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The structure and stoichiometry of C-S-H

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Abstract

This review relates to the models describing the structural evolution of calcium silicate hydrate (C-S-H) at the crystal–chemical level as a function of composition in terms of calcium to silicon ratio. The different models are compared and discussed in the light of recent spectroscopic and microscopic data. Taking into account the structure and the morphological properties of C-S-H, a surface reaction thermodynamic model has been proposed and discussed to predict and correlate the chemical and structural evolution of C-S-H with solution chemistry.

Keywords: Calcium silicate hydrate (C-S-H); Crystal size; Crystal structure; Spectroscopy; Thermodynamic calculations

1. Introduction

Calcium silicate hydrate (C-S-H) has long been the object of many studies of its structure and composition. Taylor made important contributions to the field by intensive study of the crystal chemistry of the phases of the lime–silica–water system at different temperatures [1–13]. As early as 1950, he had defined the crystal properties of tobermorite-like C-S-H, C-S-H(I) [1] and jennite-like C-S-H, C-S-H(II) [9] as well as their thermal decomposition and stoichiometry [5,9]. More recently, he proposed a nanostructural model for C-S-H occurring as hydration products of tricalcium and dicalcium silicates or Portland cement pastes based on a mix of these two limit phases [14]. Both tobermorite and jennite have a layered structure based on a calcium sheet flanked on each side by linear silicate ‘‘dreierketten’’ chains as demonstrated by ^{29}Si MAS NMR measurements [15–17]; that is, the chains are kinked in such a way as to repeat at an interval of three tetrahedra. Two adjacent tetrahedra coordinate to the calcium ions of the layer, while the third, termed a bridging tetrahedron, bridges two successive dimers. In tobermorite, two oxygens from nonbridging tetrahedra coordinate to calcium ions [18,19] while in jennite, only one oxygen of the nonbridging tetrahedra coordinate to the calcium ions of the sheet; the other oxygen is provided by hydroxide ions [13,20]. 14 Å-tobermorite may be described by the limiting formula $Ca_4H_4Si_6O_{18}.8H_2O$ (Ca/Si = 0.66) and jennite by $Ca_8H_4Si_6O_{18}(OH)_8.6H_2O$ (Ca/Si = 1.33). In each case, two protons are carried by binding bonds of each bridging tetrahedron. According to Taylor [14], to account for dehydration data, one of these two protons must be substituted by 1/2 Ca^{++} ion in the interlayer leading to the formulae $Ca_5H_2Si_6O_{18}.8H_2O$ (Ca/Si = 0.83) and $Ca_9H_2Si_6O_{18}(OH)_8.6H_2O$ (Ca/Si = 1.5) for tobermorite and jennite, respectively. According to Taylor [14], C-S-H(I) structure and stoichiometry may be derived from a tobermorite model by eliminating a part or the whole of the bridging tetrahedra and C-S-H(II) derived from the jennite model; the limiting formulae should be then $Ca_5H_2Si_4O_{16}.8H_2O$ (Ca/Si = 1.25) and $Ca_9H_2Si_4O_{16}(OH)_8.6H_2O$ (Ca/Si = 2.2), respectively, in which silicate chains are only dimers. The results of TEM microanalysis obtained by Richardson and Groves [21] about the bimodal distribution of Ca/Si in the products of early hydration of a cement paste centred around 1.2 and 2.3, suggesting that, at early age, C-S-H may be precipitated either as a defect dimeric tobermorite type, or as a defect dimeric jennite type. Taylor suggested that as the paste ages, the bimodal distribution reduces and eventually disappears because regions of low and high Ca/Si ratio slowly interact, producing material of intermediate composition having mainly a jennite-type structure. In his last view, contrary to his initial model, Taylor [22] suggested that the tobermorite-like and jennite-like regions

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could be poorly defined and could merge into each other within individual layers.

Cong and Kirkpatrick [23] apparently disagree with the Taylor model. They essentially argue that the occurrence of jennite-type C-S-H(II) is extremely rare. Based on their extensive study of synthetic C-S-H of variable Ca/Si using ^{29}Si and ^{17}O MAS and CP-MAS NMR, they proposed a defect tobermorite-like model for C-S-H with Ca/Si ratio less than 1.5. But in fact, both models are very similar and differ essentially by the fact they describe different ranges of stoichiometry: Taylor's model focused on C-S-H with Ca/Si>1.5 whereas Cong and Kirkpatrick's model focuses on C-S-H with Ca/Si < 1.5. In both models, some of the silicate portions of the structure derive from tobermorite with missing bridging tetrahedra, others from jennite with calcium of the main layer charge balanced by OH^- and a part of the protons bound as SiOH are substituted by calcium ions. In Taylor's model, the jennite-type parts would have to be preponderant to reach high Ca/Si values, whereas in Cong and Kirkpatrick's model, the tobermorite-type parts would be the most abundant but only relatively low Ca/Si ratios can be reached. Both also suppose a very disordered structure.

Nonat and Lecoq [24,25] proposed a slightly different model to account for the evolution of Ca/Si in the whole range from 0.66 to 2. Like Cong and Kirkpatrick's model, it is based on data in equilibrium (probably metastable) obtained from both $CaO-SiO_2$ mixes and fully hydrated C_3S samples in solution in which the lime concentration is maintained constant. Thus, the solid Ca/Si ratio is fixed by the value of this concentration and does not change in the course of hydration. Contrary to either Taylor's or Cong and Kirkpatrick's models, it is not essential to suppose a disordered structure. Over the whole range of Ca/Si ratios, the X-ray diffraction (XRD) patterns of C-S-H always resemble the tobermorite pattern; the d spacing corresponding to the basal plane changes only slightly even at high Ca/Si ratio close to 2. The main difference from the two previous models is that the layers would not contain jennite-like regions; that is, calcium in the main plane would not coordinate to OH^-. To reach high Ca/Si values, Nonat and Lecoq's model supposes that most of the interlayer crystallographic sites of the tobermorite model are occupied by calcium ions which are charge balanced by OH^- in interlayer positions. Indeed, each missing bridging tetrahedron makes available two crystallographic sites for OH^- and allows for accommodation of one $Ca(OH)_2$ unit in the structure. This model is just as consistent with spectroscopic data as the previous ones including those which evidence Ca–OH groups because none are sufficiently precise to state if the relevant Ca ions are in the main plane or in the interlayer, or both.

These three models essentially differ as follows: Taylor's model needs to consider a mix of two phases at a more or less large scale, whereas Cong and Kirkpatrick's and Nonat and Lecoq's models need only one phase, which, in Cong and Kirkpatrick's model, is supposed to be very disordered. The aim of this paper is on the one hand, to discuss the relevance of these different C-S-H structural models by confronting them with recent textural and structural data and, on the other hand, to unify the structural description and the evolution of the C-S-H stoichiometry by a predictive thermodynamic approach.

2. One C-S-H phase or more?

Analytical results [26,27] and NMR data [28] from previous studies suggest the existence of an invariant point in the $CaO-SiO_2-H_2O$ diagram corresponding to an equilibrium between two C-S-H phases with, respectively, Ca/Si < 1 and Ca/Si>1.1. Recent NMR data from enriched samples perfectly confirms the evidence of equilibrium between two phases from the discontinuity in the evolution of most of the physical properties versus Ca/Si, i.e., XRD d spacing, Q^n chemical shifts and proton $T_{1\rho}$ values [29]. The highest values of Ca/Si ratio of C-S-H in the reported experiments are generally lower than 1.5 when the sample is free of portlandite. These values are always lower than those found in a cement paste where portlandite is typically precipitated along with C-S-H. Thus, it appears that having a supersaturated aqueous phase with respect to calcium hydroxide, even for a short period, is required to reach the highest Ca/Si ratios. Indeed, a ^{29}Si NMR study of the products obtained by Ca_3SiO_5 hydration in, respectively, undersaturated and supersaturated solutions with respect to portlandite, reveals a discontinuity of the variation of the silicate chain length, suggesting the existence of a third C-S-H phase at high lime concentration [30]. This result has been confirmed by obtaining pure C-S-H samples by full hydration of Ca_3SiO_5 in different calcium hydroxide solutions in which the concentration is kept constant by a specific device [25]. The variation of the Ca/Si ratio versus lime concentration exhibits a discontinuity between 1.5 and 1.8 close to [CaO] = 22 mmol/kg characteristic of another invariant point at which two solid phases are in equilibrium with the solution. The author then proposed the existence of three different C-S-H phases: α-C-S-H ($0.66 \leq Ca/Si < 1$), β-C-S-H ($1 < Ca/Si < 1.5$) and γ-C-S-H ($1.5 < Ca/Si < 2$). α-C-S-H is probably typically 14 Å-tobermorite and β-C-S-H is the same as Taylor's C-S-H(I) and corresponds to the solubility curve of C-S-H (A) identified by Jennings [31]. However, in the experiments reported here, γ-C-S-H always presents a tobermorite-like XRD pattern and is different from Taylor's C-S-H(II) and does not correspond to the solubility curve of C-S-H (B) identified by Jennings, because this curve is unlikely to be a solubility curve [32]. That is why I chose the α, β and γ prefixes, to avoid confusion. Hence, except at invariant points, in equilibrium conditions, it is not likely that the Taylor model considering a mix of tobermorite-like and jennite-like phases would be relevant. This assumption is confirmed by NMR data: homonuclear and heteronuclear correlation NMR experiments allow the neighbouring sites in the structure to be identified and reveal the sites belonging to the same phase. There are rather sophisticated and lengthy experiments requiring ^{29}Si-enriched samples. The first systematic Si–Si and H–Si correlation study on C-S-H samples made by Klur et al. [29] identified different silicon sites of the silicate chain. They found that all the Q^1 and Q^2 [1] silicon sites belong to the same phase over the whole range of Ca/Si. On the other hand, the dreierketten structure of the chains was confirmed by identifying the bridging tetrahedra. Differences in chemical shifts for tetrahedra bearing either protons or calcium ions were revealed for both bridging and non-bridging tetrhedra. The possible substitution of protons of silanol groups by calcium was then structurally evidenced. They also confirm the existence of SiOH and CaOH environments. These results were recently confirmed by Brunet et al. [33] using different correlation methods: double quantum Si–Si correlation and 2D H–Si HECTOR experiments. The Si–Si correlation maps allow a distinction between Q^1 arising from dimers from end of chain tetrahedral and show the decrease of the length of silicate chains longer than dimers as Ca/Si increases which disagrees with the bimodal hypothesis of Cong and Kirkpatrick. On the other hand, H–Si correlation maps show that protons in a CaOH environment are correlated with all Q^n sites; because the intensity of correlation peaks is not proportional to the site abundance, due to cross polarisation, it is not possible until now to conclude the location of CaOH with respect to silicate chains and to decide if Ca ion of the main sheet are only charge balanced and coordinated by oxygen of silicate or also by OH^-.

3. Is C-S-H necessary a very disordered material?

One often writes about C-S-H gel. Many people associate an amorphous material with this term. Taylor [22] reminded us of Everett’s definition of gels as “dispersions in which the attractive interactions between the elements of the disperse phase are so strong that the whole system develops a rigid network structure and, under small stresses, behaves elastically”. C-S-H in hydrated tricalcium silicate paste exactly fits this definition. Atomic force microscopy (AFM) imaging of a flat surface of hydrating alite [34–36] shows that the elements of the disperse phase occur in the form of identical aggregated nanoparticles of C-S-H. The dispersion of course is very concentrated; the dispersion medium in the experiment was a saturated lime solution. One can argue that the conditions of observation are far from a real cement paste and do not reflect reality. High resolution can only be obtained using AFM with a very flat surface: the roughness has to be lower that the objects to be imaged. However, the same type of image is obtained when the surface of a real cement paste in contact with a single crystal of calcite is imaged (Fig. 1). Thus, C-S-H gel in a hydrated cement paste, consists of a network of nanoparticles; the dimensions have been measured by AFM and those of small lamellae are 60 × 30 nm^2 and 5 nm thick. Dynamic rheology tests show that this network has an elastic behavior for very weak strains [37,38]; the critical strain beyond which the network is broken does not exceed 0.02%.

Thus, C-S-H may be considered to be gel-like, but it is not necessary amorphous. It is crystallised because one always gets a defined diffraction pattern when the sample is only composed of C-S-H obtained either from CaO–SiO_2 mix or from C_3S hydration (Fig. 2). All the reflections are broad. The broadening of diffraction lines has generally two different causes: the small size of the coherent domains, the presence of microdefects, or both [39]. C-S-H particles are very small and even if they are single crystals, the thickness of 5 nm means that this dimension corresponds to only two crystalline cells according to the hypothesis in which the basal plane of lamellae corresponds to the layer plane of a tobermorite-

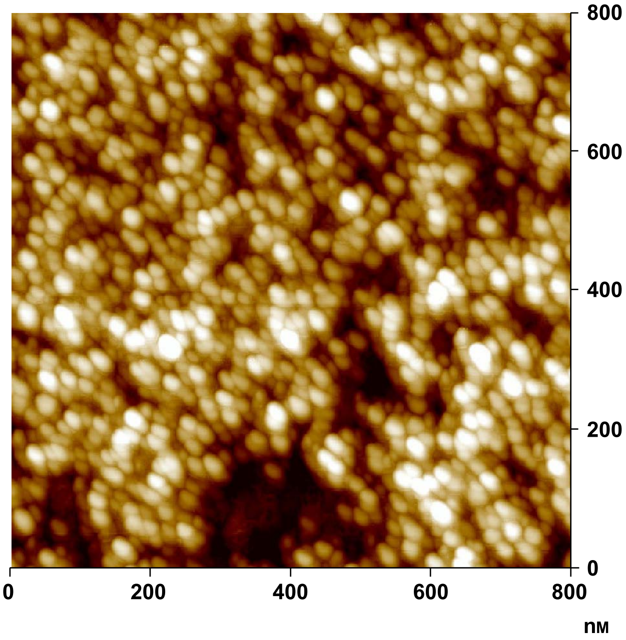

Fig. 1. AFM image of the surface of an hydrated cement paste in contact with a calcite single crystal. In this condition, the surface of the paste is flat enough to get high resolution after removing the calcite crystal. C-S-H nanoparticles are clearly identified. The darker zones corresponds to pores. (courtesy of J.-P. Perez and E. Liesniewska).

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[1] Q^1 designs the silicon sites corresponding to the dimeric and end of chains tetrahedra and Q^2 the silicon sites corresponding to the middle chains tetrahedra.

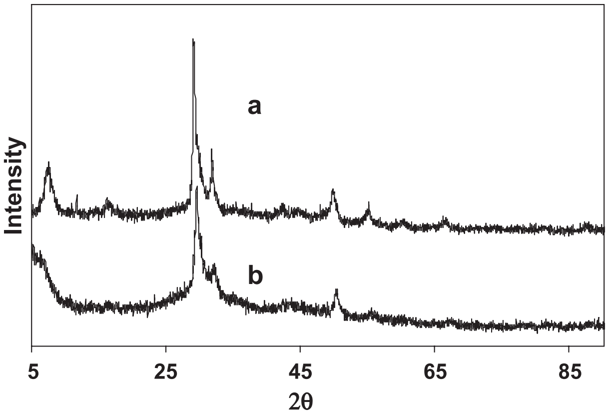

Fig. 2. XRD patterns ($\lambda Cu_{K\alpha}$) of C-S-H obtained (a) in diluted suspension from a mix of CaO and SiO_2 (w/c = 20), (b) by hydration of a mix of fine C_3S and SiO_2 in paste (w/c = 1.5). In both cases, Ca/Si ≅ 1.4 (after Ref. [42]).

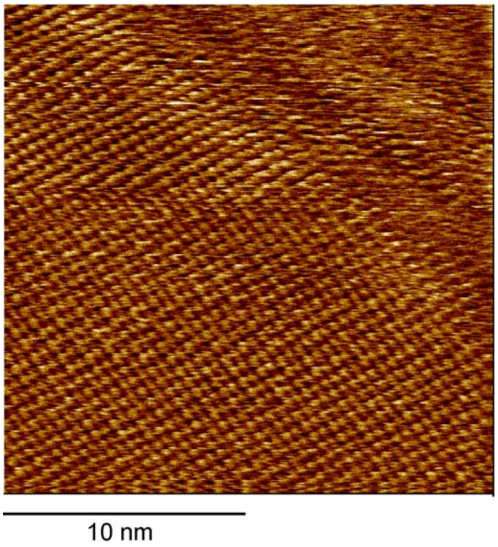

Fig. 4. Atomic scale AFM image of a C-S-H (Ca/Si = 1.5) crystallised on a calcite single crystal. One can notice the well-organised structure on a large scale (courtesy of C. Plassard and E. Liesniewska).

like structure. The XRD pattern calculated with the aid of these hypotheses, taking into account the size of the nanoparticles, is close to the experimental one (Fig. 3). It shows that, first, the structure of C-S-H is not very different from that of tobermorite structure, second, C-S-H nanoparticles are practically single nanocrystals, and third, they are not necessary defective; the line broadening of the XRD pattern can be explained on the basis of domain size.

Other experimental results do not support the idea of a very disordered structure to account for the variation of Ca/Si. It was recently observed that, according to Oswald ripening, small C-S-H nanocrystals initially formed on calcite single crystals, dissolved and crystallised again in one new single crystal under equilibrium conditions.[40]. C-S-H of different Ca/Si ratios, ranging from 0.7 to 1.5, were crystallised by ripening in solutions of calcium hydroxide of concentrations ranging from 1 to 20 mmol/l and saturated with respect to C-S-H. In each case, coherent domains of several μm^2 were observed. AFM imaging at the atomic resolution level of the sample shows a well-ordered structure over a relatively large scale (Fig. 4) and Fourier transform of the image allowed the evolution of the surface cell parameters (a, b and α, the angle between a and b) of C-S-H to be measured as a function of Ca/Si (Fig. 5) [41]. It would be difficult to explain the crystallisation in different ordered structures for each value

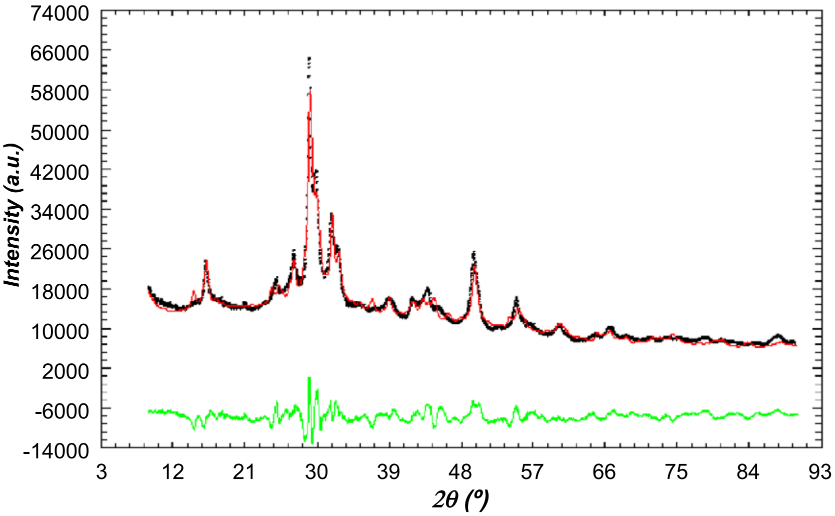

Fig. 3. Experimental and calculated XRD pattern of C-S-H ($\lambda Cu_{K\alpha}$), Ca/Si = 0.9 using the FULLPROF program. The calculation is made assuming a structure deriving from the monoclinic structure of 11 Å tobermorite proposed by Hamid [18] with a lamellar crystal shape of 50 nm in diameter and 5 nm thick. The structural model (P1, a = 0,674 nm, b = 0.761, c = 24.310 nm, γ = 123.74) does not fit exactly the C-S-H structure as revealed by the difference between the experimental and calculated pattern but the line broadening is accounted for by the size of the particles.

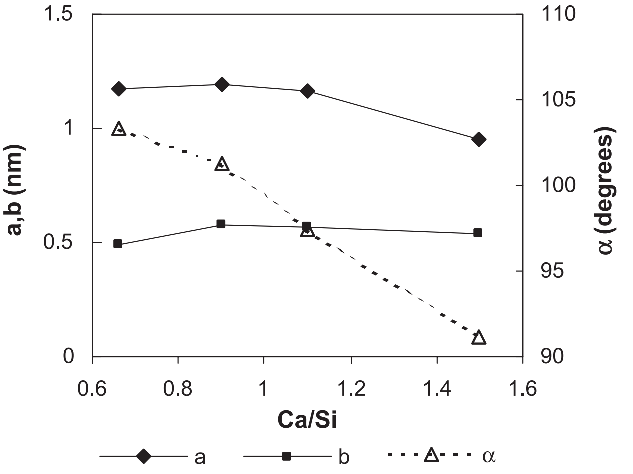

Fig. 5. Evolution of surface crystal parameters of C-S-H crystallised on single crystals of calcite determined from Fourier transform of AFM images at the atomic scale. α is the angle between a and b surface cell parameters. (after Ref. [41]).

of Ca/Si if a disordered structure was needed to achieve these Ca/Si ratios.

4. Towards a predictive model

All the models reported here are structurally descriptive; they account for a global evolution of the Ca/Si ratio observed in the samples in relation to the evolution of the structure but in any event they are able to predict the structure and the stoichiometry of the product obtained in given equilibrium conditions.[2] A phenomenological model has recently been proposed on the basis of Nonat and Lecoq's structural model by taking into account textural data [42,43]. According to this model, the structural unit of C-S-H may be described as following:

- the main layer consists of a silicate dimeric unit charge balanced by two calcium ions and the two free extremities bear two protons, $Ca_2H_2Si_2O_7$;
- two successive dimeric units may be bridged by a silicate tetrahedron; if so, the bridging tetrahedron bears the protons and we have on average $Ca_2H_2Si_2O_7(SiO_2)_x$, where $x \leq 1$
- silanol may be partially ionised and charge balanced by calcium in the interlayer, giving $Ca_2H_{2-p}Si_2O_7(SiO_2)_x Ca_{p/2}$ or $Ca_2H_{2-p}Si_2O_7(SiO_2)_x(CaOH)_p$
- finally, $Ca(OH)_2$ units may be accommodated in place of missing bridging tetrahedra, giving as the constitutional formula: $Ca_2H_{2-p}Si_2O_7(SiO_2)_xCa_{p/2}, (Ca(OH)_2)_y$.

This elemental description of C-S-H is chemically equivalent to that given by Richardson and Groves [44], but the formulation is directly related to the structural model. A thermodynamic development of this model has been performed on the basis of bulk and surface mass action laws that should be predictive and reliable in different conditions.

The first mass action law is relative to the bulk solubility according to Eq. (1)

$$Ca_2H_2Si_2O_7 + 4H^+ \leftrightarrows 2Ca^{++} + 2H_4SiO_4$$

$$K_1 = \frac{(Ca^{++})^2(H_4SiO_4)^2}{(H^+)^4} \qquad (1)$$

where (*X*) is the activity of the *X* species in solution.

The bridging of two successive dimers may be described as a surface reaction between silanol sites of two adjacent dimers and a silicate ion in solution according to Eq. (2):

$$2 - SiOH + H_4SiO_4 \leftrightarrows - SiOSi(OH)_2OSi\text{-} + H_2O$$

$$K_2 = \frac{a_{-SiOSi(OH)_2OSi-}}{(H_4SiO_4)a_{-SiOH}} \qquad (2)$$

where $a_{\text{-SiOSi(OH)}_2\text{OSi-}}$ and $a_{\text{-SiOH}}$ are the activities of the surface sites -SiOSi(OH)$_2$OSi - and −SiOH, respectively. This surface reaction may occur at the external surface of C-S-H particle as well as in the interlayer.

Concerning the partial substitution of protons by calcium ions, two cases have to be considered depending on the location of silanol, at the external surface or in the interlayer: At the external surface, to account for the surface charge of C-S-H, the ionisation of silanol groups and the complexation of calcium may intervene according to Eqs. (3) and (4), respectively

$$-SiOH \leftrightarrows SiO^- + H^+ \quad K_3 = \frac{a_{SiO^-}(H^+)}{a_{SiOH}} \exp\left(-\frac{e\Psi_0}{kT}\right) \qquad (3)$$

$$-SiOH + Ca^{++} \leftrightarrows SiOCa^+ + H^+$$

$$K_4 = \frac{a_{SiOCa^+}(H^+)}{a_{SiOH}a_{Ca^{2+}}} \exp\left(\frac{e\Psi_0}{kT}\right) \qquad (4)$$

In those equations, a_X represents the activity of the *X* surface species), and Ψ_0 is the surface potential. The factor $\frac{a_{SiO^-}(H^+)}{a_{SiOH}}$ is the intrinsic equilibrium constant for the reaction; $\exp\left(\frac{e\Psi_0}{kT}\right)$ is a factor that accounts for the work involved in moving a charged species (H^+) away from a charged surface; the basic theory for surface complexation reactions, including electrostatic potential, is presented in Ref. [45]. The balance between these two equilibria fixes the surface charge of C-S-H. The same reactions cannot be

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[2] The equilibrium conditions are restricted here to metastable equilibria between nanocrystaline C-S-H solid phases and solutions. This approximation may be used because the rate of transformation in crystalline C-S-H is very slow and no change are observed during several weeks.

written at the internal surfaces, because the interlayer must be electrically neutral: to preserve charge balance, the equilibria in Eqs. (5) and (6) in the interlayer have to be formulated as

$$2-\mathrm{SiOH}+\mathrm{Ca}^{2+}\leftrightarrows\text{-SiOCaOSi-}+2\mathrm{H}^{+}$$

$$K_5=\frac{a_{-\mathrm{SiOCa_2OSi}}\text{-}(\mathrm{H}^{+})}{(\mathrm{Ca}^{++})a_{-\mathrm{SiOH}}}\qquad(5)$$

$$-\mathrm{SiOH}+\mathrm{CaOH}^{+}\leftrightarrows\text{-SiOCaOH}+\mathrm{H}^{+}$$

$$K_6=\frac{a_{-\mathrm{SiOCaOH}^{-}}(\mathrm{H}^{+})}{a_{-\mathrm{SiOH}}(\mathrm{CaOH}^{+})}\qquad(6)$$

The equilibrium Eq. (6) may be considered to represent both the external and internal surfaces because the resulting surface species are electrically charge balanced.

The values of the equilibrium constants have been adjusted to fit the experimental data relative to the chemistry, the structure and electrokinetic surface properties of C-S-H as revealed, for example, by plotting the evolution of the silica concentration in solution (solubility), the Ca/Si ratio (stoichiometry), the Q^1/Q^2 ratio (silicate chain length) and inversion of surface charge as a function of lime concentration in solution [46,47]. The calculated evolutions (line) are compared to experimental data on Fig. 6. For the calculations, the density of surface sites used for the surface reactions may be estimated from the cell parameters and the size of the C-S-H nanoparticles.

The model fits the equilibrium state of samples prepared either in diluted suspensions or as paste. As a consequence, whatever the initial starting materials, the hydration products formed during bottle or paste experiments are similar, provided the same equilibrium state is achieved. When equilibrium is reached, there are no differences between C-S-H having the same Ca/Si ratio but synthesised by different methods.

The reported model has been best developed for β-C-S-H when $1 < \mathrm{Ca/Si} < 1.5$ because there are more experimental values in this range. However, the model does not fit lower and higher Ca/Si values well. It could probably be easily extended to these cases by changing the bulk solubility equilibria by considering the dissolution of $\mathrm{Ca_4H_4Si_5O_{15}}$ ($\mathrm{Ca/Si}=0.8$, α-C-S-H) in the lower range of Ca/Si. In the highest range of Ca/Si (γ-C-S-H), the bulk phase should be formulated as:

- $\mathrm{Ca_3HSi_2O_7(OH)}$ ($\mathrm{Ca/Si}=1.5$); one silanol proton is replaced by CaOH^{+} in interlayer,
- $\mathrm{Ca_3H_2Si_2O_7(OH)_2}$ ($\mathrm{Ca/Si}=1.5$), one silicate bridging tetrahedron is be replaced by $\mathrm{Ca(OH)_2}$ (tobermorite-like structure) or a nonbridging tetrahedron is be replaced by 2 OH^{-} (jennite-like part).

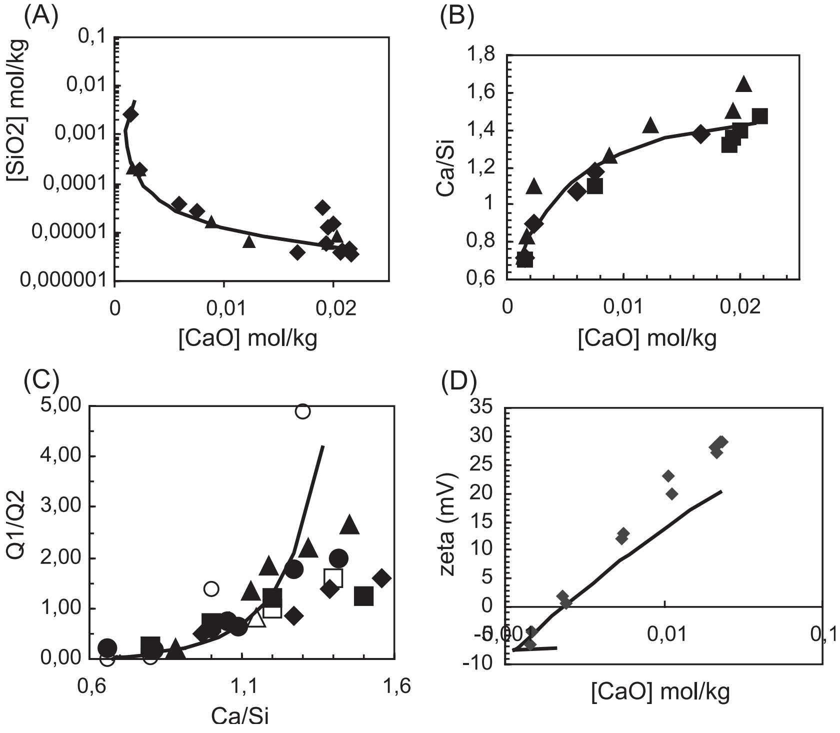

Fig. 6. Comparison of calculated properties of C-S-H with the help of the surface reaction thermodynamic model with experimental data: (A) solubility; (B) Ca to silicon ratio; (C) Q1/Q2 ratio characteristic of the length of the silicate chains; (D) calculated surface potential compared to experimental zeta potential: the important point to notice is the composition at which the charge inversion occurs. (after Ref. [50]).

5. C-S-H in hydrating cement paste

When the model described in Section 4 is an equilibrium model, it may probably also be reliable in a hydrating system in which local equilibria may be considered. According to the model, Ca/Si and structure of C-S-H are fixed by the lime concentration with which it is in contact and it should be possible to explain the observed evolution of stoichiometry and structure of C-S-H through the evolution of lime concentration during hydration. At early age, the solution from which C-S-H precipitates has a low lime concentration (6 mmol/kg); C-S-H should have a low Ca/Si ratio and long chains. But during the so-called induction period, the solution becomes supersaturated with respect to portlandite; as a result of which, Ca/Si of C-S-H increases and chains shorten drastically. During the accelerating period of hydration, the concentration gradients are probably the greatest between the pore solution and the solution directly in contact with the surface of tricalcium silicate; C-S-H which grows near or far from alite surfaces does not probably have the same composition and structure and could help to explain the bimodal distribution of Ca/Si observed by EDX. During the decelerating period of hydration, the gradients trend to equilibrate as do numerical values of the Ca/Si ratio and average silicate chain lengths. With ageing of the paste, lime concentration decreases to reach the solubility of portlandite (or lower if carbonation occurs) and as a result, the average silicate chain length increases.

6. Conclusion

The lamellar character of C-S-H has long been recognised. This textural characteristic has many consequences on several properties, such as crystal structure and chemical properties, because the surfaces (internal and external) are extremely extended. The surface chemistry is probably more important than crystal structure; it controls interactions with cations, anions, polyelectrolites and other molecules and is the origin of cohesive forces between particles [40,48,49]. However, full understanding of these properties requires investigations and simulations at the atomic level. These last tasks can only be achieved with the exact knowledge of the atomic structure of the surface of C-S-H. Much work has already been done but much more has to be done by integrating results obtained from different investigation techniques.

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References

[1] H.F.W. Taylor, Hydrated calcium silicates: part I. Compound formation at ordinary temperatures, J. Chem. Soc. (1950) 3682–3690.

[2] L. Heller, H.F.W. Taylor, Hydrated calcium silicates: part 2. Hydrothermal reactions: lime:silica ratio 1:1, J. Chem. Soc. (1951) 2397–3401.

[3] L. Heller, H.F.W. Taylor, Hydrated calcium silicates: part 3. Hydrothermal reactions of mixture of lime:silica molar 3:2, J. Chem. Soc. (1952) 1018–1019.

[4] L. Heller, H.F.W. Taylor, Hydrated calcium silicates: part 4. Hydrothermal reactions lime:silica ratios 2:1 and 3:1, J. Chem. Soc. (1952) 2535–2541.

[5] H.F.W. Taylor, Hydrated calcium silicates: part 5. The water content of calcium silicate hydrate (I), J. Chem. Soc. (1953) 163–171.

[6] E.R. Buckle, J.A. Gard, H.F.W. Taylor, Tricalcium silicate hydrate, J. Chem. Soc. (1958) 1351–1355.

[7] J.A. Gard, J.W. Howison, H.F.W. Taylor, Synthetic compounds related to tobermorite: an electron-microscope, X-ray, and dehydration study, Mag. Concr. Res. 11 (33) (1959) 151–158.

[8] H.F.W. Taylor, Structural chemistry of calcium silicates and calcium silicate hydrates, 9th International Conference of the Yugoslav Centre of Crystallography, Yugoslavia, 1974.

[9] J.A. Gard, H.F.W. Taylor, Calcium silicate hydrate (II), Cem. Concr. Res. 6 (5) (1976) 667–677.

[10] T. Mitsuda, H.F.W. Taylor, Normal and anormalous tobermorites, Min. Mag. 42 (322) (1978) 229–235.

[11] J.A. Gard, K. Luke, H.F.W. Taylor, $Ca_7Si_{16}O_{40}H_2$, a new calcium silicate hydrate phase of the truscottite group, Cem. Concr. Res. 11 (1981) 659–664.

[12] K. Luke, H.F.W. Taylor, Equilibria and non-equilibria in the formation of xonotlite and truscottite, Cem. Concr. Res. 14 (5) (1984) 657–662.

[13] E. Bonaccorsi, S. Merlino, H.F.W. Taylor, The crystal structure of jennite, $Ca_9Si_6O_{18}(OH)_6.8H_2O$. Cem. Concr. Res. 34 (2004) 1481–1488.

[14] H.F.W. Taylor, Proposed structure for calcium silicate hydrate gel, J. Am. Ceram. Soc. 69 (6) (1986) 464–467.

[15] W. Wieker, A.R. Grimmer, A. Winkler, Solid state high resolution ^{29}Si NMR spectroscopy of synthetic 14Å, 11Å and 9Å tobermorites, Cem. Concr. Res. 12 (1982) 333–339.

[16] S. Komarneni, D.M. Roy, C.A. Fyfe, G.J. Kennedy, Naturally occurring 1.4 nm tobermorite and synthetic jennite: characterisation by 27 Al and 29 Si MASNMR spectroscopy and cation exchange properties, Cem. Concr. Res. 17 (6) (1987) 891–895.

[17] T. Mitsuda, H. Toroya, Y. Okada, M. Shimoda, Synthesis of tobermorite: NMR spectroscopy and analytical electron microscopy, Ceram. Trans. 5 (1989) 206–213.

[18] S.A. Hamid, The crystal structure of the 11 Å natural tobermorite $Ca_{2.25}[Si_3O_{7.5}(OH)_{1.5}]$ 1 H_2O, Z. Kristallogr. 154 (1981) 189.

[19] C. Hoffmann, T. Armbruster, Clinotobermorite, $Ca_5[Si_3O_8(OH)]_{2.4}$ H_2O-$Ca_5[Si_6O_{17}].5H_2O$, a natural C-S-H (I) type cement mineral: determination of the substructure, Z. Kristallogr. 212 (1997) 864–873.

[20] A.B.C. Carpenter, J.A. Gard, K. Speakman, H.F.W. Taylor, Jennite, a new mineral, Am. Mineral. 51 (1–2) (1966) 56–74.

[21] I.G. Richardson, G.W. Groves, Microstructure and microanalysis of hardened ordinary Portland cement pastes, J. Mater. Sci. 28 (1993) 265–277.

[22] H.F.W. Taylor, Nanostructure of C-S-H: current status, Adv. Cem. Based Mater. 1 (1993) 38–46.

[23] X. Cong, R.J. Kirkpatrick, ^{29}Si MAS NMR study of the structure of calcium silicate hydrate, Adv. Cem. Based Mater. 3 (1996) 144–156.

[24] X. Lecoq, Etude de l'hydratation à concentration controlée du silicate tricalcique Ca_3SiO_5 et des caractéristiques de ses produits de réactio. Université de Bourgogne, Dijon, 1993.

[25] A. Nonat, X. Lecoq, The structure, stoichiometry and properties of C-S-H prepared by C_3S hydration under controlled solution, in: P. Colombet, A.-R. Grimmer, H. Zanni, P. Sozzani (Eds.), Nu-

clear Magnetic Resonance Spectroscopy of Cement Based Materials, Springer, Berlin, 1996, pp. 197–207.

[26] E.P. Flint, H.F. McMurdie, L.S. Wells, Formation of hydrated calcium silicates at elevated temperatures and pressures, Natl. Bur. Stand. 21 (1938) 617.

[27] H.H. Steinour, The System $CaO-SiO_2-H_2O$ and The Hydration of the Calcium Silicates, Portland Cement Association, Skokie, IL, USA, 1946.

[28] M. Grutzeck, A. Benesi, B. Fanning, Silicon^{29} magic angle spinning nuclear magnetic resonance study of calcium silicate hydrate, J. Am. Ceram. Soc. 72 (4) (1989) 665–668.

[29] I. Klur, B. Pollet, J. Virlet, A. Nonat, C-S-H structure evolution with calcium content by multinuclear NMR, in: P. Colombet, A.-R. Grimmer, H. Zanni, P. Sozzani (Eds.), Nuclear Magnetic Resonance Spectroscopy of Cement Based Materials, Springer, Berlin, 1996, pp. 119–141.

[30] D. Damidot, A. Nonat, P. Barret, D. Bertrandie, H. Zanni, R. Rassem, C_3S hydration in diluted and stirred suspensions: III. NMR study of C-S-H precipitated during the two kinetic steps, Adv. Cem. Res. 7 (25) (1995) 1–8.

[31] H.M. Jennings, Aqueous solubility relationships for two types of calcium silicate hydrate, J. Am. Ceram. Soc. 69 (1986) 614–618.

[32] P. Barret, D. Bertrandie, Comment on aqueous solubility relationships for two types of calcium silicate hydrate, J. Am. Ceram. Soc. 71 (2) (1988) C-113–C-115.

[33] F. Brunet, Ph. Bertani, Th. Charpentier, J. Virlet, A. Nonat, Application of ^{29}Si homonuclear and ^{1}H/^{29}Si heteronuclear NMR correlation to structural studies of Calcium Silicate Hydrates. J. Phys. Chem. B (in press).

[34] S. Garrault-Gauffinet, Etude expérimentale et par simulation numérique de la cinétique de croissance et de la structure des hydrosilicates de calcium, produits d'hydratation des silicates tricalciques et dicalciques. Université de Bourgogne, Dijon, 1998.

[35] S. Gauffinet, E. Finot, E. Liesniewska, A. Nonat, Observation directe de la croissance d'hydrosilicate de calcium sur des surfaces d'alite et de silice par microscopie à force atomique, C.r. Acad. Sci. Paris 327 (4) (1998) 231–236.

[36] S. Gauffinet, E. Lesniewska, S. Collin, A. Nonat, AFM and SEM studies of C-S-H growth on C_3S surface during its early hydration. In XXth International Conference on cement microscopy. Guadalajara, Mexico, 1998.

[37] M.A. Schultz, L.J. Struble, Use of oscillatory shear to study flow behaviour of fresh cement past, Cem. Concr. Res. 23 (2) (1993) 273–282.

[38] L. Nachbaur, J.C. Mutin, A. Nonat, L. Choplin, Dynamic mode rheology of cement and tricalcium silicate pastes from mixing to setting, Cem. Concr. Res. 31 (2) (2001) 183–192.

[39] A. Guinier, X-Ray Diffraction in Crystals, Imperfect Crystals, and Amorphous Bodies, Dover Publications, New York, 1994.

[40] S. Lesko, E. Lesniewska, A. Nonat, J.C. Mutin, J.P. Goudonnet, Investigation by atomic force microscopy of forces at the origin of cement cohesion, Ultramicroscopy 86 (1–2) (2001) 11–21.

[41] C. Plassard, E. Lesniewska, I. Pochard, A. Nonat, Investigation of the surface structure and elastic properties of calcium silicate hydrates at the nanoscale, Ultramicroscopy 100 (2004) 331–338.

[42] A.-C. Courault, Simulation Experimentale Des C-S-H Dans Les Bétons Modernes: Etude De La Composition Et Des Propriétés À L'équilire Dans Des Milieux Complexes, Université de Bourgogne, Dijon, 2000.

[43] A. Nonat, A.-C. Courault, D. Damidot, A new model describing the variation of C-S-H Ca/Si ratio with lime concentration in solution, Cem., Wapno, Beton 5 (2001) 184–191.

[44] I.G. Richardson, G.W. Groves, A reply to Discussions by H.F.W. Taylor of the Papers "models for the composition and structure of calcium silicate hydrate, C-S-H, gel in hardened tricalcium silicate pastes" and "the incorporation of minor and trace elements into calcium silicate hydrate, C-S-H, Cem. Concr. Res. 23 (4) (1993) 999–1000.

[45] D.A. Dzombak, F.M.M. Morel, Surface Complexation Modeling-Hydrous Ferric Oxide, John Wiley, New York, 1990.

[46] L. Nachbaur, P.C. Nkinamubanzi, A. Nonat, J.C. Mutin, Electrokinetic properties which control the coagulation of silicate cement suspensions during early age hydration, J. Colloid Interface Sci. 202 (1998) 261–268.

[47] H. Viallis-Terrisse, A. Nonat, J.C. Petit, Zeta-potential study of calcium silicate hydrates interacting with alkaline cations, J. Colloid Interface Sci. 244 (1) (2001) 58–65.

[48] A. Delville, Electrostatic interparticle forces: from swelling to setting, in: A. Nonat (Ed.), Second Rilem Workshop on Hydration and Setting: "Why does Cement Set?", Rilem Editions, Cachan, 1997, pp. 37–62.

[49] R.J.-M. Pellenq, M. Crespin, N. Lequeux, C. Menager, L. Costalin, A. Caillol, J.M. Caillol, H. Van Damme, A (NTV) Monte-Carlo study of the stability of charged interfaces application to cement and clay minerals, in: A. Nonat (Ed.), Second Rilem Workshop on Hydration and Setting: "Why does Cement Set?", Rilem Editions, Cachan, 1997, pp. 63–86.

[50] A. Nonat, A.-C. Courault, D. Damidot, A surface reaction model describing the structure and stoichiometry of calcium silicate hydrate (C-S-H) with calcium hydroxide concentration in solution, J. Colloid Interface Sc. to be published.