



# Calcium silicate hydrates: Solid and liquid phase composition



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## ABSTRACT

This paper presents a review on the relationship between the composition, the structure and the solution in which calcium silicate hydrate (C–S–H) is equilibrated. The silica chain length in C–S–H increases with the silicon concentration and the calcium content in the interlayer space with the calcium concentrations. Sodium and potassium are taken up in the interlayer space, preferentially at low calcium concentrations and thus by low Ca/Si C–S–H. Aluminium uptake in C–S–H increases strongly at higher aluminium concentrations in the solution. At low Ca/Si, aluminium substitutes silica in the bridging position, at Ca/Si > 1 aluminium is bound in TAH. Recently developed thermodynamic models are closely related to the structure of C–S–H and tobermorite, and able to model not only the solubility and the chemical composition of the C–S–H, but also to predict the mean silica chain length and the uptake of aluminium.

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## 1. Introduction

The objective of this article is to assemble the latest state of research on the structure and the composition of C–S–H and their relation with the composition of the solution in which it forms. C–S–H precipitates from the ions produced in the pore solution by the dissolution of anhydrous calcium silicates (C<sub>3</sub>S or C<sub>2</sub>S), but also from other soluble siliceous materials which may be present in blended cements such as silica fume, fly ash or slag. The relation between composition and structure of pure synthetic C–S–H, for which the calcium to silicon ratio ranges from ~0.7 to ~1.45, has been studied for a long time [1–17]. It is now generally agreed that the silica arrangement in C–S–H is parallel linear rows of dimers of silica tetrahedra more or less bridged by a third tetrahedron (bridging tetrahedron). If all the dimers are bridged, the chains are infinite and correspond to the dreierketten arrangement of the silica chains found in natural calcium silicates such as tobermorite, jennite and wollastonite. <sup>29</sup>Si NMR studies have largely contributed to show that the number of bridging tetrahedra decreases when the Ca/Si increases [13,16,18,19]. For synthetic C–S–H, which is also representative of C–S–H in blended cements with a high content of reactive silica (low pH cements), it has been demonstrated that the composition of the solid phase is determined by the composition of the solution. The highest Ca/Si is limited by the solubility of portlandite. Recent experimental studies [20–24] confirm that the structure of C–S–H with this range of composition can be described as a defect tobermorite structure; this is the subject of the first part of this paper.

The composition of C–S–H in a cement paste is generally higher than 1.5, 1.7 on average, and could be as high as 2 in certain conditions [25–28]. Such high ratios are observed, because during the hydration of alite, the solution is supersaturated with respect to portlandite. In other words, the calcium hydroxide concentration is higher than the solubility of portlandite which leads initially to a higher calcium content in C–S–H. Structural experimental data on C–S–H at this composition are rare [7,13,29,30]. The structure of such high Ca/Si C–S–H is still under discussion, some new input comes from molecular modelling [31–35]. The tobermorite like structure seems to be preserved; the nature of the defects and the extent to which the material can be considered as amorphous or not, are discussed in the second section.

Beside the silicate phases, the reaction of calcium aluminates in the clinker as well as of fly ash and slag, releases some aluminium in the solution, i.e. Al(OH)<sub>4</sub><sup>-</sup> species at the pH of 12.5 imposed by the solubility of portlandite. The presence of aluminium in solution leads to its uptake in C–S–H, essentially by substitution of silica, although other mechanisms are also possible. Clinkers contain also alkali and alkalis are used as activators for blastfurnace slags, which contribute to increase the pH of the pore solution. The consequences on the composition and the structure of C–(A)–S–H are discussed in the third part of this paper.

Finally, in the last part, the different approaches reported in literature to model C–S–H/solution equilibrium are presented and discussed.

## 2. CaO–SiO<sub>2</sub>–H<sub>2</sub>O system

It has been known for a long time that mixing lime and silica in water at ambient temperature leads to the formation of calcium silicate hydrate, C–S–H, of variable composition. Depending on the composition

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of the initial mixture, i.e. the amount of lime, silica and also water, the final product contains either residual amorphous silica and C–S–H, C–S–H and portlandite or C–S–H only. The composition of C–S–H varies depending on the activity of the ions in the equilibrium solution. Although C–S–H is not well crystalline,  $^{29}\text{Si}$  NMR data indicate that the C–S–H structure can be described using a defect tobermorite structure consisting of a calcium oxide layer with silica chains attached on both sides organized in “dreierketten” structures, i.e. repeating chains of three silica tetrahedra as discussed in detail by Richardson [23,36]. Fig. 1 shows a schematic representation: two of the silica tetrahedra, the pairing tetrahedra, are linked to the calcium oxide layer, while the third bridging tetrahedron links the two pairing tetrahedra. A number of sheets can be connected by an interlayer containing water, calcium, alkalis and other ions.

### 2.1. Relationship between the solid and the composition of the solution

The composition of C–S–H is generally characterised by its calcium to silicon ratio, Ca/Si or C/S in the nomenclature used in cement chemistry. The C–S–H composition is mirrored in the composition of the aqueous phase. The correlation between calcium and silicon concentrations and the pH values with the calcium to silica ratio is well documented as shown by the data compiled in Fig. 2. The lowest Ca/Si in C–S–H is about 0.7 and the highest is about 1.45, both depending on the temperature. If the Ca/Si of the solid is lower, it is a mix of C–S–H and amorphous silica or if it is higher than 1.45 it is a mix of C–S–H with portlandite. It is important to keep in mind that, in this system with 3 components, the Ca/Si at equilibrium conditions cannot be lower than 0.7 because the activity of ions is fixed by the solubility product of amorphous silica, or higher than 1.45 as the activity of calcium ions is fixed by the solubility of portlandite. This range of Ca/Si corresponds to what it is generally called C–S–H(I) [2].

A recent careful reinvestigation [13] of the solution in equilibrium with the solid phases (see Fig. 3) tends to show that this range of composition is actually covered by two C–S–H phases as previously proposed [5,30,37–39]. The measured activity of  $\text{H}_4\text{SiO}_4$  can be plotted

as a function of the logarithm of the activity of  $\text{Ca}^{2+} + 2 \text{pH}$  [13], which corresponds to a linearized form of the solubility product written as  $(\text{CaO})_x(\text{SiO}_2)_y(\text{H}_2\text{O})_z + 2x\text{H}^+ = x\text{Ca}^{2+} + \text{H}_4\text{SiO}_4 + z\text{H}_2\text{O}$ , where  $x$  is the Ca/Si ratio and  $z = y + x - 2$  (for details see [13]). The Ca/Si ratios (triangles) vary over the range in two steps, first with a shallow slope from 0.75 to 1 and then steeply from 1 to 1.6. In Fig. 3 the y-intercepts give the log K values and the slopes the calcium to silica ratio in the solid. The first line with a slope equal to zero corresponds to the equilibrium solubility of amorphous silica,  $\text{SiO}_2$ . The second and the third have slopes equal to 0.81 and 0.96, corresponding to two different C–S–H phases, with Ca/Si  $\approx 0.8$  and 1 such that:

$$\begin{aligned} \alpha - \text{C-S-H} : \log K_1 \\ = 0.82 \log (\text{Ca}^{2+}) + \log (\text{H}_4\text{SiO}_4) - 1.64 \log (\text{H}^+) \approx 11.2 \text{ for } 0.75 < \text{Ca/Si}_{\text{eff}} < 1 \end{aligned} \quad (1)$$

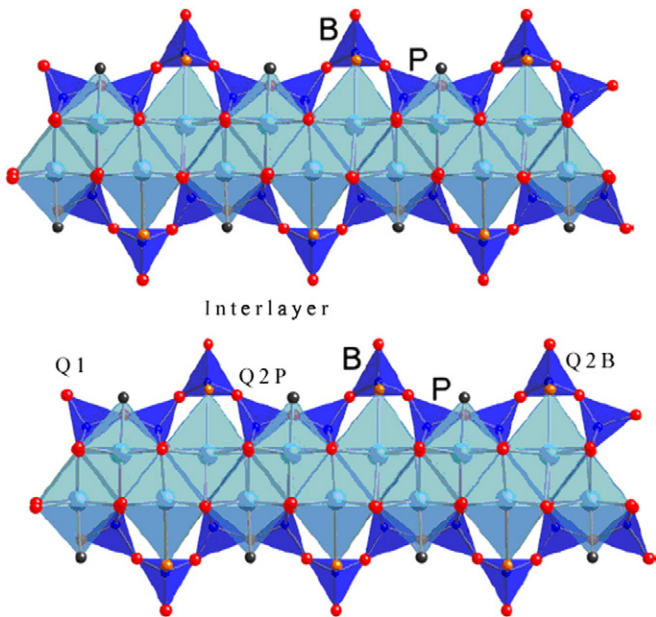
$$\begin{aligned} \beta - \text{C-S-H} : \log K_2 \\ = 0.98 \log (\text{Ca}^{2+}) + \log (\text{H}_4\text{SiO}_4) - 1.96 \log (\text{H}^+) \approx 14.2 \text{ for } 1 < \text{Ca/Si}_{\text{eff}} < 1.5. \end{aligned} \quad (2)$$

Although the linearization of the solubility products gives a single value of Ca/Si for each phase, Fig. 3 clearly shows that their composition varies on a larger range:  $\alpha$ -C–S–H:  $0.7 < \text{Ca/Si}_{\text{eff}} < 1$ ,  $\beta$ -C–S–H:  $1 < \text{Ca/Si}_{\text{eff}} < 1.5$ . This increase is due to two simultaneous mechanisms, the uptake of calcium in the interlayer and the depolymerisation of the silicate chains which result in changes of the C–S–H structure. It is now generally agreed to consider that C–S–H(I), which covers both alpha and beta C–S–H, has a structure close to the tobermorite structure [22,23]. In the last decades,  $^{29}\text{Si}$  NMR studies demonstrated unambiguously that the higher the Ca/Si, the shorter the silicate chains (see Fig. 4a). The shortening is due to the partial elimination of the bridging tetrahedra. The main features of the linear parallel chains of dimer of silica tetrahedra, also named pairing tetrahedra, are preserved because the calcium cations of the main plane of the tobermorite are coordinated by the oxygen atoms of the silica. The shortening of the chains is due to the lowering of the silicon concentrations in solution (see Fig. 4b) as the calcium concentration increase. As a consequence, Ca/Si of C–S–H increases.

If the calcium hydroxide concentration in solution increases, the activity of the protons decreases (pH increases) and the activity of calcium increases: calcium ions replace protons in the interlayer space of C–S–H. This process can be simply described by the following reaction:  $2\equiv\text{SiOH} + \text{Ca}^{2+} = (\equiv\text{SiO})_2\text{Ca} + 2\text{H}^+$ , where  $\equiv\text{SiO}$  represents one of the SiO bounds of the silica tetrahedra. Fig. 5 illustrates the increase of the interlayer Ca with the calcium concentration in solution.

### 2.2. Composition–structure relationship

Except for the variation of the chain length for which evidence comes from Si NMR, the changes in the structure are difficult to study experimentally. Little advance has been made in the use of X-ray diffraction to determine C–S–H structure in the last 50 years, despite considerable improvements in diffraction techniques and the use of very high resolution synchrotron diffraction experiments, data is not better because the resolution is limited by the C–S–H samples and not by the experimental broadening. The X-ray diffraction patterns are broad because of the small size of the coherent domains and the defect structure of C–S–H. It is difficult to extract structural information from these patterns. Some recent attempts to fit C–S–H diffraction patterns by Rietveld methods using tobermorite structures illustrate this [21,22,24,42,43]. All of them give a good agreement with the experiments but use different structural constraints. The system is highly correlated; the structural parameters (cell parameters, atom coordinates) and profile parameters with anisotropy and preferred orientations include



**Fig. 1.** Schematic diagram representing the tobermorite structure showing the dreierketten chains of silica (4-fold coordinated, with in theory infinite chain length) and the 7-fold coordination of calcium atoms. P denotes pairing, B bridging tetrahedra,  $Q^1$  are the different silicon environments identified by NMR,  $Q^1$  are end of chains (1 neighbour),  $Q^2$  middle chain (2 neighbours). The interlayer hosts calcium (or others) ions and water molecules. Adapted from [36].

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