A ^{29}Si MAS NMR study of modified C–S–H nanostructures

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ABSTRACT

The sustainability of cement-based materials is a core technical issue of national importance. The service-ability of the concrete infrastructure, especially bridges, has recently received considerable media attention. Concurrently, the nanoscience of cements has emerged as a new discipline with the potential to positively manipulate the nanostructure of calcium silicate hydrate (C–S–H) in order to achieve sustainability objectives. Organic/inorganic C–S–H nanocomposites are being developed to enhance durability and long-term engineering behavior. Results of a ^{29}Si MAS NMR study of phase pure C–S–H (prepared with C/S ratios 0.6–1.6) modified by interaction with hexadecyltrimethyl ammonium (HDTMA), methylene blue (MB), polyethylene glycol (PEG), polyvinylalcohol (PVA) and polyacrylic acid (PAA) are reported. It is apparent that the degree of silica polymerization is affected by the presence of the various organic molecules and the C/S ratio of the C–S–H. Possible mechanisms responsible for this effect are described. The implications of these nanostructural changes for sustainability are discussed. It is suggested that the interaction of polymers with the nanostructure of C–S–H that increases silicate polymerization may improve volume stability and promote mechanical properties of such systems. The resistance of polymer-modified C–S–H systems in chemically aggressive environments is likely to be increased as the defect sites in the silicate structure are eliminated by the presence of polymer molecules.

1. Introduction

Sustainability issues have become paramount for the construction materials industry [1]. Cement-based materials are microporous and subject to attack from aggressive media including gases (carbon dioxide) and liquids (salt solutions) [2]. Pore structure and composition of the solid phase are determining factors for performance. Changes to the nanostructure of calcium silicate hydrate (C–S–H, the primary binding phase in Portland cement concrete) can have a significant effect on the micro and macroscopic behavior of concrete. One approach involves the development of modified cement-based nanocomposites. These materials are generally comprised of polymer-modified C–S–H. There are only a few studies that have been reported [3–14]. There is an indication that the mechanical properties can be enhanced. It is also evident that access to the internal structure of C–S–H can be impeded by integration of a polymer phase within the nanostructure. Penetration of aggressive ions into the interlayer regions from layers ends or at defect points (e.g. missing bridging tetrahedra on the silicate chain) is likely to be resisted by the presence of polymer either in the interlayer or grafted on the silicate surface. The nature of the C–S–H–polymer interaction has not been resolved although a clearer picture is emerging. C–S–H has a disordered layered structure made of "dreierkette" linear silicate chains elongated in a twisted pattern in one direction, analogous to that of tobermorite or that of jennite, with a layer thickness in the nanometer range [15,16]. These silicate chains are grafted to a double plane of calcium ions coordinated by oxygen ions, thus creating stacks of layers sandwiched between calcium ions and water molecules. Solid state NMR studies such as ^{29}Si MAS NMR have revealed the existence of variable chain lengths of silicates, where a silicon site Q^1 represents an end group of a chain, Q^2 a middle group, Q^3 a branching site and Q^4 a fully cross linked group. Recent studies on the nanostructure of C–S–H provided considerable information on this semi amorphous material, including a number of structural analogies as well as notable differences with natural clays (smectites) [7,17]. Several papers describe efforts to incorporate different entities such as polyethylene glycol (PEG), hexadecyltrimethylammonium (HDTMA), dimethyl sulfoxide (DMSO) and methylene blue (MB) and others into aluminosilicates, e.g. smectites, montmorillonite, or kaolinite [18–21]. Pioneer work in the field was led by Lagaly and Lagaly et al [22,23] including the dependence of the extent of intercalation of different molecules on the surface chemistry of these aluminosilcates. Since layered aluminosilicates are rather hydrophobic, to facilitate the transport of the organic molecules into the interlamellar space, it is essential to first modify the silicate surface. Replacement of the inorganic interlayer cations (Na, Ca, K, etc.) by cationic surfactants such as alkylammonium or by the use of different solvents as a pre-swelling agents,

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promote exchange with a wider range of molecules. The ^{29}Si MAS NMR spectroscopy can discriminate the nature of the bonding in proximity to the silicon sites. A ^{29}Si MAS NMR study was designed to assess the effects of the interactions between C–S–H of variable stoichiometry and several polymers e.g. PEG, HDTMA, DMSO and MB. The implications of using these types of organic molecules and polymers for the nanostructural improvement of layered silicates have been extensively studied in clay science. The use of these selected organic molecules has allowed clay scientists to obtain better insights of the structural properties of these inorganic materials. This has also provided researchers with tools to tailor their properties and improve performance for different applications. The analogy of clay minerals with the calcium silicate hydrates in the assembly of silicate structure makes them suitable candidates for relevant experimental studies in cement science. The achievement of improvements in the properties of C–S–H using similar polymers to those used in clay investigations is therefore promising. The results of ^{29}Si MAS NMR experiments on the organically modified C–S–H systems are reported in this paper.

2. Experimental

2.1. Synthesis of C–S–H

C–S–H samples with C/S ratios of 0.60, 0.80, 1.00, 1.20, 1.50, 1.60 were prepared using stoichiometric amounts of CaO and amorphous silica mixed at a water–solids ratio of about 10:1. The CaO was produced using precipitated $CaCO_3$ heated at 900 °C for 24 h. The CaO was purged with nitrogen gas and stored in a desiccator until required. The amorphous silica was heated at 110 °C to dry the material thoroughly. The reactants for producing C–S–H were placed in high-density polyethylene (HDPE) bottles that were continuously rotated (16 rpm) for periods up to 1 year. The reaction temperature was 23 °C. The material was then filtered to remove excess water and dried under vacuum for 4 days. The resulting products were placed in HDPE bottles, purged with nitrogen and stored until further use. Samples of the various C–S–H preparations were put aside for immediate characterization using thermogravimetric analysis (TGA) and X-ray diffraction (XRD) methods.

2.2. Characterization of C–S–H

2.2.1. ^{29}Si MAS NMR Spectroscopy

The ^{29}Si MAS NMR spectra were recorded at 39.6 MHz on a Tecmag Apollo 200 spectrometer. Samples were packed into a 7 mm Zirconia rotor and spun about the magic angle at about 4.5 KHz, in a probe supplied by Doty Scientific. A simple pulse and acquire pulse sequence was used. The sweep width was 10 KHz and the 90-degree pulse length was 7 μs. A relaxation delay of 60 s was normally used. The final spectra took up to 48 h to obtain. Chemical shifts are reported relative to tetramethylsilane (TMS).

Fig. 1. ^{29}Si MAS NMR spectra of C–S–H: C/S = 0.6, 0.8, 1.0, 1.2, 1.5, 1.6.

Table 1
^{29}Si MAS NMR parameters for C–S–H nanocomposites

C–S–H preparation	Q[2]/Q[1]	Mean chain length[a] (MCL)
Ref. C–S–H (C/S = 1.6)	0.60	3.20
C–S–H–PEG 300	1.91	5.82
C–S–H–PEG 450	2.02	6.04
C–S–H–PEG 1000	1.37	4.74
C–S–H–HDTMA	1.99	5.96
Ref. C–S–H (C/S = 1.0)	1.12	4.24
(C/S = 1.20)	0.31	2.62
(C/S = 1.50)	0.24	2.48
C–S–H–MB (C/S = 1.0)	7.20	16.40
C–S–H–MB (C/S = 1.2)	0.70	3.40
C–S–H–MB (C/S = 1.5)	0.74	3.48
C–S–H–Na	3.06	8.12
Ref. C–S–H[b] (C/S = 1.3)	0.64	3.28
C–S–H–PVA	0.52	3.04
C–S–H–PAA	2.67	5.34

[a] MCL = [(Q[2]/Q[1]) + 1] × 2.
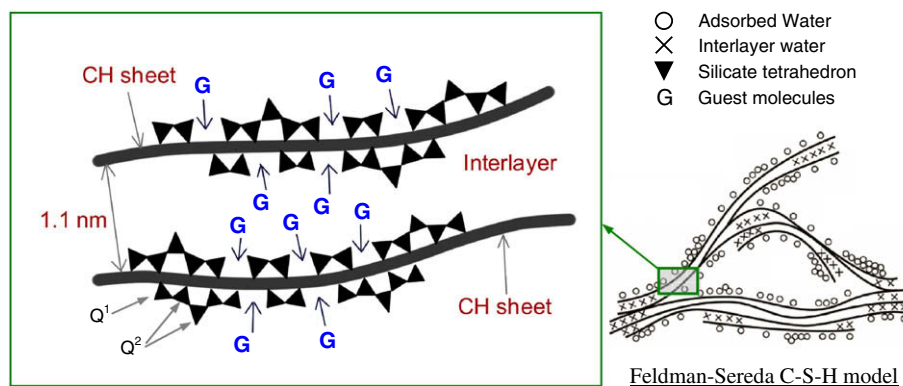[b] Matsuyama and Young, Ref. [3].

Fig. 2. A schematic of C–S–H nanostructure showing possible site for grafting of guest molecules (organic and inorganic).

2.2.2. TGA

The various C–S–H samples were placed in a TAQ 600 TGA (TA Instruments) and heated at a rate of 10 °C/min from room temperature to 1050 °C. The analysis was conducted in a nitrogen environment. The thermogravimetric curves (mass loss versus temperature) for the C–S–H preparations (for C/S ratios up to 1.6) were qualitatively and quantitatively similar to that reported for the C–S–H gel [24,25]. The mass loss in the region 400–600 °C was very small for the latter. An even smaller loss was observed for the C–S–H used in this study, suggesting that the residual amount of Ca(OH)₂ is small or negligible. Constitutional water loss likely contributes to the small mass loss in this region.

2.2.3. XRD

The XRD measurements were performed with a Scintag XDS 2000 diffractometer using CuK$_\alpha$ radiation. Characterization of the C–S–H was carried out in the range 5 < 20 < 60° using a continuous scan rate of 2°/min. Background correction was performed on the XRD patterns. The X-ray patterns indicated the presence of the primary peaks previously reported for C–S–H. A change in the peaks positions and shapes were observed for all the nanocomposite materials as a result of C–S–H interaction with Na and different organic molecules.
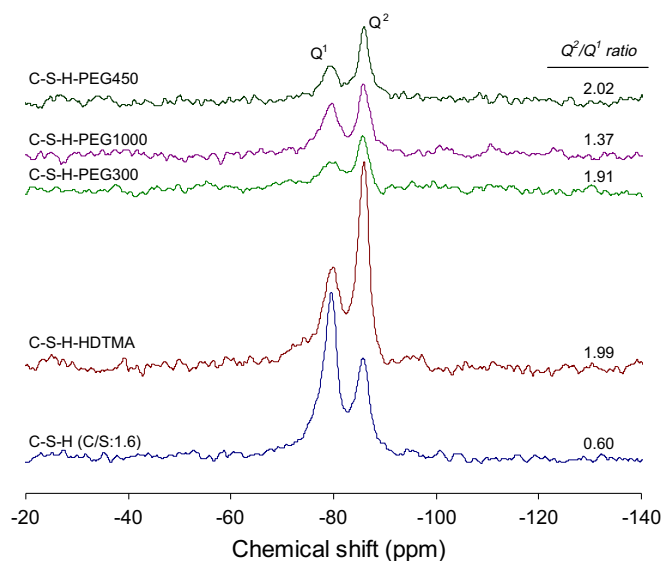

Fig. 3. ^{29}Si MAS NMR spectra for C–S–H (C/S = 1.60) and C–S–H–polymer nanocomposites where the organic molecules is PEG (MW300, 450, 1000), HDTMA, DMSO.

2.3. Preparation of C–S–H nanocomposites

2.3.1. C–S–H–HDTMA

Preparation of hexadecyltrimethylammonium C–S–H designated C–S–H–HDTMA using the reference C–S–H (C/S = 1.60) as a precursor was carried out by reacting C–S–H with an excess of aqueous 0.01 M HDTMA-Br (molecular weight = 354.46) solution for 24 h followed by washing with distilled water until the halide (Br) was not detected with AgNO₃. The material was then vacuum dried for 12 h.

2.3.2. C–S–H–PEG

Polyethylene glycol of MW 300 (PEG 300), MW 450 (PEG 450), or MW 1000 (PEG 1000) was heated between 65–70 °C. The C–S–H (C/S = 1.6) was dispersed in the polymer melt under N₂ with vigorous magnetic stirring for 24 h. At the end of the reaction run, the product was filtered and washed with methanol to remove the excess polymer.

2.3.3. C–S–H–MB

The initially dry C–S–H samples (C/S = 0.6–1.6) were resaturated in methylene blue (MB) solutions having a MB concentration of 15 mg/L. MB adsorption is very rapid and equilibrium is attained in a few minutes. All C–S–H samples were kept in the MB solution for 24 h. Following immersion in the MB solution the samples were removed from solution and dried under vacuum for 4 h. ^{29}Si MAS NMR measurements were performed on both untreated and samples treated with MB solution.

2.3.4. C–S–H–Na

Preparation of C–S–H–Na was carried out by reacting the C–S–H (C/S = 1.6) with NaCl solutions (20 g/L) for 24 h followed by filtration and washing with distilled water until the halide (Cl) was not detected with AgNO₃. The materials were dried under vacuum at 50–60 °C.

2.3.5. C–S–H–PVA and C–S–H–PAA

C–S–H nanocomposites with different PVA (MW = 70,000–100,000) contents (0.0–0.75 g/g Ca salt) and PAA (MW = 5000) contents (0.0–2.0 g/g Ca salt) were synthesized by gradually adding a calcium nitrate solution (1 mol/l) with continual stirring under nitrogen to a sodium silicate solution, in which PVA or PAA was pre-dissolved in CO₂-free de-ionized water. The initial C/S molar ratio was 0.7 for nanocomposites with PVA and 1.4 for those prepared with PAA. During the hydrothermal synthesis, the pH was kept between 13.1–13.4 by adding NaOH solution (4.0 M). After aging the suspension at 60 °C for seven days with continuous

stirring, the precipitate was separated by vacuum filtration and washed with CO_2-free de-ionized water to remove excess sodium, nitrates and residual polymeric entities. Prior to analysis, the precipitates were washed with acetone and dried at 60 °C/vacuum for 7 days.

3. Results and discussion

The objective of the ^{29}Si MAS NMR study was to assess the nature of the interactions between C–S–H and various organic species. The interaction of Na with C–S–H as a pre-treatment to facilitate possible intercalation was also investigated. Interpretation of the spectroscopic evidence is intended to provide some insight about the location and structural role of the organic species. The NMR spectra for the control C–S–H specimens (C/S = 0.6–1.6) are shown in Fig. 1. They are very similar to those reported by Cong and Kirkpatrick [26]. Low C/S ratio preparations (0.6 and 0.8) are characterized primarily by a single sharp Q^2 peak indicating the presence of relatively long silicate chains (a higher degree of polymerization). A tiny Q^3 peak is present for the C/S = 0.6 preparation indication a small degree of crosslinking. The peaks on the shoulder of Q^2 peak for C/S = 0.6 and 0.8 are attributed to the difference in the local environment of Q^2 sites as in the bridging positions and paired groups [27,28]. The chemical shift of bridging sites may also vary depending on the chemical attachments such as OH^- or Ca^{2+}. Q^1 peaks appears at C/S = 1.0 with the Q^2/Q^1 intensity ratio exceeding 1.0. At higher C/S ratios ($\geqslant$1.2), the Q^2/Q^1 ratio is significantly less

Fig. 5. ^{29}Si MAS NMR spectra for C–S–H (C/S = 1.60) and C–S–H–Na.
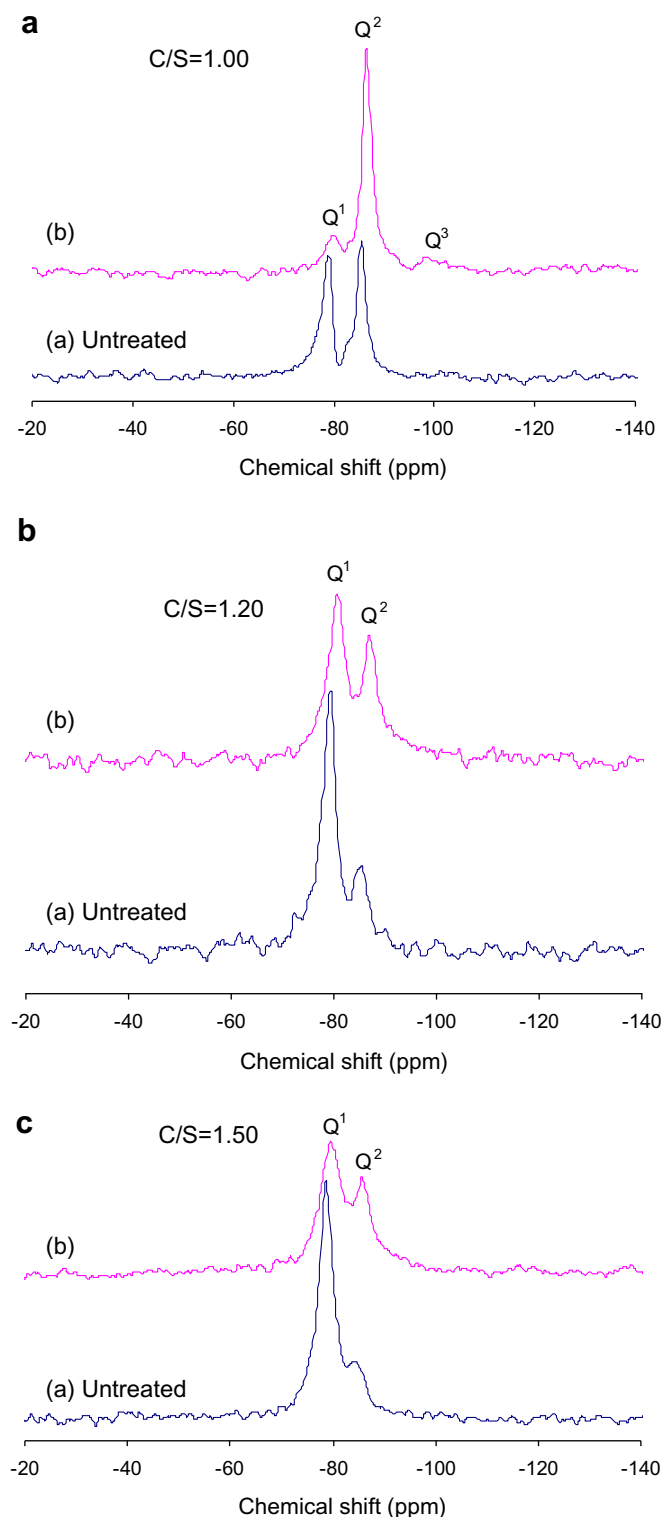

Fig. 4. ^{29}Si MAS NMR spectra for C–S–H (C/S = 1.0, 1.2 and 1.50) and the corresponding spectra for C–S–H–MB nanocomposites.
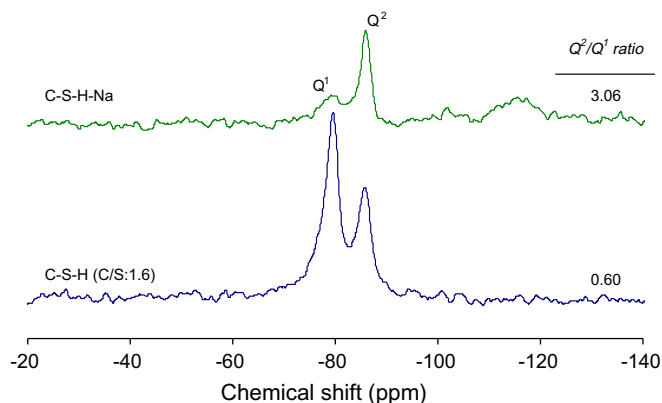

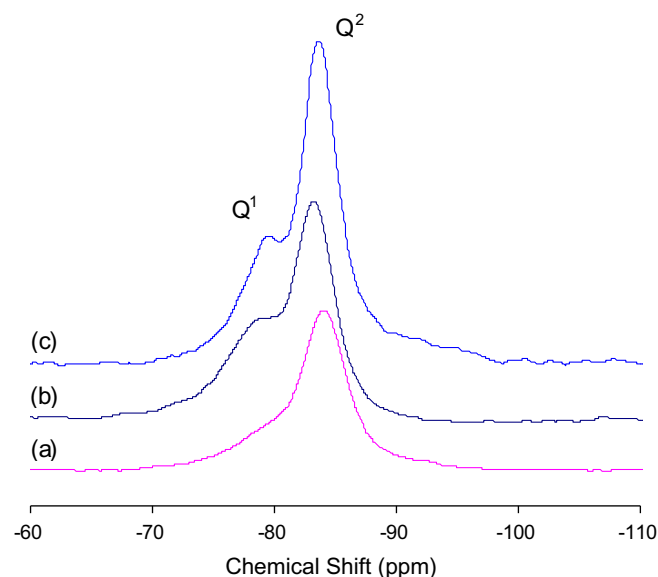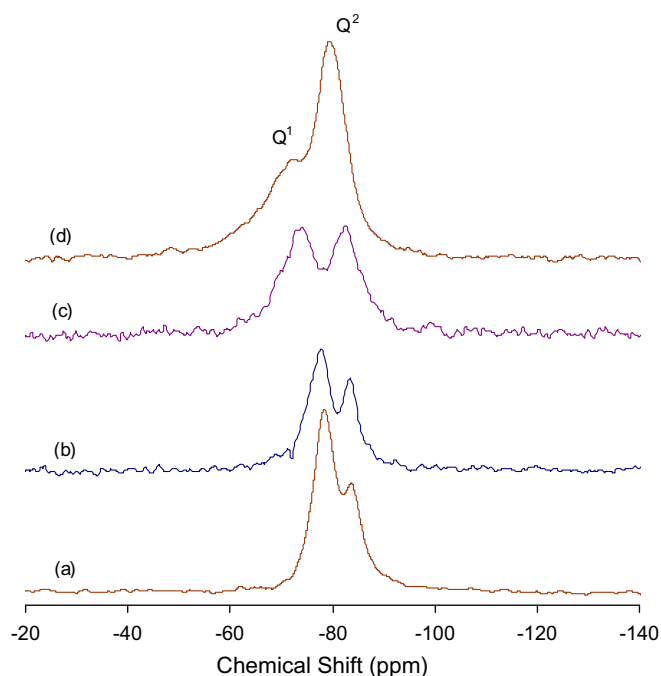**Fig. 6.** ^{29}Si MAS NMR spectra for: (a) C–S–H (C/S = 0.7); (b) C–S–H/PVA (0.7–0.5) and (c) C–S–H/PVA (0.7–0.75).

Fig. 7. ^{29}Si MAS NMR spectra for: (a) C–S–H (C/S = 1.4); (b) C–S–H/PAA (1.4–0.02); (c) C–S–H/PAA (1.4–0.15) and (d) C–S–H/PAA (1.4–0.35).

than 1, indicating that the silicate chains are comprised primarily by dimers. Locations along the silicate chain where there are missing bridging tetrahedra can be considered as nanostructural defects and possible sites for polymer grafts. It is also possible that some polymer molecules can intercalate into the interlayer space.

The ^{29}Si MAS NMR results of polymer–C–S–H nanocomposites produced in this study will now be discussed. In this context, reference to Matsuyama and Young will be useful [3]. They concluded that the addition of a polymer such as polyacrylic acid (PAA) results in lengthening of the chains. At C/S = 1.3, they observed a significant expansion of the basal spacing for polyvinylalcohol (PVA) modified C–S–H. This was, however not accompanied by a change in the Q^2/Q^1 ratio in the ^{29}Si MAS NMR spectrum. The implication is that the PVA was resident primarily in the interlayer region and did not graft onto the silicate at the sites of the missing bridging silica tetrahedra in contradistinction to the PAA nanocomposites which exhibited a significant increase in Q^2/Q^1 ratio (see Table 1 for ^{29}Si MAS NMR parameters). It would appear likely from this work that several organic species can be involved in different types of interaction with C–S–H i.e. intercalation, grafting at sites of missing silica tetrahedra or possibly combinations of both. A schematic of the C–S–H structure showing possible sites for polymer grafts is provided in Fig. 2.

Grafting at sites of missing tetrahedra has been reported for silylated polymers [29]. It is known that electrons of the atoms in the vicinity of existing –O–Si–O bonds can shield the silicon nuclei resulting in a detectable chemical shift. These shifts depend on the extent and strength of shielding. A chemical shift for the silicon atom will occur in the following cases: –O–Si–O–H; –O–Si–O–Na; –O–Si–O–Si–; –O–Si–O–[Polymer]. The chemical shift is different most of the time but it is theoretically possible to have two different attachments that result in a similar chemical shift. In other words the chemical shift of Si in the vicinity of the polymer can be similar to that obtained with a Si–O–Si bond and mimic the latter which is called Q^2. This would explain the increase in the Q^2/Q^1 ratio observed for C–S–H–PVA by Matsuyama and Young [3].

The ^{29}Si MAS NMR spectra for the referenced C–S–H (C/S = 1.60) and C–S–H treated with polyethylene glycol (PEG molecular weight: 300, 450 and 1000), hexadecyltrimethyl ammonium (HDTMA) and dimethyl sulfoxide are shown in Fig. 3. It is clear for all these spectra that there is a significant increase in the Q^2/Q^1 ratio (degree of silicate polymerization) ranging from 1.37 for PEG 1000 modified C–S–H to 2.0 for the HDTMA and PEG (MW 450). The Q^2/Q^1 ratio C–S–H modified with PEG (MW 300, 450 and 1000) are 1.91, 2.02 and 1.37, respectively. The Q^2/Q^1 results and chain length calculations are summarized in Table 1. It would appear that for the HDTMA–C–S–H and PEG–C–S–H nanocomposites both intercalation and grafting of the surface of the silicate sheets may occur. The authors have previously observed expansion of the (002) basal spacing (the mean distance between the C–S–H layers) in these nanocomposite preparations [30,31] supporting the view that intercalation is likely a contributing mechanism to nanocomposite formation.

The ^{29}Si MAS NMR spectra for C–S–H (C/S = 1.0, 1.2 and 1.5) treated with methylene blue (MB) along with those of the untreated reference samples are presented in Fig. 4a–c. The Q^2/Q^1 ratio and length of the silicate chains have significantly increased for all these preparations. These values are also summarized in Table 1. It is suggested that the methylene blue dye molecules are also grafted at sites of missing bridging tetrahedra in the silicate chains of the C–S–H nanostructure. The authors have shown that the X-ray basal spacing (002) peaks significantly increase in intensity after treatment with MB solution supporting the evidence for increased C–S–H polymerization [32].

The authors have also examined the interaction between sodium ions and C–S–H. It is known that sodium can be incorporated into the C–S–H structure [17]. This information was thought to be useful for interpreting the effect of the polymers on the C–S–H nanostructure.

The Q^2/Q^1 ratio of the Na treated with C–S–H (C/S = 1.60) was also significantly increased (see Table 1 and Fig. 5). The C–S–H in this case was preformed prior to immersion in a NaCl solution (20 g/L) for 24 h followed by vacuum drying at 50–60 °C. A similar increase in the Q^2/Q^1 ratio of Na treated C–S–H (C/S = 1.0) was observed by Mitchell et al. [33]. In their experiments, C–S–H was synthesized in a 1 M solution of NaOH. It is suggested that sodium is incorporated in the silicate chains at sites of missing silica tetrahedra bonding to oxygen in the chain –O–Si–O–Na. This mechanism of increased silicate polymerization appears to be operative independent of whether the C–S–H is preformed prior to interaction with Na or the interaction occurs insitu formation of C–S–H.

It is suggested that the C–S–H nanocomposites have the potential to mitigate the effects of deleterious processes e.g. decalcification due to leaching and other interaction with aggressive species e.g. magnesium salts. These benefits should arise due to the limiting effects of silicate polymerization on the ingress of aggressive species into the layered silicate structure. This would be a result of the elimination of defects at sites of missing bridging silica tetrahedra along the silicate chains. The authors are currently designing experiments (based on helium diffusion techniques) to validate development of these concepts. Helium gas can be used as a nanostructural probe to estimate the volume of nanospaces that are not instantly accessible. The conventional diffusion of helium into the interlayer regions may be restricted by the presence of organic molecules at the silicate defect sites or at the entrance locations of the interlayer space. It is expected that a new generation of polymer-modified cement-based materials may have an impact on sustainability. These modifications are likely to improve the resistance of C–S–H, and thus concrete microstructure, to several types of aggressive media. This, in turn, may contribute to more sustainable use of concrete materials.

The effect of polymer concentration on the Q^2/Q^1 ratio was studied for C–S–H made at C/S = 0.7 and 1.4. The ^{29}Si MAS NMR spectra are shown in Figs. 6 and 7 for PVA and PAA respectively. In the case of PVA, the mean length of the silicate chain determined by the Q^2/Q^1 ratio is increased in all nanocomposites as a result of an increase in the polymer concentration. A broadening of the Q^2 peak as well as a transformation of the Q^1 signal from a peak to a shoulder was observed. This behaviour is explained by a change in the local neighbour of the Si nuclei caused by the interaction of the polymer molecules with the silicate chains.

For nanocomposites made with PAA and C–S–H at C/S = 1.4, the ^{29}Si MAS NMR spectra shows a Q^2/Q^1 ratio increase with the concentration of PAA. The starting material, C–S–H (C/S = 1.4) exhibits a Q^2/Q^1 ratio smaller than the C–S–H with C/S = 0.7 due to missing of bridging silica tetrahedra in the dreierketten chains. Defects in the main silicate chains create new hosting "nests" for PAA molecules. These organic moieties are therefore grafted on the edges of the silica chains leading to more Q^2 groups presence and hence to an increase of Q^2/Q^1. Nanocomposites with higher PAA concentration (Fig. 7d) show a spectrum similar to that for pure C–S–H at C/S = 0.7 (Fig. 6a).

4. Conclusions

1. ^{29}Si MAS NMR spectroscopy can provide useful nanostructural information about the nature of polymer–C–S–H interactions.
2. The interaction of several organic species e.g. polyethylene glycol, hexadecyltrimethyl ammonium, methylene blue, polyacrylic acid with C–S–H promotes an increase in the degree of polymerization of the silicate chains.
3. An increase of organic molecules concentration generates an increase of the Q^2/Q^1 ratios.
4. The interaction of organic molecules with C–S–H may involve the following: grafting at sites of missing bridging silica tetrahedra, intercalation or both.
5. The chemical shift (^{29}Si MAS NMR) of silicon in the vicinity of the organic molecule located in the C–S–H nanostructure can be similar to the chemical shift of a silicon bond. This accounts for increases in the Q^2/Q^1 ratio of the C–S–H–polymer nanocomposites studied.
6. Sodium bonds to the C–S–H silicate structure at sites of missing bridging tetrahedra. This reaction can occur in situ during the synthesis of C–S–H or when pre-formed C–S–H is immersed in solution containing sodium cations.
7. C–S–H nanocomposites have the potential to mitigate the effects of deleterious processes e.g.: decalcification. It is expected that a new generation of cement-based materials may have an impact on sustainability of concrete infrastructure.

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