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.

Keywords: C-S-H, pore solution, aluminium, potassium, sodium

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_3S or C_2S), 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. ^{29}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 modeling [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, is 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, release some aluminium in the solution, i.e. $\text{Al}(\text{OH})_4^-$ 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-SiO₂-H₂O 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 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, ²⁹Si 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]. Figure 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.

Figure 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^n 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].

2.1 Relationship between the solid and the composition of the solution

The composition of C-S-H is generally characterized 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 Figure 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].

Figure 2: Relation between solid Ca/Si ratio of synthetic C-S-H and aqueous phase composition in the absence of aluminium or alkalis. Data from [1-17]; Data compilation courtesy of Colin Walker.

A recent careful reinvestigation [13] of the solution in equilibrium with the solid phases (see Figure 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 H₄SiO₄ can be plotted as a function of the logarithm of the activity of Ca²⁺ + 2pH [13], which corresponds to a linearized form of the solubility product written as (CaO)_x(SiO₂)(H₂O)_y + 2xH⁺ = xCa²⁺ + H₄SiO₄ + zH₂O, 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 Figure 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, 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 $\text{Ca/Si} \approx 0.8$ and 1 such that:

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

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

Figure 3: Solubility (diamonds) and stoichiometry (triangles) of C-S-H as a function of the calcium hydroxide concentration in solution reproduced from [13]. The activity of H_4SiO_4 is plotted as a function of the logarithm of the activity of $\text{Ca}^{2+} + 2\text{pH}$ (diamonds), which corresponds to a linearized form of the solubility product written as $(\text{CaO})_x(\text{SiO}_2)_y + 2x\text{H}^+ = x\text{Ca}^{2+} + \text{H}_4\text{SiO}_4 + z\text{H}_2\text{O}$, where x is the Ca/Si ratio and $z = y + x - 2$ (for details see [13]).

Although the linearization of the solubility products gives a single value of Ca/Si for each phase, Figure 3 clearly shows that their composition varies on a larger range: $\alpha\text{-C-S-H: } 0.7 < \text{Ca/Si}_{\text{eff}} < 1$, $\beta\text{-C-S-H: } 1 < \text{Ca/Si}_{\text{eff}} < 1.5$. 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}Si NMR studies demonstrated unambiguously that the higher the Ca/Si , the shorter the silicate chains (see Figure 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 Figure 4b) as the calcium concentration increase. As a consequence, Ca/Si of C-S-H increases.

Figure 4 : Evolution of the mean chain length of silica in C-S-H determined by ^{29}Si NMR in function of a) Ca/Si: circles [13], squares [16], triangles [40], empty diamonds [5], full diamonds [41] b) the concentration in silicon in solution: triangles [13], diamonds [14], squares [16].

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. Figure 5 illustrates the increase of the interlayer Ca with the calcium concentration in solution.

Figure 5 : Evolution of Ca content of the interlayer, calculated from data in [13], assuming a tobermorite like structure for C-S-H.

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, atoms coordinates) and profile parameters with including anisotropy and preferred

orientations include more than 100 parameters to be determined from 5 broad peaks! Among them, the approach developed by Battocchio [24] using the fragment method with MAUD software is particularly interesting; it preserves the geometry of the coordination polyhedra and the bond length during the refinement method which is a critical point as underlined by Richardson [23]. In the end these approaches merely confirm the tobermorite-like structure of C-S-H.

The pair distribution function extracted from total X-ray scattering [20] also supports a tobermorite-like structure and shows that the local environment of Si and Ca atoms remains unchanged with the evolution of the Ca/Si. The calcium atoms are mainly hepta-coordinated with CaO bonds length of 2.44 Å, in agreement with the values given by Richardson in his recent review of calcium silicate structures [23]. The authors mentioned a more important contribution of six fold coordinated Ca at high Ca/Si but this is probably attributed to portlandite which is observed in the diffraction patterns.

Finally, all the authors agree on the fact that the diffraction patterns are characteristic of a material with very small coherent diffraction domains, in the order of magnitude of the crystal cell, with a smaller dimension perpendicular to the plane of the interlayer (≈ 5 nm).

2.3 Water content

The water content of C-S-H is certainly the most difficult to determine precisely. The measured values depend on the drying conditions and on the discrimination between the C-S-H crystal water and the pore water. Proton NMR relaxometry is a good tool to separate the contributions [44-48] (see Figure 6. Figure 7a from [23] shows a large scattering of the data expressed in term of H_2O/Si in function of Ca/Si. Two parallel trend lines are obtained showing an increase of H_2O/Si with Ca/Si. The top line corresponds to preparations that were lightly dried and is more consistent with crystal-chemical arguments [23] and is in a good agreement with NMR data (Figure 7b). H_2O/Si varies between 1.5 and 2.2 when Ca/Si increases from 0.8 to 1.45. It has to be kept in mind that H does not represent only water molecules in C-S-H, but includes also OH from Si-OH and Ca-OH if present. The fraction of Si-OH decreases with Ca/Si while Ca-OH increases. One could assume from the representation given in Figure 7 that the water content increases with Ca/Si. In fact, if one considers tobermorite structural units, it is not the case: for example if we consider $Ca/Si=1$, with a chain length of 5, one obtains 1.6-2.0 H_2O per pairing silica ($1.3-1.6 \cdot 5/4$), while for a dimer structure ($Ca/Si = 1.5$) it is similarly 1.6-2.0 H_2O per pairing silica ($1.6-2.0 \cdot 2/2$).

3 C-S-H in cement paste

C-S-H obtained from a pure tricalcium (or dicalcium) silicate paste and in Portland cement paste has a Ca/Si higher than 1.45, an average value of 1.7 is generally reported [51] (and references therein), [52] [25-27, 48, 53]. The reason for the formation of high Ca/Si C-S-H is the high initial calcium concentration when alite dissolves and the pore solution is supersaturated with respect to the portlandite. Under these conditions the activity of calcium hydroxide is higher than in the case of synthetic C-S-H prepared in diluted solutions (described above) and thus a C-S-H richer in calcium precipitates. The silica concentrations are comparable to those of synthetic C-S-H in equilibrium with portlandite as also the chain length is close to 2, i.e. most of, but not all the bridging tetrahedra have disappeared.

This higher Ca/Si results also in a higher density. The density of 2.6 g/cm³ [28] and 2.7 g/cm³ [48] reported for C-S-H in cement paste are significantly higher than the tobermorite density (2.2 g/cm³ [54]). Published X-ray diffraction patterns of fully hydrated C₃S or C₂S are very few but all of them are very close to the C-S-H(I) patterns [30, 51, 55], characteristic of a tobermorite like structure. One can reasonably expect a structural continuity with C-S-H(I).

In a recent work it has been demonstrated from ab-initio calculations that the ²⁹Si NMR spectra of C-S-H in cement paste correspond to a silicon environment similar to the one in tobermorite and is significantly different from the one in jennite [56]. The question on how such a high Ca/Si can be compatible with a tobermorite – like structure has been discussed for a long time [57-59]. The two processes allowing the increase the Ca/Si of a tobermorite-like structure is the presence of calcium in interlayer and the removal of bridging silica tetrahedra [30, 55]. Pellenq et al. [32] proposed a model of C_{1.65}-S-H mainly based on the random elimination of silica tetrahedra in bridging position and pairing position. The removal of pairing silica would result in the formation of monomeric silica, which is not consistent with Si-NMR data. The removing of dimers results in local environments similar to jennite.

This is inconsistent with the molecular modeling reported above [56]. In addition the density of this modeled C-S-H, 2.45 g/cm³, is lower than the experimental one. In fact, all processes based on the elimination of silica tetrahedra decreases the density relative to C-S-H(I) as the volume of the crystal cell does not change significantly [21]. On the contrary the addition of calcium in interlayer increases the density in agreement with the experimental observations.

Energy minimization of molecular dynamics simulations on models based either on the elimination of silica tetrahedra or on the addition of calcium in the interlayer shows that addition of calcium in the interlayer gives more stable structures [35]. However, the structures obtained from molecular modeling have to be taken with caution. The bond length, cell parameters depend on the force fields used in case of molecular mechanics, they could be smaller or larger than the experimental one. In any case, the modeled structure should respect the crystal chemical features of calcium silicates in term of coordination and bond length [60] which is not always the case. The origin of the very small coherent diffraction domains, giving a quasi amorphous material, is not completely clear. The small size of the particles, the fact that millions of structures with the same composition but with different location of the defects in the crystal cell exist and the high contribution of the surface could contribute to that.

4 Effect of other ions in solution

The pore solution of a cement paste is much more complex than a C_3S paste and contains ions other than calcium, silicon and hydroxides. The alkali sulphates dissolving from the clinker give concentration in solution 5 to 6 orders of magnitude higher than the silicon concentration. Hydroxide concentration can be 5 to 10 times higher. As a consequence, the calcium concentration is lower than in the synthetic C-S-H samples discussed in section 2.1. Once the sulphates are depleted in the pore solution to form ettringite, the aluminium concentration in solution can reach a few mM [61-63]. All these ions interact with C-S-H and similar to calcium and silicon, also aluminium, alkali and sulphate uptake in (synthetic) C-S-H show a strong correlation with dissolved aluminium [64-66], alkali [67-70] and sulphate concentrations [71, 72]. Most of the studies discussed below have been performed with synthetic C-S-H and in more or less diluted suspensions to make the analyses possible but the results should apply to cement paste as well.

4.1 Sodium and potassium

More alkalis are taken up by C-S-H in the presence of higher alkali concentrations and lower calcium hydroxide concentration, conditions which correspond to low-Ca/Si C-S-H, in synthetic C-S-H ([69, 70, 73] and Figure 8a) and for low pH cements [74-76].

This behaviour reflects the competition between alkali cations with calcium cations to compensate the surface charge of C-S-H. Indeed, a net negative charge occurs at the C-S-H surface due to the deprotonation of $\equiv\text{SiOH}$ to $\equiv\text{SiO}^-$ sites. The higher the pH value, the higher the negative charge on the surface [73, 77, 78] as shown in Figure 8c. Calcium can balance this negative charge and even overcompensate it, as $\equiv\text{SiOCa}^+$ may be formed at the C-S-H surface, which leads to positive zeta potentials in the presence of higher calcium concentrations ([73, 78], Figure 8c). An increased deprotonation of the silanol sites at higher pH values leads to the sorption of more calcium on C-S-H and thus to higher measured positive charge. The term sorption is used in the present paper in a broad sense indicating uptake in the interlayer or on the surface of C-S-H and does not imply any specified uptake mechanism or binding site of C-S-H.

Figure 8: a) Na/Si and K/Si and b) calcium concentrations in C-S-H in equilibrium with 100-400 mM NaOH or KOH. Experimental data from [69, 70, 79, 80]. The experimental data from different authors show some scattering as the measurement of alkali uptake by C-S-H is associated with a significant experimental error and different factors such as equilibration time, water to solid ratio, alkali concentration and phase separation techniques can influence the result. c) Zeta potential versus bulk solution pH for i) 20 mM calcium (empty triangles), ii) pure Ca(OH)_2 solution (empty circles) and iii) <1 mM Ca(OH)_2 (empty squares). Curves: simulations; symbols: experiments. Adapted from [78].

As the alkali ions compete with calcium ions to compensate the negative charge and as bivalent cations such as calcium are strongly preferred compared to monovalent sodium or potassium [73] due to stronger electrostatic interaction, high calcium concentrations can inhibit alkali uptake. As a consequence, the alkali uptake by high Ca/Si C-S-H, which is in equilibrium with high calcium concentrations, is low [69, 70, 73, 80, 81] as shown in Figure 8b, even if the alkali concentration is much higher than the calcium concentration, 2 orders of magnitude in the case of the data presented in Figure 8b. In contrast the alkali uptake is strongly enhanced in the presence of low Ca/Si C-S-H; the maximum Na/Si and K/Si ratios reported are in the range 0.3-0.5 [69, 80, 81].

The replacement of calcium by sodium or potassium ions is mirrored by an increase of the calcium concentrations in the presence of high concentrations of alkali nitrates or chlorides as shown in Figure 9a for Ca/Si = 0.8. Similar observations are reported for Ca/Si ranging from 0.67 to 1.3 [10, 12, 68, 82, 83]. At high Ca/Si ratios, the increase in calcium concentration is not very distinct, as calcium concentration is limited by the solubility of portlandite.

In the presence of alkali hydroxides the pH increases which leads i) to a higher de-protonation of the silanol sites at low Ca/Si ratios and thus to more negatively charged C-S-H [73, 84] and ii) to lower calcium concentrations in equilibrium with C-S-H as shown in Figure 9a. Both factors contribute to an increased binding of sodium and potassium in solutions containing hydroxides compared to solutions with nitrates or chlorides as shown by the higher alkali/Si ratio of the C-S-H in Figure 9b.

Figure 9: a) Effect of alkalis on the calcium concentrations in the aqueous solution. b) Alkali binding. Solutions in equilibrium with synthetic C-S-H ($\text{Ca/Si} = 0.8\text{-}0.83$) in equilibrium with alkali nitrate [68]:

squares; alkali chlorides: circles [85] and crosses [12]; alkali hydroxides: diamonds [68] and triangles [80].

Some researchers report higher sodium than potassium sorption [86, 87] on C-S-H, while others [68, 88] observed a clear preference of potassium compared to sodium uptake. Bach et al. [68] argued that the larger size of solvated sodium ions compared to smaller size of solvated potassium ion would hinder the uptake of sodium in the interlayer sites of the C-S-H. Other studies showed no significant difference between sodium and potassium uptake in synthetic C-S-H [69, 70, 80] or in hydrated Portland cements [61, 62, 67]. The scatter of results reported in the literature could be related to i) the large experimental error associated with the measurement of alkali uptake, ii) an influence of the synthesis protocol (alkali addition to prefabricated C-S-H versus co-precipitation) and iii) different mechanisms responsible for alkali uptake in C-S-H, such that the results may vary depending on the alkali concentration, the C-S-H composition and the presence of other ions or solids. In fact, ^{23}Na NMR data indicate the presence of two different environments for sodium in C-S-H [18, 89]. A broad signal at ≈ 10 ppm has been assigned to Na with a low mobility, "bound Na". A sharper signal was assigned either to "mobile Na" or NaCl or to highly symmetrically bound Na. The fraction of bound Na is observed to decrease strongly with increasing Ca/Si ratio in the presence of relatively low Na concentration (total Na/Si = 0.1; [89]) and to decrease much less in the presence of higher Na concentration (NaCl = 0.5 M; [18]).

Figure 10: Relative fraction of signals observed by ^{23}Na -NMR determined by [89]. A sharp resonance has been assigned to symmetrically bound or mobile Na, a broad signal at -10 ppm to “bound” sodium.

The presence of charge balancing potassium or sodium instead of calcium in the interlayer and on the surface does not significantly change the structure of C-S-H. However, it can lead to the availability of more calcium to form the main calcium oxide layer at a constant total Ca/Si ratio as shown schematically in Figure 11b. The resulting increase of the calcium oxide to silica ratio in the C-S-H main layer (while the total Ca/Si which includes both main layer calcium and charge balancing calcium remains constants), results in shorter silica chain lengths and a decrease of the “dreierketten” chain length which can be observed by ^{29}Si NMR for Ca/Si ≤ 1 (Figure 11a) in the presence of alkali hydroxide. A comparison of Si-NMR data reported for synthetic C-S-H prepared in the absence and presence of different alkali salts [18, 66, 90, 91] confirms the decrease of the silica chain length in the presence of high alkali concentrations as illustrated in Figure 11c.

At higher Ca/Si ratios, where dimer chain length and high calcium concentrations dominate, and where portlandite can possibly be present, no significant changes are visible as at higher calcium concentrations the alkali uptake is suppressed [69, 70, 73] such that no significant changes in the C-S-H structure occur.

Figure 11: a) ^{29}Si NMR of synthetic C-S-H ($\text{Ca/Si} = 1$) without and with 0.5 M KOH, b) schematic redistribution of charge balancing calcium from the interlayer to the main calcium oxide layer, adapted from [66]. Dark circles: calcium; light (blue) circles: K; triangles; silica tetrahedra. c) silica chain length as a function of the Ca/Si in C-S-H determined in solutions with and without alkalis (C-S-H: circles [13, 18, 40], crosses [16], diamonds [66, 92, 93], and triangles [91]; white Portland cement (WPC) [94]: squares). The lines are eye-guides.

The replacement of charge balancing calcium in C-S-H by alkali ions also leads to a decrease of the basal spacing of C-S-H at lower Ca/Si ratios [66, 68] and to changes in the chemical shifts observed

by ^{29}Si NMR. However, the main factor affecting the basal spacing is the amount of water present, such that the measured basal spacing varies strongly depending on the drying applied before the measurement. Typically the shielding of silica sites by alkalis and protons is weaker than by calcium such that a less negative chemical shift of silica neighbouring alkali ions are observed by ^{29}Si -NMR measurements [95-97]. In fact, a 1-3 ppm less negative chemical shift is observed for Q^1 and Q^2 silica in the presence of high alkali concentrations ([18, 66, 90], Figure 11a) supporting the replacement of calcium by alkalis in the vicinity of the silica chains. Corresponding observations have also been made for C-S-H with aluminium [66, 92].

4.2 Aluminium

The comparison of the Al/Si ratio measured in C-S-H and dissolved aluminium concentrations in Figure 12a confirms a clear relation between aluminium concentrations and Al/Si ratio in C-S-H.

On this figure Al/Si in C-S-H shows a quasi linear relationship with the logarithm of the aluminium concentration in solution except the vertical trends at very low aluminium concentrations. The quasi linear regime corresponds to experiments made with both synthetic C-S-H and cement pastes as shown in Figure 12b. The vertical trends correspond to long term experiments with synthetic C-S-H at low Ca/Si ratios ($= 0.6$ and 0.8), where Al/Si ratio of 0.1 or higher are in equilibrium with very low aluminium concentrations in the aqueous phase, i.e. below the detection limit of 0.004 mM aluminium. In these experiments in addition the precipitation of strätlingite, katoite and/or AH_3 has been observed which limits the aluminium concentration in the aqueous solution, however the Al/Si remains high[14, 66]. In contrast in short-term experiments, where aluminium solutions are added to C-S-H, for Al/Si ratios of the same order no precipitation of such phases is observed, either because the solution is undersaturated or because the degree of supersaturation is too low to observe the precipitation during the experiment. This observation indicates a high affinity of aluminium uptake at low Ca/Si and possibly an irreversibility of the binding. It seems that a high aluminium concentration during the synthesis is needed to get a high Al/Si and high Al/Si is conserved even if the aluminium concentration decreases finally due to the precipitation of low soluble phases. It is also what it was observed for a C-A-S-H sample with high Al/Si obtained in high Al concentration after re-equilibration in pure water ([98], p77). This is also in agreement with the strong stabilisation of the C-S-H structure by substituting silicon by aluminium in bridging tetrahedra predicted by ab-initio calculations [84].

Figure 12: Effect of dissolved aluminium concentrations in the aqueous solution on the aluminium uptake in C-S-H a) with different Ca/Si ratio in the absence of alkalis and b) with $\text{Ca/Si} \geq 1$ in the absence and presence of KOH and in cements. Short-term experiments (equilibration time 1 week, addition of aluminium to pre-synthesised C-S-H): squares [64, 65], triangles: [13], diamonds [71]. Long-term experiments (equilibration time 3-24 months, co-precipitation): circles [14, 66]. Data for Portland cements (PC) [99, 100], for Portland-fly ash cements (PC+FA) [99, 101] and for portlandite-free blends [74, 75, 99, 102, 103].

The presence of alkali hydroxide increases the pH values and destabilises strätlingite, aluminium hydroxide and katoite, which leads to higher aluminium concentrations and thus to increased aluminium uptake in synthetic C-S-H [66] as shown in Figure 12b. In the presence of 0.5 M KOH a

maximum Al/Si of 0.23 is observed. This agrees with the observation of an increased aluminium uptake by Portland cement in the presence of NaOH and NaAlO₂ containing solutions [94].

The incorporation of aluminium in C-S-H is well characterised by ²⁷Al-NMR. Aluminium is present in 3 different coordination environments, tetra-, penta- and hexa-coordinated, noted as Al_{IV}, Al_V and Al_{VI}, which indicates different binding sites.

As shown in Figure 13, Al_{IV} is the dominant environment in C-S-H of low Ca/Si, i.e. at low calcium hydroxide concentrations. Al substitutes Si in bridging tetrahedra, in both Q² and Q³ position. The Q³ position in anomalous tobermorite corresponds to the crosslinking of two chains of different layers. This is not the case in C-A-S-H, Q³ positions correspond to the cross linking of two adjacent chains of a same layer, other wise the basal spacing between the layers would be much smaller than that observed experimentally by XRD [14, 104]. As the Ca/Si increases, the Al in Q³ position disappears and the fraction of Al in bridging position, Q^{2b}, decreases. A third Al_{IV} signal appears at Ca/Si above ≈1. It is attributed to Al in bridging position, Q^{2b}, charge balanced by calcium cations [105] or to aluminium in pairing position, Q^{2p} [64, 89, 106, 107]. The chemical shift of this signal, its quadrupolar constant and mass / charge balance calculations favour the second hypothesis [64], which is also compatible with the ²⁹Si NMR spectra. Ab initio calculation of the Si-Al substitution in a tobermorite-like structure show that aluminium in pairing position is energetically very unfavourable [84]. However those calculations have been made using a fully protonated structure, while the surface of C-S-H tends to be deprotonated particularly for high Ca/Si C-S-H [77]. Thus the nature of this third Al_{IV} signal needs to be clarified.

Figure 13: Evolution of the population of the different environment of Al in C-S-H in function of its calcium to silicon ratio; from Renaudin et al. (Al/Si=0.1) [89] and Pardal et al. (Al/Si=0.19) [64] Lines are intended as eye-guides only.

Whatever the total Al/Si ratio, the Al_V contribution remains roughly constant with Ca/Si and is close to 10% of total aluminium. The location of the Al 5-fold coordinated is not clearly identified yet. It has been postulated that could correspond to aluminium present in the interlayer [89, 105, 106, 108].

For 6-fold coordinated aluminium, three different types of environment have been identified to be present in C-A-S-H, assigned Al_{VIa} , Al_{VIb} and Al_{VIAFm} in Figure 13. The data summarised in Figure 13 results from two different sets of experiments. The data indicated by filled symbols have been prepared by mixing appropriate amounts of lime and silica in a calcium aluminate solution (Renaudin et al. [89]) using Al/Si=0.1. The data indicated by empty symbols were obtained equilibrating pre-prepared C-S-H in a calcium aluminate solution using Al/Si=0.19 (Pardal et al. [64]). In both cases, hexa-coordinated aluminium species labelled Al_{VIa} are observed corresponding to about 10% of the

total Al with no variation or a slight decrease if the Ca/Si of C-S-H increases. Al_{Vla} is observed even at low Ca/Si ratio, i.e. under conditions where the pore solution is undersaturated with respect to AFm phases such as strätlingite and monocarbonate. Al_{Vla} is probably present in interlayer of C-S-H. The presence of Al_V and Al_{Vla} results in an increase of the basal spacing of C-S-H obtained from XRD pattern refinements on dried C-S-H samples. A second signal, labelled Al_{VIAFm} , is observed only in the second type of preparation when pre-synthesized C-S-H was in contact with aluminium in solution (empty circles) when the equilibrium solution were supersaturated with respect to AFm phases which were observed in the XRD patterns. In the first type of preparation (filled circles), when C-S-H precipitated in contact with aluminium in solution, not a signal corresponding to Al_{VIAFm} , but to Al_{Vlb} was observed [64]. Its intensity increased significantly if the solution were supersaturated with respect to AFm even if no other phases are observed in the XRD patterns. Al_{Vlb} is attributed to an amorphous aluminate hydrate associated with the C-A-S-H precipitation called third aluminium hydrate (TAH) [109]. It could correspond to the intercalation of a single layer of AFm between precipitating C-S-H or to a separate phase at the surface of C-S-H.

As discussed above, at Ca/Si of 1.0 and higher, i.e. at higher calcium hydroxide concentration, aluminium binding in octahedral sites, the so-called third aluminium hydrates (TAH), becomes more important ([64, 89, 109], Figure 13). At $Ca/Si \geq 1.0$, the Al/Si ratio in C-S-H increases with the aluminium concentration; the same trends are observed both in short-term experiments [13, 64, 65] and long-term experiments [14, 66]. Also the aluminium uptake in the C-S-H of ordinary Portland cements and Portland cements blended with silica fume or fly ash [75, 99] shows the same behaviour as shown in Figure 12b and in different studies [66, 75, 99]. In agreement with the ^{27}Al -NMR results, which indicate the presence of different sites for Al-binding in C-S-H depending on the Ca/Si ratio of the C-S-H [64, 89, 109], the comparison between aluminium concentrations and the Al/Si ratio in C-S-H confirms the presence of at least two different binding sites. At low Ca/Si the preferential uptake of Al in the silica chain seems very favourable as confirmed by the very low equilibrium concentrations. At higher Ca/Si ratios, where the chain length decreases aluminium is partly taken up in TAH resulting in higher equilibrium aluminium concentrations in the solution. If at intermediate Ca/Si ratio two or three different aluminium binding sites with different affinity are present in C-S-H, sorption isotherms recorded as function of the aluminium concentration could indicate the relative amount of such sites. Such measurements, however, are presently hampered by the small experimental window between the analytical detection limits of aluminium by ICP-OES or IC measurements (generally 0.004 mM)

and the aluminium concentrations where strätlingite or katoite precipitate (0.01 - 0.05 mM, depending on the Ca/Si ratio). The use of alkali hydroxides and/or of measurements methods with lower detection limits such as ICP-MS may allow in the future the record of sorption isotherms over a reasonable range of aluminium concentrations.

5 Thermodynamic modelling

5.1 Modelling of the C-S-H-solution interface

Due to its very high surface/solid ratio, most of the properties of C-S-H are governed by the interface with the pore solution. Minerals develop a charge at their surface when they are immersed in an aqueous solution and so does C-S-H. Due to electrostatic interaction between the charged surface and ions in solution and due to thermal agitation, solvated ions accumulate at the surface-solution interface and form an ionic cloud, the so-called electric double layer (EDL), which charge balances the surface. The electrostatic interactions in the EDL depend on the surface charge density and control many properties which are important in cement science such as aggregation, growth, material cohesion, ion retention and transport, and interaction with admixtures. In the case of C-S-H the formation of the surface charge results from the ionisation (deprotonation) of the silanol groups present at the surface of the layers in the alkaline solution: $\equiv\text{SiOH} + \text{OH}^- = \equiv\text{SiO}^- + \text{H}_2\text{O}$. These silanol groups are present for pairing silica (Q^1) and for bridging silica (Q^{2B}). According to the tobermorite-like structure, the silanol density is estimated to be 4.8 SiO/nm^2 [110]. When the pH of the solution increases more and more silanol sites are deprotonated and the surface charge density increases.

The determination of the surface charge density as a function of the ionic content of the solution is not trivial. The most used theory is based on the Poisson-Boltzmann equation (PB) but this fails to describe the C-S-H/solution interface as it is applicable only to monovalent ions and weakly charged solids [110]. The PB equation is, for example, not able to explain the charge reversal of C-S-H identified by zeta potential measurements as a function of the Ca(OH)_2 concentration (see Figure 8c). Thus, it is necessary to take into account all the interactions, i.e. ion-ion, ion-site and site-site correlations. This has been done with a simple microscopic model where the surface is described by a plane with uniformly distributed sites in contact with water described by its dielectric permittivity and ions described as hard spheres. Labbez et al. developed a Monte Carlo simulation method in the Grand Canonical ensemble (constant volume, temperature and chemical potential) that permits the

simultaneous prediction of surface charge, zeta potential and the content of the EDL as a function of the composition of the solution [73, 78, 110, 111]. In a first approach, an arbitrary pK equal to the first deprotonation constant of the silicic acid (pK=9.8) has been used, which gave a very good agreement with experimental results [73]. More recently, the pKs of the different silanol sites have been calculated from ab-initio molecular dynamics (AIMD) simulations [77]. Four different acidities were obtained depending on the configuration of the silanols in the structure, two sites with a low pK and two with a high pK. This model allows also the determination of adsorption isotherms of different poly electrolytes [112, 113]. However it does not allow for the ionic specificity to be accounted for yet. The ions of the same valence can only be differentiated by the diameter of the hard sphere. Ion specificity could be introduced by developing an effective potential determined, e.g. by ab-initio calculation, and used in place of the purely coulombic interaction potential.

5.2 Geochemical modelling

A number of models able to describe the solubility of C-S-H have been published during the last decades. These models for C-S-H are based either on simple empirical fits [4, 114-116], on the definition of a number of different solid C-S-H compositions [117-119] to represent the gradual changes observed in the aqueous solutions, on solid solution between different end-members [120-123] or on the sorption of calcium, silica and other ions on C-S-H [13]. These models are generally able to describe the experimentally observed solubility data satisfactorily as shown in Figure 14. The comparison of the results of different geochemical models, i.e. i) the use of 3 stoichiometric C-S-H compositions [124]: orange dotted line, ii) solid solution model [122]: blue dashed line and iii) sorption model [13]: black solid line, shows in all cases roughly similar trends. The biggest difference is observed for the model (i) using 3 stoichiometric C-S-H compositions [124], as the use of only 3 solid phase compositions ($C_{1.6}SH_{2.58}$, $C_{1.2}SH_{2.06}$, and $C_{0.8}SH_{1.54}$) leads to step wise changes of the aqueous composition, which follow the observed changes less well than the other two approaches shown in Figure 14. In many cases such a simplified representation can be sufficient to follow the changes in the solid and liquid phases as e.g. shown in [119, 125]. Some differences can also be observed between the solid solution model (ii) based on an ideal solid solution between $C_{1.5}SH_{2.5}$ (dimer), $C_{1.25}S_{1.25}H_{2.5}$ (pentamer) and $CS_{1.5}H_{2.5}$ (infinite chain) [122]) and the sorption model (iii) based on $C_6S_4H_2$ (dimer), C_2S_2H (pentamer) and $C_4S_5H_2$ (infinite chain) [13]). These differences are mainly related to the different data sets used to fit the models, i.e. the data of Chen and Thomas [16] for the

solid solution model [122] and the data set of Haas and Nonat for the sorption model [13]. Another difference between these two models can be observed in the higher Ca/Si ratio (up to 1.73), which can be reached in the sorption model due to the uptake of Ca as charge balancing ion, while the Ca/Si in the tobermorite based C-S-H is limited to 1.5. It should be noted, however, that higher Ca/Si can be reached if the other the solid solution model, CSHQ, by [122] is used (not shown here). Each of these models has some additional possibilities. The stoichiometric C-S-H composition model [124] and the solid solution model [122] can also be used at higher temperatures, while the sorption model [13] calculates in addition surface charge.

Which thermodynamic model to use, thus, rather depends on the parameters to be calculated, the personal preferences, on the ability of the software used (some softwares do not allow the use of solid solution models) and on the general database used. The stoichiometric C-S-H composition model [124] should be used together with the Thermoddem database [126], the solid solution model [122] with the psi/nagra database [127, 128] (which contains in contrast to other two databases a aqueous $\text{CaSiO}_2(\text{OH})_2^0$ complex) and the sorption model [13] with the PHREEQC database [129].

Figure 14: Relation between solid Ca/Si ratio of C-S-H and aqueous phase composition in the absence of aluminium or alkalis. Concentration data from [1-17], mean silica chain length (MCL) data from [5, 13, 14, 16, 18, 40, 91, 97, 130]. Modelled: i) three stoichiometric solid C-S-H compositions [124]: orange dotted line, ii) solid solution model [122]: blue dashed line and iii) sorption model [13]: black solid line.

The recently developed sublattice solid solution models [122, 131, 132] and the sorption model [13] are closely related to the structure of C-S-H and tobermorite, and therefore able not only to model the solubility and the chemical composition of the C-S-H, but also to predict the mean silica chain length consistent with the ²⁹Si NMR data (see Figure 14). In such models, the C-S-H stoichiometry is represented by building units to describe the C-S-H structure, such as silica dimer, CaO in the main layer, bridging tetrahedra, charge balancing ions, A model of this kind seems complicated, but has

the advantage that it has the closely related to the C-S-H structure. In addition, such models can easily be extended to account for the uptake of aluminium, calcium, alkalis or other ions by adding them to the respective building units. Recent extensions of such C-S-H models allow aluminium uptake to also be modelled based on the sorption approach [13] or aluminium and alkali uptake in low Ca/Si C-S-H using a solid solution approach [133]. Figure 15 compares experimental results from [13, 64, 66] with the calculations using the two different models (at Ca/Si = 1; the precipitation of strätlingite and aluminium hydroxide was suppressed in the calculations to correspond to the conditions of the short-term experiments). Both models are able to reproduce the gradual increase of Al/Si. Both models indicate a slightly higher aluminium uptake at lower Ca/Si, for details see [13] and [133]. The surface sorption model, which was optimized based on the data shown in Figure 15 thus shows a very good agreement with these data. The solid solution model, which was optimized for alkali activated slags, i.e. the presence of high alkali concentrations, overestimates the aluminium uptake moderately but predicts the increase of the MCL very well. However, as in the case of C-S-H, both modelling approaches are well able to reproduce the observed changes in these low Ca/Si C-S-H systems.

Figure 15: Effect of dissolved aluminium concentrations on the aluminium uptake and mean chain length (MCL) in C-S-H. Short-term experiments: squares [64], triangles: [13]; long-term experiments: circles [66]. Modelled Al/Si and MCL: solid solution model [133]: dashed lines; sorption model [13]: solid lines. The dotted vertical line indicates the aluminium concentrations above which strätlingite and AH₃ are expected to precipitate in long-term experiments at Ca/Si = 1.

449 6 Conclusions and outlook

450

451 Calcium silicate hydrates (C-S-H) gels prepared from mixing lime and silica in water have a Ca/Si
452 between 0.7 to about 1.5. Their structure can be described using a defect tobermorite model, where
453 bridging tetrahedra are removed at higher calcium to silica ratios and more calcium is present in the
454 interlayer. The variation of C-S-H composition is mirrored in the composition of the aqueous phase.
455 The silica chain length in C-S-H increases with the silicon concentration. Similarly the calcium content
456 in the interlayer space increases with the calcium concentrations. C-S-H present in Portland cement
457 pastes or from alite pastes has a higher Ca/Si ratio, on average $\text{Ca/Si} = 1.7$, due to initially the higher
458 availability of calcium in such systems.

459 Sodium and potassium are taken up in the interlayer space, preferentially at low calcium
460 concentrations and thus by low Ca/Si C-S-H as present in e.g. in Portland cements blended with fly
461 ash or silica fume. At a constant Ca/Si ratio, more alkalis are bound at higher pH than at lower pH
462 values, as high pH values lower the calcium concentrations. The presence of sodium and potassium in
463 the interlayer does not significantly change the structure of C-S-H but can at high concentrations
464 decrease the interlayer distance and shorten the silica chain length.

465 Aluminium uptake in C-S-H increases strongly with higher aluminium concentrations in the solution.
466 Aluminium in C-S-H can be present in different sites depending on the calcium to silica ratio. At low
467 Ca/Si, aluminium substitutes silicon in the bridging position, the uptake of aluminium increases the
468 chain length and crosslinking of adjacent chains has been observed. At higher Ca/Si, aluminium in Q^3
469 position disappears and the fraction of aluminium in bridging position, Q^{2b} , decreases. At all Ca/Si
470 ratios approximately 10% of the aluminium is present as penta-coordinated, Al_V , which has been
471 postulated to represent aluminium present in the interlayer. Hexa-coordinated aluminium, Al_{VI} ,
472 becomes important at $\text{Ca/Si} > 1$ and is attributed to the presence of an amorphous aluminate hydrate
473 associated with C-S-H.

474 Recently developed sublattice solid solution models and the sorption thermodynamic models are
475 closely related to the structure of C-S-H and tobermorite, and therefore able not only to model the
476 solubility and the chemical composition of the C-S-H, but also to predict the mean silica chain length

consistent with the ^{29}Si NMR data. In addition, such models have been extended to account for the uptake of aluminium, calcium, alkalis or other ions.

In the last few years many experimental studies have been published which focus on investigating synthetic C-S-H structure and solubility and the effect of the presence of different ions and many more such studies are expected to appear in the next years. This growing collection of systematic data of the relation between aqueous and solid phase composition, of spectroscopic and XRD data and the advancement in molecular modelling has led in the last years to a better and more detailed understanding of the C-S-H structure and the different factors influencing it. This more detailed understanding has also enabled the development of geochemical models which take into account the structure of C-S-H are able to model aluminium uptake and the changes in the mean chain length. However, there are still some open questions associated with C-S-H such that both the investigations of the effect of different parameters (e.g. presence of other ions, temperature, relative humidity, rate of formation, ...) as well as the development of geochemical and molecular models will continue in the next years.

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