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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 (C_3S) 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 (Ca^{2+}) 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.

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, SiO_2 and H_2O (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

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silicates, C_3S and C_2S, are hydrated under water-saturated conditions at temperatures in the normal concrete use range (0–60 °C) has an average composition close to $C_{1.7}SH_n$; 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_3S) and "belite" (impure dicalcium silicate, C_2S). 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:

$$C_3S + 5.3H \Rightarrow C_{1.7}SH_4 + 1.3CH \quad (1)$$

$$C_2S + 4.3H \Rightarrow C_{1.7}SH_4 + 0.3CH \quad (2)$$

It is observed that pure C_3S 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

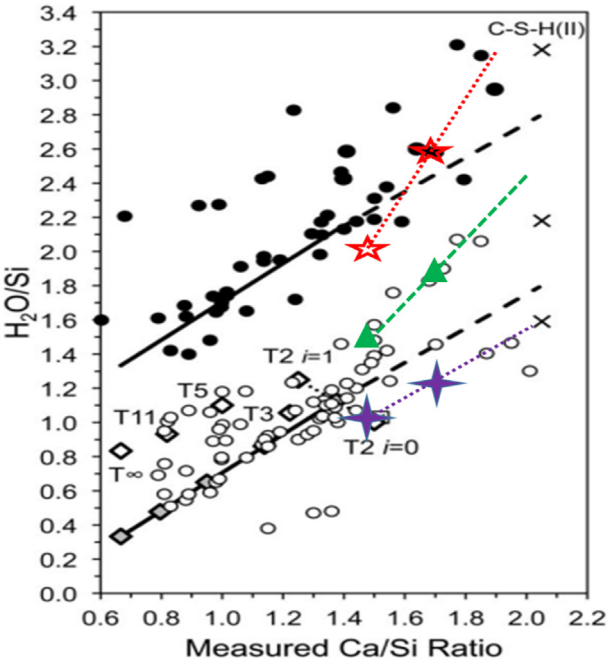

Fig. 1. Plot of H/S against C/S for C-S-H(I) preparations (Fig. 2 from Ref. [7], reproduced here for convenience). The filled circles represent samples that were lightly dried (e.g. in flowing N_2 at room temperature) and the unfilled circles represent samples that were more strongly dried, i.e. at around 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.)

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-SiO_2 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