the author's opinion that many aspects of the growth and properties of C-S-H in C_3S and cement pastes could be accounted for, in principal, by a model like this, if it can be extended to three dimensions. The extension to three dimensions is not trivial, because the nature of curvature is more complex. However, it might make more sense of the C-S-H actually grows in the form of thin ribbons, rather than in broad sheets. Ribbon-like growth would make the product rather similar to many solidified organic polymers with amorphous and crystalline regions, and would be consistent with the kinetics worked out above. It is also more likely that curvature would persist in a ribbon-like product than in a product consisting of broad sheets.

In addition to the points already noted, we might also consider that the influence of foreign chemical species on the relative rates of the two main processes (nucleation of new sheets, and growth of existing sheets) can clearly influence the fundamental physical properties of the gel during its formation. Once the gel has formed, the nucleation regions act as links between hydrate sheets but cannot grow easily to increase the total crystallinity of the product because, if they do, they induce severe local stresses in the linking sheets. This can probably explain the kinetic stability of the gel, even though it is inherently a non-equilibrium product. As for its binding properties, the presence of many buckled sheets or ribbons extending into the solution away from the surface of the cement grains gives ample opportunities for weak bonds to occur between two grains, simply by interactions between two sheets that happen to align in a favorable way and have the right local composition to form bridges.

Summary

A simple model has been presented that can reconcile the autocatalytic hydration kinetics of C_3S with the unusual porous and apparently amorphous nature of the C-S-H product formed. The structure of the product is postulated to be a consequence of the way in which it grows, which is assumed to be in the form of sheets, probably rather narrow and ribbon-like, that can buckle and curve as a consequence of the local ionic concentrations when they formed. These sheets are linked in localized nanocrystalline regions that represent nucleation sites for new sheets during the growth process. The nanocrystalline regions can be tobermorite-like, jennite like, or possibly even portlandite like, accounting for a very wide range of possible C/S ratios; the actual average C/S ratio will depend on the proportion of such regions as well as the composition of the amorphous regions in between them. The early-age kinetics of C-S-H growth are essentially exponential because of the interplay between growth of existing sheets and nucleation of new sheets at certain sites on the existing sheets; however, as soon as they begin to interfere with one another, the rate will no longer increase exponentially because some ends and nucleation sites will become hindered. Once the hydrates have formed, the crystalline and amorphous regions become essentially locked in for kinetic reasons, even though the structure is probably chemically metastable with respect to a differentiated set of crystalline hydrates. The presence of curved regions along the sheets can allow for a wide range of binding energies for various adsorbed species. The high porosity of the gel is inherent in its structure because of the curvature of the sheets in the amorphous regions, and this results in the observed high drying shrinkage capacity. It is interesting to note that a solid consisting of small crystalline regions linked by amorphous regions containing (curved) chains is very common in organic polymer systems.

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