

Cement-polymer and clay-polymer nano- and meso-composites: spotting the difference†

Fabrice Merlin, H el ene Lombois, St ephane Joly, Nicolas Lequeux, Jean-Louis Halary and Henri Van Damme*

*Ecole Sup erieure de Physique et Chimie Industrielles (ESPCI), 75231 Paris cedex 05, France.
 E-mail: henri.vandamme@espci.fr*

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Calcium silicate hydrate (C-S-H), the most important reaction product of Portland cement with water, is a layered lattice silicate which has much in common with smectite clays. Both materials may be synthesised (C-S-H) or found in nature (smectites) in the form of particles which are stacks of negatively charged nanometre-thick platelets separated by water molecules and charge-compensating cations. Smectite clays are well known for their ability to intercalate molecular species including polymers, to “swell” in a remarkable variety of solvents and to form nano-composites with polymers in which total delamination may eventually be obtained. In this work, we explore the possibility of intercalating cationic, anionic and neutral water-soluble polymers in C-S-H. Contrary to recent reports, no clear signs for intercalation of the macromolecules were observed. Nevertheless, the significant amount of polymer retained by the silicate suggests that the composite materials formed may be considered as meso-composites in which the individual solid units are not the individual C-S-H sheets but crystallites thereof. The localisation of electric charges and the strong Coulombic forces acting in cement hydrates are thought to be responsible for this difference.

1. Introduction

The intimate association of inorganic entities with macromolecules is an intrinsic feature of many biological hard materials such as bones, shells, or spines.^{1–4} This may lead to a remarkable improvement of mechanical properties such as strength, toughness or ductility. As far as dense synthetic materials are concerned, two main biomimetic routes have been developed: hybrids on one hand and nano-composites (NC) on the other hand.⁵ Hybrids are usually defined as materials in which the association of organic and inorganic species is at a molecular level *via* iono-covalent bonds whereas, in nano-composites, nanoscale clusters or particles may still be identified and distinguished from the embedding matrix.

Clay-polymer nano-composites have received considerable attention in recent years.^{6–8} Smectite clays (also called swelling clays) are particularly suited for development as nano-composites due to their wide availability, their capacity to intercalate a wide variety of organic species^{9,10} and the ease with which they may be surface-treated and dispersed, by various methods, in polymer matrices. So far, most of the attention has been devoted to materials in which the polymer is by far the major component, the smectite clay loading being typically of the order of a few percent by weight. Yet, provided a good dispersion is obtained, such small loadings are enough to obtain a significant improvement of the polymer properties: modulus, strength, heat and fire resistance, gas barrier properties.¹¹ The quality of dispersion may range from poor, when the polymer does not penetrate into the interlamellar galleries of the particles (the particles are stacks of negatively charged nanometre-thick lamellae separated by charge-compensating cations and water or solvent molecules), to excellent, when the particles are totally delaminated and randomly dispersed in the matrix (Fig. 1).⁶ In the latter case, the clay-polymer interface area may approach $800 \text{ m}^2 \text{ g}^{-1}$, leading to a material in which virtually all the polymer is in an interfacial configuration. An

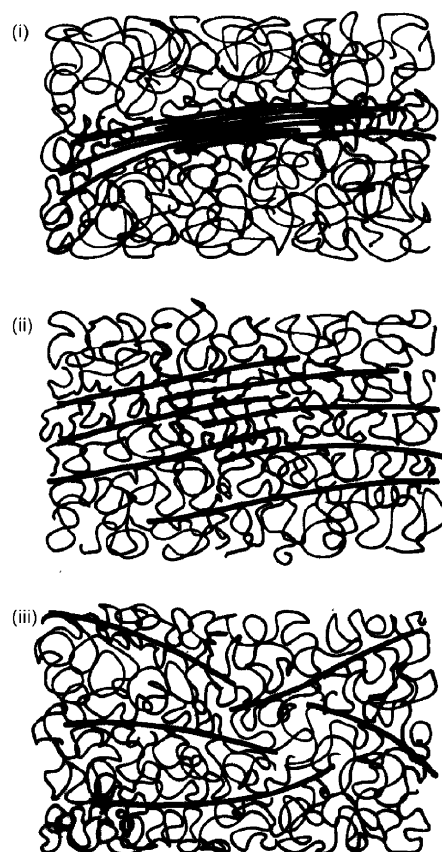


Fig. 1 Sketch of three possible textures of a polymer composite with layered nano-particles. (i) Meso-composite: the polymer does not penetrate into the interlamellar state. (ii) Intercalated nano-composite: the polymer penetrates into the interlamellar space and increases the interlayer spacing, but orientational and positional correlations are maintained. (iii) Delaminated nano-composite: the layers are separated and randomly distributed in the matrix.

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intermediate situation is that of the so-called intercalated NC, when the polymer penetrates into the galleries but the particles, with expanded galleries, are still recognisable (Fig. 1). To what extent interfacial gradients of properties and molecular confinement contribute to mechanical reinforcement of the polymer remains to be established.

Much less effort has been devoted to NC in which the mineral is the dominant phase.¹² In the case of clays, this may be of limited interest but with cement-based materials, a bio-inspired approach may prove to be very valuable. Indeed, concrete is the most widely used material in the world, but it suffers from some drawbacks. Hardened cement, mortars and concrete are intrinsically fragile porous materials, with a low tensile or flexural strength due to a distribution of pore sizes ranging from nm to μm .^{13,14} The introduction of polymers into the pores may not only reduce the critical flaw size and limit crack initiation but also control crack propagation, as in natural biocomposites such as nacre. Reduction of the critical flaw size is the basis of the Macro-Defect-Free (MDF) cements concept, developed by Birchall *et al.* in the eighties at ICI in the UK.^{15,16} The term MDF refers to the absence of large voids. The best mechanical properties have been achieved by mixing high-alumina cements, whose main components are calcium aluminates, with water and a water-soluble polymer, poly(vinyl alcohol) (PVA) or poly(vinyl alcohol)-poly(vinyl acetate) (PVA-co-Vac). Very little water is added, so that most of the cement remains anhydrous. The microstructure of MDF materials is characterised by grains of unreacted cement embedded in the polymer matrix, with an amorphous interphase region containing fine crystallites of hydrates (the products of the reaction of anhydrous cement with water).¹⁷ Elimination of the largest pores gives the material a much larger flexural strength than polymer-free hardened cement (up to 150 MPa, compared to 10 MPa for ordinary cement, typically), but the material is still fragile. Crack propagation is still catastrophic.

The next step in a biomimetic approach is to introduce the polymer, not only between the non-hydrated cement grains, but also between the elementary nanoscopically sized particles of the hydrates. The alternation of hard and soft regions, ranging from the nm scale up to the μm scale and above, is indeed expected to make crack propagation much more difficult. Nacre is a good example of this logic.¹⁸ It turns out that two hydration products of cement, calcium aluminate hydrate (C-A-H) and calcium silicate hydrate (C-S-H), are both nano-sized layered solids (when they are well crystallised, see Section 2).¹⁹ The lamellae of C-A-H, which has a crystal structure akin to that of layered double hydroxides (LDHs), are positively charged, with charge-compensating anions in the interlayer space. The charge of the C-S-H lamellae is less obvious, but it should be negative and depend on the Ca : Si ratio (see Section 2). Intercalation of anionic molecular species—including sulfonated polymers—in C-A-H is a facile process provided the hydrate is precipitated from its precursor calcium and aluminium salts in a polymer solution.^{20,21} Recent reports claim that intercalation of polymers in C-S-H during its precipitation is also a facile process.^{22–25} A broad range of anionic, neutral and cationic polymers could be intercalated, but intercalation was very much dependent on the Ca : Si ratio of the solid and on the polymer molecular weight. Cationic polymers were reported to intercalate at a low Ca : Si ratio and anionic polymers at a high Ca : Si ratio. Considering the tremendous benefit that would be obtained from an improvement of cement-based materials, the present paper is a critical study of this intercalation reaction, focusing on C-S-H, the most important component of hydrated Portland cement. As will be shown below, our results suggest that the materials obtained are better described as ill-organised meso-composites rather than intercalated nano-composites. The difference between C-S-H and smectite clays will be discussed in terms

of recent molecular simulation studies of cement and clay cohesion and swelling.

2. C-S-H and smectite clays

Cement is the (grinded) product of the non-equilibrium cooling of a sintered mass of the system $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3$, with magnesium and iron impurities, starting from a mixture of clay and limestone as raw material.¹⁹ It is a mixture of several mineral phases, the most abundant being an impure tricalcium silicate, $3\text{CaO}\cdot\text{SiO}_2$ (alite). When cement is mixed with water, it undergoes a dissolution reaction generating, among others, calcium, silicate and aluminate ions in the interstitial solution. Very soon, new products precipitate, the most important being calcium silicate hydrate (C-S-H) and calcium hydroxide (portlandite). As this dissolution-diffusion-precipitation hydration reaction proceeds, more and more anhydrous material is converted into hydrates, with an overall decrease of the porosity since the volume of hydrates produced by the thorough reaction of tricalcium silicate with water is more than twice the initial anhydrous volume.²⁶

C-S-H is basically a non-stoichiometric compound.¹⁹ The average Ca : Si ratio in ordinary hardened cement paste is around 1.7 but it may decrease locally to much lower values. Local values, measured by analytical electron transmission microscopy, fluctuate between 0.6 and 2 or more.^{27–29} Pure C-S-H may also be synthesised directly from its elementary oxide or hydroxide constituents—lime, silica and water—in dilute suspension and mild thermal conditions. This is the so-called pozzolanic synthesis route¹⁹ which gives much greater flexibility in the control of the Ca : Si ratio than the simple mixing of cement and water. The reason is that the Ca : Si ratio in C-S-H is thermodynamically controlled by the activity of the calcium ions in equilibrium with it¹⁹ and this activity is much easier to control in the pozzolanic method. Even simpler than the pozzolanic method is the direct precipitation of C-S-H from its precursor salts, calcium nitrate and sodium silicate for instance. However, this method has the drawback of leaving excess ions (nitrate and sodium) in the synthesis solution. Thus, C-S-H with a Ca : Si ratio varying from 0.66 to 1.5 may be prepared both by the pozzolanic and the precipitation method. In order to prepare C-S-H with higher and well-controlled Ca : Si ratios, tricalcium silicate has to be hydrated in lime solutions supersaturated with portlandite.³⁰

Though generally poorly organized (hence the widespread use of the words “C-S-H gel”), C-S-H is widely recognised to have a layered crystal structure, akin to that of the mineral tobermorite (Fig. 2) or to that of jennite, with a layer thickness in the nanometre range.^{19,31–35} This morphology is hardly recognizable in real hardened cement paste but it becomes evident from X-ray diffraction and from direct transmission electron microscopy (TEM) observations of pozzolanic C-S-H (Fig. 3). High resolution ²⁹Si, ¹H and ¹⁷O NMR, X-ray absorption spectroscopy, IR and Raman spectroscopy³⁶ have provided considerable information on the structure of the layers. It is now generally admitted that their two-dimensional backbone is a double plane of Ca^{2+} ions 6-coordinated by central O^{2-} ions, to which disordered silica chains are grafted on each side. These composite layers stack along the 001 direction, being separated by Ca^{2+} ions and water molecules.

In the reference mineral tobermorite, with Ca : Si = 0.66, the chains are infinite and run parallel to the *b* axis.³⁷ The repeating units along the chains are so-called dreierketten, with two pairing tetrahedra linked to the CaO polyhedra by sharing edges with them, and one bridging tetrahedron pointing away from the CaO polyhedra layer (Fig. 2). In perfect tobermorite, all the oxygen atoms involved in the dangling bonds of the silicate chain are protonated, as hydroxy groups, so that the structure is neutral. The interlayer is

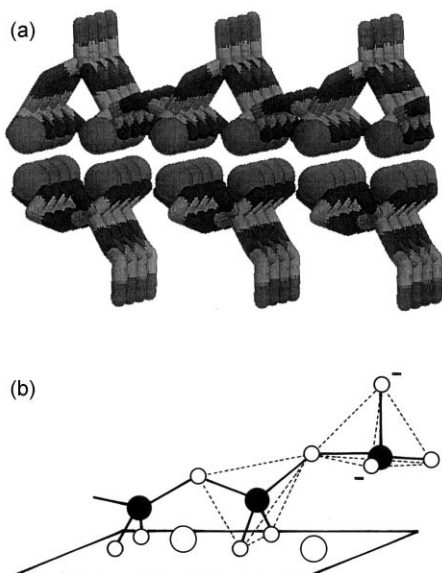


Fig. 2 The structure of tobermorite, with a central double layer of calcium ions and chains of silica tetrahedron triads (dreierketten) on each side. Also shown is the arrangement of silica tetrahedrons in the dreierketten units.

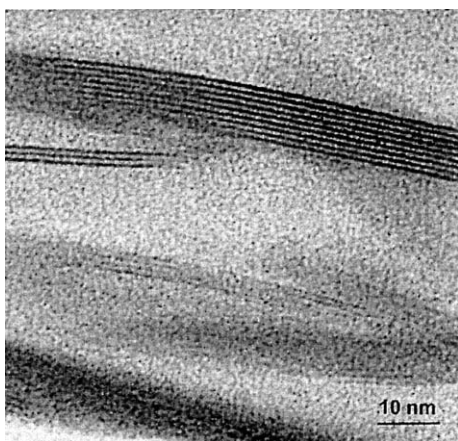


Fig. 3 TEM micrograph of C-S-H at Ca : Si = 1 prepared by reaction of silica with lime (pozzolanic reaction) (courtesy of C. Clinard), showing the nanoscale lamellae and the mesoscale lamellae stacks (or crystallites).

occupied by water molecules. Two interlayer distances are observed: 1.1 and 1.4 nm, the difference being one additional layer of water molecules.

Up to Ca : Si = 1.5, C-S-H may be considered as a defect tobermorite structure³⁶ (Fig. 4). A crucial point is that the solution in equilibrium with C-S-H is always at a very high pH. For Ca : Si = 1, it is already beyond 10. In the low ratio Ca : Si regime, the structural evolution appears to be the progressive replacement of the protons of the initially doubly protonated bridging tetrahedra by Ca²⁺ ions, which move into the hydrated interlayer space. At Ca : Si = 1, the first phase transition occurs and a new type of C-S-H with a lower degree of polymerization of the chains appears. The main defects are missing bridging tetrahedra. The higher the Ca : Si ratio, the larger the number of missing bridging tetrahedra and the shorter the average chain length. This length changes from an average of pentameric units at Ca : Si = 1 to dimeric units at Ca : Si = 1.5. Ionization of the hydroxy groups of the dangling bonds generated by this chain shortening maintain the negative charge of the layers and the number of Ca²⁺ ions in the interlayer space. At Ca : Si = 1.5, a second phase transition seems to take place. The structure of C-S-H in this

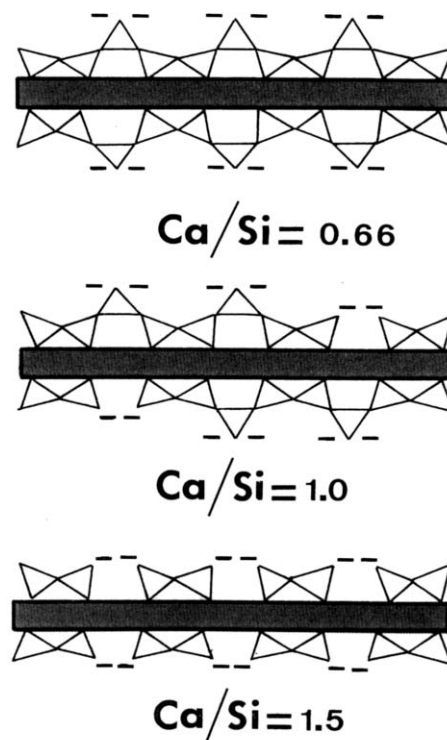


Fig. 4 Evolution of the C-S-H structure as the Ca : Si ratio increases from 0.66 to 1.5. The electric charges are localised on the surface of the lamella.

high ratio Ca : Si regime, above 1.5, is the most controversial point.³⁶

The simplest picture for C-S-H which emerges from the above description, in the scale of a few nanometres or tens of nanometres, is a stack of negatively charged lamellae separated by hydrated calcium ions and perhaps, at a Ca : Si ratio above 1.5, OH⁻ ions. Whether these calcium ions should be considered as adsorbed onto the lamellae or mobile within the interlayer space has still to be clarified. This picture immediately points to the similarity between C-S-H and clays of the smectite family, like montmorillonite for instance^{38,39} (Fig. 5). In montmorillonite, the layer thickness is also close to 1 nm and the layers are also negatively charged. However, beyond this first-order similarity, several differences should be kept in mind. In montmorillonite, the lateral extension of the layers is much larger than in C-S-H (more than 1 μm is common for montmorillonite). More important, the origin and the localisation of the layer charge are also different. In smectites, the charge stems from ionic substitutions in the octahedral or tetrahedral layer, or both (Fig. 6). Hence, the

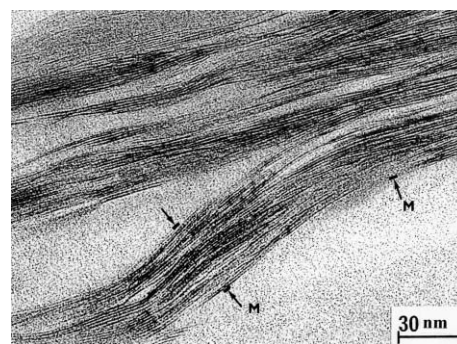


Fig. 5 TEM micrograph of calcium montmorillonite, showing the nanoscale lamellae and the intricate texture of the lamellae packets, merging in some places, separating in other places and generating a complex void space (courtesy of H. Gaboriau and C. Clinard).

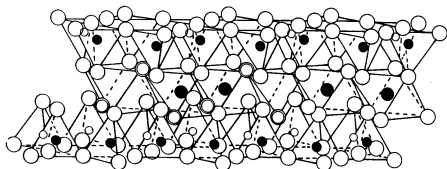


Fig. 6 Structure of montmorillonite. Large open circles are oxygen (single circles) or hydroxide (double circles) ions, large filled circles are aluminium ions in octahedral coordination and small filled circles are silicon ions in tetrahedral coordination. The ionic substitutions generating the layer charge (aluminum substituted by magnesium for instance) occur most frequently in octahedral sites and occasionally in tetrahedral sites (silicon substituted by aluminium or iron for instance). Note the different arrangement of the silica tetrahedrons as compared to tobermorite and C-S-H.

charge is embedded within the lamellae and, for a molecule located in the interlayer space, it is screened by one or more layers of oxygen atoms. In contrast, in C-S-H, the charge is located on the surface of the lamellae. A final difference is that the charge compensating cations in the interlamellar space are readily exchangeable in smectites, but hardly so in C-S-H, probably due to the previous point and to the greater charge density in C-S-H.

3. Experimental

3.1. Polymers

Neutral (PVA, PVME, PEO), anionic (PSS) and cationic (PDC, PVBC) polymers were used.

Poly(vinyl alcohol) (PVA). Two PVAs from Polyscience ($\bar{M}_w = 78\ 000$ Da), hydrolysed at 98 and 88% respectively (PVA98 and PVA88), were used in order to assess the influence of the number of polar groups per chain.

Poly(vinyl methyl ether) (PVME). A chromatographic standard from Scientific Polymer Process ($\bar{M}_w = 99\ 000$ Da, $\bar{M}_n = 46\ 500$ Da), was purchased as a 50% aqueous solution. It was dried under vacuum ($T_g = -31\ ^\circ\text{C}$) before use.

Poly(ethylene oxide) (PEO). A short chain PEO from Acros ($\bar{M}_w = 8\ 000$ Da) was chosen in order to assess the influence of chain length, by comparison with previous results.

Poly(styrene sulfonate) (PSS). PSS ($\bar{M}_w = 70\ 000$ Da) was used either as the sodium or potassium salt (PSSNa from Acros and PSSK from Polyscience, respectively).

Poly(diallyldimethyl ammonium chloride) (PDC). PDC (\bar{M}_w between 100 000 and 200 000 Da) was purchased from Aldrich as a 20 wt% solution. It was used after freeze-drying.

Poly(4-vinylbenzylammonium chloride) (PVBC). PVBC was synthesised from a mixture of isomers of 3- and 4-vinylbenzyl(trimethyl)ammonium chloride in degassed water at 50 °C under reflux and nitrogen, using 2,2'-azobis(2-aminidopropane) dihydrochloride[‡] as initiator. Two batches were prepared, leading to $\bar{M}_w = 300\ 000$ Da and $\bar{M}_w = 100\ 000$ Da, respectively, as estimated from viscosity measurements.

3.2. C-S-H and composite synthesis

The two direct synthesis methods mentioned in Section 2 were used: reaction of silica with lime ("pozzolanic method") and precipitation from soluble salts ("precipitation"). Both methods

may be applied to the synthesis of C-S-H and for the synthesis of the composites. In the former case the reaction medium is water, in the latter it is an aqueous polymer solution.

Pozzolanic method. Lime was prepared by heating calcium carbonate (Aldrich) at 1100 °C for 3 hours and used within 12 hours after preparation in order to avoid carbonation. Lime and silicic acid (Aldrich, particle size smaller than 20 μm), in the desired ratio for a given Ca : Si ratio in the final product, were added to deionized water or polymer solution at a solution : solid ratio of 20. The mixture was kept at 50 °C for at least three weeks in a CO₂-free atmosphere, with periodic shaking. After filtration, the product was washed twice, either with 5 ml of water or with an aqueous solution containing calcium and silicate ions at concentrations in equilibrium with the solid, unless otherwise stated. Drying was performed at 11% relative humidity until constant weight. In some cases, to be mentioned, drying was performed by washing the filtered product with acetone first, followed by ether and then drying at room temperature under vacuum. The same filtering, washing and drying methods were applied to the products obtained by the other methods described below.

Precipitation. Sodium metasilicate (Aldrich) was dissolved in water or in the polymer solution. The pH was adjusted to 13.2 with NaOH and the solution was flushed with nitrogen in order to remove dissolved CO₂ before the introduction of the calcium salt solution, prepared separately (calcium nitrate, Aldrich). The pH was kept constant during addition of calcium solution. The total solution : solid ratio was 20. The final solution was kept at 60 °C for one week under gentle stirring in a CO₂-free atmosphere.

Hybrid method. In some cases, a combination of the two previous methods was used. A sodium metasilicate solution was prepared as before and lime was then added as the source of calcium.

Post-intercalation. This method consists in mixing a pre-prepared pozzolanic C-S-H with a polymer solution. The mixture was then kept at 60 °C for two months under gentle stirring.

3.3. Characterisation

XRD spectra of powdered samples were recorded using a Philipps PW1729 diffractometer and Cu-K α radiation. In a standard procedure, data were collected using a 0.1 mm detection slit, $2\theta = 2.5^\circ$ to 60° in 0.03° steps, with a collection time of 5 s per step. In cases where a large interlamellar swelling was suspected, a 1/2 mm slit was used, allowing 2θ to start at 1.9° .

We were primarily interested in detecting a shift in the 001 reflection, which should be the signature of intercalation. In order to improve the accuracy of shift measurement, a background subtraction operation was performed between $2\theta = 2.5^\circ$ and 12° using a second degree polynomial fit of the background with a correlation coefficient higher than 0.99, which was then subtracted from the spectrum.

4. Results

4.1. Polymer-free hydrates

The XRD spectra of the C-S-H samples prepared by the two main methods and their variants contain the $hk0$ peaks expected for tobermorite, characteristic of the in-plane lamellar structure (see Section 2). However, the intensity and the width of the diffraction line undergoes significant variations, depending on the method used, on small differences in the

[‡]The IUPAC name for 2,2'-azobis(2-aminidopropane) dihydrochloride is 2,2'-azo(2-methylpropionamidine) dihydrochloride.

procedure (temperature, duration, particle size of the precursor materials in the pozzolanic method,...) or even on the batch, everything being kept (as much as possible) constant. Beyond these fluctuations, the general trend is a decrease of the in-plane crystal order as the Ca : Si increases, as inferred from the peak widths, in agreement with literature data.¹⁹

The fluctuations that were observed in crystallinity depending on the synthesis method and parameters were also observed for the lamellar stacking order and the [00 ℓ] reflections. In the overwhelming number of cases, only the [001] reflection is observed, at a position consistent with the structure of tobermorite, at spacings between 1.15 nm and 1.4 nm. A peak at 1.03 nm corresponding to jennite may also be observed with the pozzolanic method. The 001 peak of the samples prepared by the pozzolanic method show the already reported shift towards smaller distances as the Ca : Si ratio increases. The peak shifts from \sim 1.40 nm at Ca : Si = 0.7 to \sim 1.15 at Ca : Si = 1.5, revealing the decrease in the interlamellar hydration state. The shift was much less pronounced with the samples prepared by precipitation (average at 1.3 nm).

4.2. Polymer introduction in pozzolanic synthesis

We consider first the evolution of the small angle domain of the XRD spectra when the C-S-H synthesis was performed in solutions of PVME and PVBC, respectively. The samples were dried by washing with water-miscible organic solvents (Section 3.2). In what follows, the concentration of polymer in the synthesis solution will always be expressed as the "total number of Ca ions in the hydrate : total number of monomer units in the solution" ratio (Ca : m). Thus, as illustrated in Fig. 7 for PVME, only a modest increase in the lamellar repeat distance is generally observed, of the order of 0.07 nm at Ca : Si = 0.8 and Ca : m = 1.5, rising to 0.16 nm at Ca : Si = 1.4 and Ca : m = 1.00. The expansion is of the same order for PVBC. This is much less than the thickness of the stretched polymer

chain, which is, as calculated from van der Waals radii, 0.45 nm for PVME and 0.62 nm for PVBC. Hence, no clear evidence for polymer intercalation is observed.

At this stage, three possibilities may be considered. The first is that the expansion observed is due to an increase in the interlamellar hydration state. The second is that the intercalated polymer displaced the interlamellar water and is "keyed" in the atomic scale surface roughness of the C-S-H lamellae due to the silica chains (Section 2), so that the expansion is less than expected. The third is that the distance we measure at the maximum of the broad 001 reflection is an average of intercalated and non-intercalated domains, due to interstratification. In order to explore these possibilities, two series of experiments were performed on the PVME/C-S-H samples with complementary drying treatments: (i) drying the samples at 60 °C under vacuum or (ii) freeze-drying, and recording the XRD spectra immediately after drying. Although the 001 peak was considerably broadened by freeze-drying, it was observed that, with these treatments, the peak maximum shifted to the same position as that of the blank (polymer-free) samples submitted to the same treatment. Thus, of the three possibilities that we considered, only the first is left, namely that some samples retained more water in the standard (and mild) drying conditions than the others.

In spite of the absence of clear evidence for intercalation from XRD, chemical analysis shows that the carbon content is not negligible. In C-S-H/PVME at Ca : Si = 0.8, the Ca : m ratios in the products are 4, 7.3 and 9.5 for initial ratios of Ca : m in the reaction medium of 1.5, 1 and 0.75, respectively. Thus, up to one monomer per 4 calcium ions may be retained in the solid. This suggests that the polymer retained may be coating the C-S-H crystallites, thereby limiting the diffusion of water out of the interlamellar spaces during drying. In order to see whether this is coherent or not with the other observations, we washed particularly thoroughly the samples for which the largest expansion was observed (Ca : Si = 1.4 and initial Ca : m = 1.0), with aqueous solutions in equilibrium with the C-S-H in order to avoid Ca dissolution. The standard organic drying treatment was then applied. The 001 reflection is then observed at the same position as the polymer-free sample, further confirming that the polymer retained is not in the interlamellar space of the C-S-H crystallites. The lack of evidence for intercalation was similar for PSSNa, PSSK and PVA.

4.3. Post-intercalation

According to previously published results,²²⁻²⁴ post-intercalation is particularly facile with cationic polymers like PDC in C-S-H with Ca : Si = 0.8 or less. We used C-S-H prepared by the pozzolanic method at Ca : Si = 0.8. The solid was filtered and the filtrate was recovered. Its pH was 11.7. Since control of pH above 13 is reported to be important for successful intercalation,^{23,24} we performed two sets of experiments. In the first the pH was left at 11.7. In the second, the pH was first adjusted to 13.1 by adding KOH. Polymer solutions were prepared with each filtrate and C-S-H was added in various ratios. As illustrated in Fig. 8, no XRD evidence for intercalation is observed, even in what are supposed to be very favourable conditions (pH = 13.1).

PVBC behaves similarly. In this case, intercalation was attempted using a wide range of Ca : Si values (0.7, 0.8, 1.0, 1.1, 1.2, 1.3, 1.4, 1.5) and with Ca : m = 1.5 and 1. As illustrated in Fig. 9 for Ca : Si = 0.6 and Ca : Si = 1.0, no XRD evidence for intercalation was observed. In the latter case, the initial C-S-H is a mixture of tobermorite-like and jennite-like phases, with 001 peaks at 1.37 and 1.05 nm, respectively. Neither peak was found to shift significantly after contact with PVBC solutions.

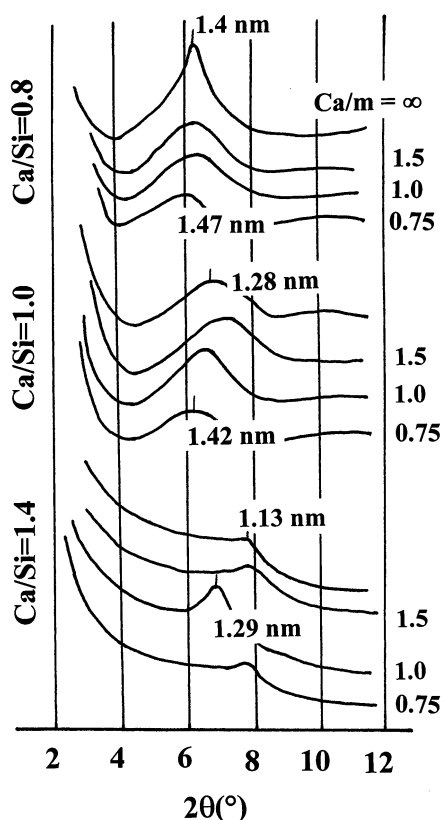


Fig. 7 Evolution of the low angle XRD diagram of pozzolanic C-S-H prepared in PVME solution, at different Ca : Si and Ca : m ratios.

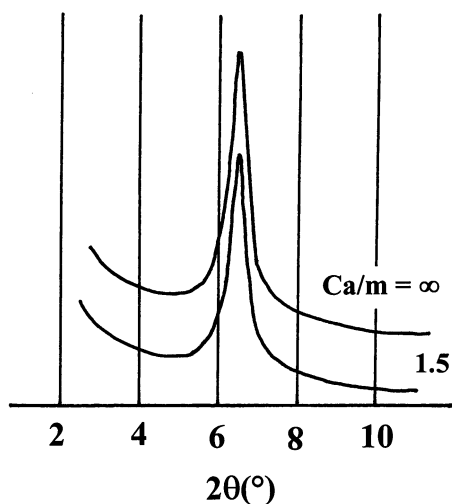


Fig. 8 Post-intercalation attempt: evolution of the 001 reflection of pozzolanic C-S-H at Ca : Si = 0.8 when treated with a PDC solution.

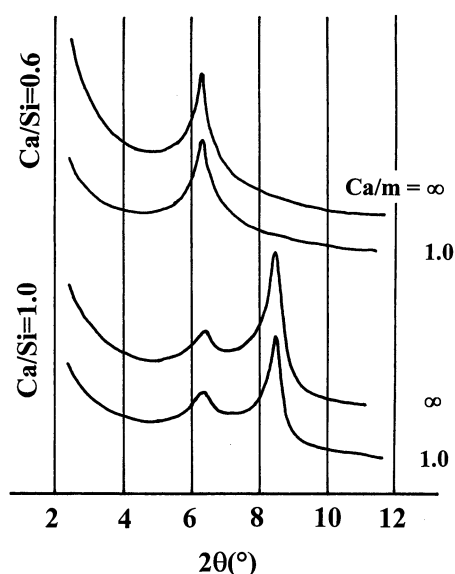


Fig. 9 Post-intercalation attempts: evolution of the 001 reflection of pozzolanic C-S-H at Ca : Si = 0.6 and 1.0 when treated with a PVBC solution at Ca : m = 1.0. The sample at Ca : Si = 1.0 is a mixture of tobermorite-like and jennite-like C-S-H.

4.4. Polymer introduction in precipitation synthesis

This is the main composite synthesis method used in the work of Matsuyama and Young.²²⁻²⁴ Once more, we focused our efforts on PDC and PVBC, with additional experiments with PVME. Intercalation was attempted both without and with pH adjustment above 13, at 13.1, by addition of NaOH during addition of the calcium salt to the silicate + polymer solution. Without adjustment, the pH drops to values slightly lower, between 12.7 and 13. The reason for the possible importance of pH adjustment above 13 is that this is the pK_{a3} of silicic acid. $[\text{SiO}_2(\text{OH})_2]^{2-}$ is the dominant form above pH = 13, whereas $[\text{SiO}(\text{OH})_2]^-$ is most abundant below 13.

C-S-H precipitation in PVME solutions was performed at "natural" pH, at three Ca : Si ratios (0.9, 1.1 and 1.5) and two Ca : m ratios (1.0 and 0.75). A slight expansion of the order of 0.07 nm was observed in one case (Ca : Si = 0.9 and Ca : m = 0.75), but the general situation is either no change, or even a slight but repeatable contraction at Ca : Si = 1.1. With PVBC at the same Ca : Si ratios and in the same pH conditions, a modest expansion (0.2 nm) is observed only in one case (Ca : Si = 0.9 and Ca : m = 1.0). Under all the other conditions,

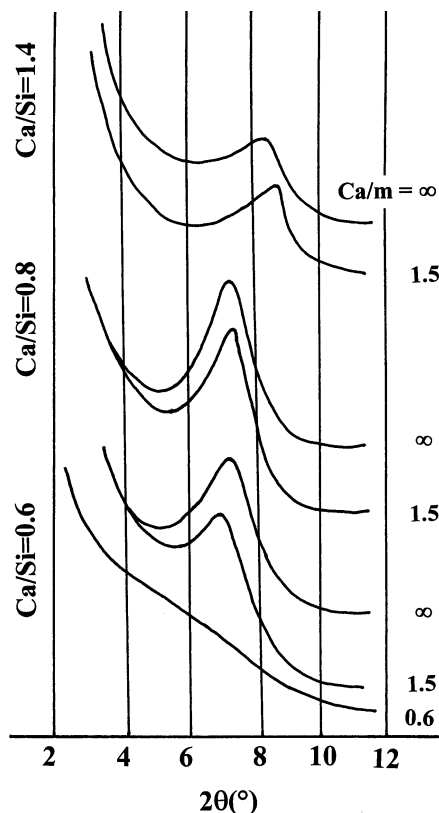


Fig. 10 001 X-ray diffraction peak of C-S-H prepared by precipitation in PDC solutions at Ca : m = 1.5 or 0.6 and at different Ca : Si ratios. Notice the strong amorphisation of the stacking order in the sample prepared at very high polymer concentration (Ca : m = 0.6; 42.5 g L⁻¹).

there is either no change or a contraction. POE and PVA behave in the same way.

Another series of precipitation syntheses were performed with PVME and PVBC, with pH adjustment at 13.1 for Ca : Si = 0.9, 1.1 and 1.5, respectively. Several syntheses in this series were also performed with the lower molecular weight (100 000) PVBC. Once more, only a negligible expansion was observed in a few cases. Thus, pH control above 13 did not prove to be a decisive factor. In addition, comparison of PVBC 100 000 with PVBC 300 000 shows that a smaller molecular weight does not facilitate intercalation. PDC, which was previously reported to intercalate with a strong interlayer expansion,²² does not behave differently. As shown in Fig. 10 for attempts performed at pH = 13.1, Ca : m = 1.5 and Ca : Si = 0.6, 0.8 and 1.4, no significant interlayer expansion was observed. A special attempt was made at a polymer concentration higher than in all the other experiments, with Ca : m = 0.6, pH 13.1 and Ca : Si = 0.6. The most noticeable feature is the strong and reproducible broadening of the 001 reflection (Fig. 10), which reflects the strong polymer-induced disorder of the C-S-H lamellae stacking. Remarkably, the carbon content of these samples is 10 mass%, which is comparable to the carbon content of the samples prepared with a similar polymer by Matsuyama and Young.

5. Discussion

The general conclusion of this work is that neither the intercalation of polymers in pre-grown C-S-H nor their introduction in the interlamellar space during C-S-H growth, by pozzolanic or precipitation reactions, are facile reactions. In spite of a few clues which suggest that some polymer may have been introduced in the interlamellar space of C-S-H in a few cases, the overwhelming majority of our data point to the

absence of intercalation. This is in disagreement with the work of Matsuyama and Young (MY),^{22–24} but is in agreement with the conclusion of Popova *et al.*⁴⁰ who studied the interaction of anionic copolymers with C-S-H during its pozzolanic synthesis and found no evidence of interlayer adsorption. The disagreement of our results with those of MY is strongest in the case of the cationic polymers, which were unambiguously able to induce a strong interlayer expansion in the experiments performed by MY, but in our work, in the best case, only a very moderate expansion was observed. In spite of this, there is often a modification of the XRD 001 peak profile when the synthesis is performed in a polymer solution. In addition, carbon analysis shows that the amount of polymer retained may be in some cases almost as high when there is no XRD evidence for intercalation as when there is clear evidence of intercalation.

When taken together, our results, those of Popova *et al.*⁴⁰ and those of MY point to what is notoriously the essential structural feature of C-S-H: its non-stoichiometric and nano-crystalline nature, which makes the structural analysis of its complexes with organic molecules much more complex than in the case of smectite clays. In order to understand what intercalation means in the case of a nano-crystalline material and to what extent it differs from simple adsorption, it may be worth thinking in terms of a tentative model, as sketched in Fig. 11. In a well-ordered layered material with large lamellae, like a graphite single crystal for instance, intercalation is a clear concept. The external surface area of the crystal is negligible as compared to the area of the interlayer space within the crystal. In a disordered layered material made of more or less deformable lamellae of limited lateral extension, like the structure sketched in Fig. 11, the regions which correspond to what could be called the interlayer space represent only a small fraction of the total porosity. Some regions are indeed in a *local* configuration in which the platelets are parallel to each other and separated from each other by a small and regular spacing, but the major part of the void space is composed of ill-defined regions in which the platelets are not parallel or are separated by a larger distance. In smectite clays, this situation has long been recognised and the locally ordered regions have been called “quasi-crystals”.⁴¹ The relative importance of the ordered regions, *i.e.* their volume fraction and their thickness, determines to a large extent the mechanical properties of the material, its adsorption properties and its transport properties (permeability).^{42–44} The thickness of the quasi-crystalline domains and their stiffness is directly correlated to the interlayer forces which are themselves controlled by the ionic or molecular species present in the material. Quantitatively, in a material like Na montmorillonite, in the form of a self-standing film prepared by slow sedimentation (hence, in a case where local order is favoured), interlayer adsorption may represent only 50% of the total amount of molecules adsorbed at saturation.⁴⁵ Considering the poor local stacking order and

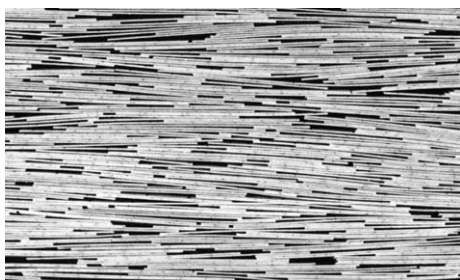


Fig. 11 Cartoon of the possible texture of a disordered layered material forming ordered and compact stacks (“quasi-crystals”) at some places and voids of various shapes at other places. The volume of these voids is comparable to the total volume of the interlayer space between lamellae in the stacks.

the smaller lateral extension of the platelets in C-S-H, the ratio of interlayer void space to total void space should be even less. It is therefore not surprising that the amount of polymer retained may be significant, even without intercalation.

Yet it remains to be explained why smectite clays intercalate some neutral or cationic polymers, like PVA,^{9,10} PEO^{10,46} or DMAEM (2-dimethylaminoethyl methacrylate)^{9,10} and not C-S-H, at least in the experiments reported here. As already pointed out in Section 2, smectites and C-S-H differ in two important respects: the localisation of the layer charge on one hand (within the layer for smectites, on the layer surface for C-S-H) and the charge density on the other hand. Although the real surface charge of C-S-H lamellae has never been directly measured, its maximum value may be estimated by assuming complete ionisation of all the surface OH groups of a tobermorite lamellae.⁴⁷ This leads to a surface charge density of the order of 0.03 e nm^{-2} for C-S-H, compared to 0.005 e nm^{-2} or less for smectites. Thus, the charge density is high in C-S-H and very localised, whereas it is low and smeared out in smectites. One consequence of this is that cation exchange is easy with smectites and difficult with C-S-H. Another and more important consequence is that C-S-H does not swell in water, whereas smectites do.⁴⁸ Recent Monte Carlo simulations show that ion correlation forces, which increase in strength with the layer charge density and the valence of the counterions in the interlayer space, are particularly strong between adjacent C-S-H lamellae and are probably responsible for the strong cohesion of C-S-H crystallites.^{47,49} It is likely that this strong cohesion is a limiting factor for polymer penetration in the interlamellar space.

6. Conclusions

The synthesis of C-S-H/polymer nanocomposites with water-soluble polymers has been attempted. Intercalation of polymers into the interlamellar space of C-S-H is a difficult reaction, whatever the synthesis method. Neither the intercalation of polymers in pre-grown C-S-H nor their introduction into the interlamellar space during C-S-H growth, by pozzolanic reaction or by precipitation, were found to be effective. Nevertheless, there is evidence that the polymer interacts with the stacking order of the hydrate lamellae and that it is adsorbed in significant amounts on the surface or in the void space left by the lamellae “stacks”. Thus, the composite materials obtained could be described as meso-composites. Their mechanical properties remain to be studied.

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