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FORMATION AND CHARACTERIZATION OF CALCIUM SILICATE HYDRATE- HEXADECYLTRIMETHYLAMMONIUM NANOSTRUCTURE

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Abstract

Results of an investigation of the interaction potential of synthetic and pre-treated C-S-H (with hexadecyltrimethylammonium (HDTMA)) are reported. The effective and strong interaction of these molecules with the C-S-H surface was shown using ^{13}C and ^{29}Si CP MAS NMR, XRD, TGA, SEM and FTIR analysis. The HDTMA-C-S-H interaction is influenced by the poorly crystallized layered structure of C-S-H. An indefinite number of layers and an irregular arrangement are confirmed by the SEM images. The position and shape of the 002 reflection of C-S-H are affected by drying procedures, chemical pre-treatment and the reaction temperature. Recovery of the initial 002 peak position after severe drying and rewetting with distilled water or interaction with HDTMA is incomplete but is accompanied by an increase in intensity. It is inferred that the stability of C-S-H binders in concrete can be affected by a variation in nanostructure resulting from engineering variables such as curing temperature and use of chemical admixtures.

INTRODUCTION

The volume stability of hydrated Portland cement and concrete is central to durability issues concerning exposure to aggressive media [1]. Disruptive expansions often occur in concert with deleterious reactions between hydrated cement phases (or cement minerals themselves) and ions in the pore solution present as a result of various transport processes [2]. Mechanisms of expansion due to reactions with specific ions e.g., sulfate and chloride, have been extensively discussed in the literature [3, 4].

Recently clay scientists have had considerable interest in the volume stability and formation of organomineral derivatives because they combine the structural, physical and chemical properties of both the inorganic host material and the organic guest species at a nanometer scale [5]. Generally polymer/layered silicate (PLS) nanocomposites have attracted great interest, both in industry and in academia, because they often exhibit remarkable improvement in material properties when compared with virgin polymer or conventional micro and macro-composites. These improvements can include high elastic moduli [6], increased strength and heat resistance [7], decreased gas permeability [8] and flammability [9], and increased resistance to biodegradation [10]. Methods based on the modification of pre-existing inorganic structures offer considerable potential for the design of new nanocomposites of interest to the construction and building material industries. The intercalation of organic molecules is well established in clay mineralogy [5, 11-14] and related layered structures such as calcium aluminate hydrates [15, 16].

There is a paucity of information available on the behavior of synthetic calcium silicate hydrate (C-S-H) modified with surfactants and polymers. The nature of C-S-H is

determined by many factors, including the composition of the cement, the water to cement ratio (w/c), the curing temperature, the degree of hydration, and the presence of chemical and mineral admixtures. Significant variation in its composition, nanostructure, and morphology can occur [17]. The objective of this work was to study the behavior of modified quasi-crystalline synthesized C-S-H in order to understand the potential impact of its composition, nanostructure and morphology on the durability of concrete structures. Results of a systematic study of the modification of C-S-H structure by surface interaction of hexadecyltrimethylammonium (HDTMA) molecules in its structure are reported. The modifications are characterized using several techniques.

The present study is designed to determine to what extent the surface interaction processes could affect the durability of the concrete structures. This is relevant as anionic polymers are used as plasticizers and set-modifying admixtures in concrete technology. The results of a study to assess the relationship between the behavior of hydrated calcium silicate and clay, based on the similarity of their structural assembly and upon modification with alkyl ammonium salts and polymers of different molecular weight are reported. The method of C-S-H synthesis, effect of Na exchange and surfactant on interactions with polymers, nature of organic guest molecules, their molecular weight and size as well as the mechanism of ion interaction and specific adsorption at surfaces will be discussed. The ^{13}C CP and ^{29}Si CP MAS nuclear magnetic resonance (NMR) spectroscopy, x-ray diffraction (XRD), thermal gravimetric analysis (TGA), Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM) and energy dispersive x-ray (EDX) techniques were used to characterize and follow changes and behavior of the C-S-H modifications.

Calcium Silicate Hydrates

C-S-H phases are the major reaction products (50-70% by mass) and primary binding phases in hydrated Portland cement [17, 18]. Recent models of hydrated Portland cement nanostructure attest to the layered nature of the silicate phases. These include those of Richardson, Jennings, Feldman and Sereda and Taylor [17,19-21]. Calcium silicate hydrate structure is often referred to that of tobermorite [17, 22, 23]. It has similarities to the clay minerals in crystal structure assembly [5, 23]. The composite 2:1 sheets are made up of a distorted calcium hydroxide sheet flanked on both sides by parallel rows of wollastonite-type chains having composition $\text{Ca}_4\text{Si}_6\text{O}_{18}$ [23]. The remaining or interlayer calcium atoms and water molecules reside between them. Generally, two types of calcium are considered: “nonlabile” Ca linked to silica chains and “labile” Ca linked to Si-OH (silanol) groups. C-S-H has a surface pH dependent charge due to the existence of silanol sites carried by bridging silica tetrahedra or by the end chain tetrahedra [17, 18, 22, 24]. Other characteristics in which C-S-H resembles clay are (to some degree) the variability of basal spacing with water content, wide variability in degree of crystallinity, and variability in C:S ratio from 0.83 to 1.75 [5].

EXPERIMENTAL

Materials

All chemicals used were of reagent-grade quality and were not further purified unless otherwise specified.

C-S-H Synthesis

Calcium silicate hydrate (C-S-H) is the principal hydration product and primary binding phase in hydrated Portland cement. C-S-H was synthesized by mixing of CaO and reactive SiO₂ in stoichiometric proportions in distilled water (preferably decarbonated) under N₂ to avoid exposure to the atmospheric CO₂. The preparation of CaO consisted of heating pure CaCO₃ at 900°C for at least 3 hours and cooling in a N₂ atmosphere. Amorphous silica (Cabosil) was heated at 110°C for 3 hours and mixed intimately with the CaO (in 500 mL high density polypropylene bottles) to obtain a C/S molar ratio of 1.6. The required amount of demineralized decarbonated water was added and the system was flushed with N₂ before sealing. The reaction was conducted at room temperature with the bottles rotated for up to 14 days. Longer hydration periods were not studied in this investigation. The above synthesis procedure involved subjecting the slurry mixture to high speed shearing for 5 min. before placing the bottles on rotating rollers. The high speed shearing was at 6100 rpm/min. using a Silverson Laboratory Mixer. The C-S-H was filtered under N₂ and dried under vacuum for 12 hours without heating. Extreme care was taken during the drying procedure to ensure the reproducibility of the results and stability of the material.

Four batches of C-S-H with a C/S ratio of 1.6 were prepared as described above but at different drying temperatures. They were labeled C-S-H01, C-S-H02, C-S-H03 (A and B) and C-S-H04. C-S-H01 was vacuum dried at 65°C, C-S-H02 at 70-75°C, C-S-H03A at 47-50°C, C-S-H03B at 50-60°C and C-S-H04 at 25°C, all for 12 hours. Previous work by the authors on the volume stability of this C-S-H indicated that length change after

immersion in distilled water was significantly reduced when vacuum drying occurred at temperatures above 50°C.

Pre-treatment of Pre-formed C-S-H

Selected C-S-H preparations were chemically pretreated to assess their potential to accommodate organic intercalates. The treatment involved the following cation exchange and intercalation procedures:

Na – C-S-H

Preparation of Na – C-S-H from the originally prepared C-S-H material was carried out by reacting the C-S-H with NaCl solutions (20 g/L and saturated) 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 and labeled Na- C-S-H03B1 and Na – C-S-H03B2 to differentiate the concentration of the NaCl solution. In an alternate experiment an aqueous solution of NaCl (20 g/L) was used directly during C-S-H synthesis. The mixture was submitted to high-speed shear at 6100 rpm for 5 min and reacted for 6 days. The sample obtained was dried at 50-60°C and labeled Na – C-S-H hs6d.

HDTMA – C-S-H

Preparation of hexadecyltrimethylammonium (HDTMA) treated C-S-H designated HDTMA – C-S-H using the reference C-S-H and Na – C-S-H as a precursor was carried out by reacting C-S-H with an excess of aqueous 0.01M HDTMA – Br (MW 354.46)

solution for 24h followed by washing with distilled water until the halide (Br) was not detected with AgNO_3 . The material was then vacuum dried for 12h and designated HDTMA – C-S-H or HDTMA – Na – C-S-H. In an alternate experiment an aqueous solution of HDTMA was used directly during C-S-H synthesis (using high speed shear mixing at 6100 rpm/5 min.) with different reaction times. The samples obtained were designated HDTMA – C-S-H hs15 min., HDTMA – C-S-H hs 24h, HDTMA – C-S-H hs3d, HDTMA – C-S-H hs6d (hs = high shear, d = days).

Summary – Specimen Designations

A summary of the specimen designations is provided in Table 1 for easy reference.

ANALYTICAL PROCEDURES

Nuclear Magnetic Resonance

^{13}C CP MAS NMR (50.33 MHz), and ^{29}Si CP MAS NMR (39.76 MHz) spectra were obtained using a Bruker ASX-200 instrument with NMR magic angle spinning rates ranging between 3 and 6 kHz. ^{13}C CP MAS NMR spectra were referenced to hexamethylbenzene at $\delta = 14.9$ ppm; the ^{29}Si CP MAS spectra were referenced to tetramethylsilane at $\delta = 0.0$ ppm.

Powder x-ray diffraction (XRD):

Powder x-ray diffraction measurements were performed with a Phillips PW3710 based diffractometer (at 45 kV and 40 mA) using CuK α radiation. Powder XRD patterns were recorded using step scanning with a step size of 0.02° 2 θ at 0.5° 2 θ /min between the interval 1.41° to 35° 2 θ , 1.41° to 15° 2 θ or 1.41° to 4° 2 θ when a low angle detailed pattern was needed. A background subtraction correction (empty sample holder scan) was performed on all XRD patterns.

Scanning Electron Microscopy (SEM)

A Hitachi S-4800-FEG high-resolution (1 nm) scanning electron microscope was used for microstructural investigation of the various C-S-H preparations.

Thermal Analysis

The study of the thermal stability of all the samples was conducted using TGA/DTA (Thermo Gravimetric Analysis/Differential Thermal Analysis) measurements obtained with a Polymer Labs STA 1500H instrument at a nitrogen flow rate = 25 cc/min and a heating rate = 20°C/min from 30 to 1000°C.

Fourier Transform Infrared (FTIR)

FTIR spectra were obtained using a Bomem-Michelson MB 100 FTIR spectrometer with 30-50 averaged scans at 4 cm⁻¹ resolution. The samples were prepared as KBr pellets.

Carbon Content Determination

The amount of carbon in the C-S-H–HDTMA material was determined from the mass loss in a TGA instrument at 600 °C. The atmosphere was changed from nitrogen (after a 1 hour hold time) to air. This mass loss is a result of the oxidation of the carbon in the organic component of the material. The carbon content of the material was calculated to be 0.33% of the total mass assuming that all the C and H in the HDTMA molecule (with the chemical formula of $C_{19}H_{42}BrN$) has reacted with the oxygen. An estimate for the HDTMA content is 0.53% of the total mass.

RESULTS AND DISCUSSION

The results of the various characterization techniques (^{13}C CP MAS NMR and ^{29}Si CP MAS NMR, XRD, FTIR and TGA) applied to the various C-S-H preparations and test regimes are presented in the following sections.

EVIDENCE for INTERACTION of HDTMA MOLECULES WITH C-S-H SURFACES

NMR

^{13}C CP MAS NMR spectra of HDTMA-C-S-H (Figure 1) preparations were obtained in order to investigate structural properties of the organic component in this organo-calcium silicate hydrate. ^{29}Si CP MAS NMR spectra were also obtained to assess the nature of modifications to the silicate-based C-S-H nanostructure due to the interactions with HDTMA molecules. Figure 1a provides evidence of the effective presence of HDTMA molecules in the C-S-H matrix. The only significant ^{13}C resonance signal of HDTMA appears at 29.32 ppm corresponding to the three methyl groups. For the dipolar dephasing technique, the ratio of I_{DD}/I_0 , where I_{DD} and I_0 are the peak intensities of the ^{13}C resonance obtained respectively with and without dipolar dephasing conditions, is a semi quantitative measure of the dynamic state of the molecular group [25-27]. If a molecular group is rigidly fixed, the ratio I_{DD}/I_0 will be decreased or disappear. The overall signal decay for carbons strongly coupled to protons, such as methylene carbons has been shown to be best described by the following equation [28]:

$$I_{\text{DD}} = I_0 e^{\left[\frac{-\tau^2}{2T_2^3} \right]}$$

where τ is the dipolar dephasing delay time and T_2 is the transverse relaxation time constant.

A dipolar dephasing (DD) experiment (^{13}C CP DD MAS) was performed for HDTMA-C-S-H (Figure 1b) where the ^{13}C signal was allowed to dephase for 40 μs under cross polarization. It showed that 98% of the signal intensity was maintained compared to the

A dipolar dephasing (DD) experiment (^{13}C CP DD MAS) was performed for HDTMA-C-S-H (Figure 1b) where the ^{13}C signal was allowed to dephase for 40 μs under cross polarization. It showed that 98% of the signal intensity was maintained compared to the simple CP MAS conditions (Figure 1a). This confirms that the methyl groups of HDTMA are functional and located at the surface of the hydrate, presumably from rapid rotation about the C_3 axis.

^{29}Si CP MAS NMR spectra of C-S-H, Na-C-S-H, HDTMA-Na-C-S-H are presented in Figure 2. In all cases, the spectra are dominated by a doublet (Q^1 , Q^2) located respectively at (-79.3, -85.2 ppm); (-79.7, -85.9 ppm); (-79.3, -84.8 ppm). These two resonances are characteristic of silicate dreierketten feature of the C-S-H structure. The Q^2/Q^1 ratio, which determines the mean chain length for the silicate entities present in the structure significantly increases with the Na (Fig 2b) and HDTMA (Fig. 2c) treatment, the latter

having the largest value. This observation implies that the polymerization state of silicates is increased by the HDTMA and Na interactions with C-S-H. This is analogous to an increase in the Q^2 contribution when Ca/Si ratio decreases [27,28]. At C/S ratios >1.0 the silicate chains consist primarily of dimers with defect sites at locations of

missing bridging tetrahedra. It is possible that the polymer can bond to the oxygens associated with the Q^1 silicon i.e. $-\text{Si-O}[\text{polymer}]$. These types of external bonding lead to shifts in the Q^1 peaks. It is theoretically possible that these Q^1 peaks can shift to Q^2 sites. This would account for the increase in Q^2/Q^1 ratio in the spectra of the treated samples. Evidence for these type of surface interactions have been obtained for C-S-H modified with polyvinylalcohol (PVA) and silylated polymers [29,30].

It is instructive to examine the work of Viallis et. al. with respect to the interaction of Na and C-S-H [28]. Their results suggest that Na has an affinity for the C-S-H surface. They report ^{29}Si NMR data with the Q^2/Q^1 ratio much smaller than observed in the present work. This could be due to differences in sample preparation methods (NaCl was added to their C-S-H preparations after 3 weeks) including the chloride concentration. The results in this study indicate a significant increase in the Q^2/Q^1 ratio of the Na-C-S-H preparation (degree of silicate polymerization). This could be a result of decalcification of the C-S-H following immersion in NaCl solution and the subsequent washing with distilled water. Evidence based on x-ray diffraction methods support this view and will be presented in the following section on XRD.

A grafting mechanism operative at sites of missing silica tetrahedra has been reported for silylated polymers [30]. It is known that atoms in the vicinity of existing $-\text{O-Si-O}-$ bonds can attract some of the electron cloud of the silicon resulting in a detectable chemical shift. These shifts depend on the strength of the new atoms in affecting the electrons. A shift for the first silicon atom will occur in the following cases: $-\text{O-Si-O-H}$; $-\text{O-Si-O-Na}$;

-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 silicon in the vicinity of the polymer can be similar to that obtained with a silicon bond to the oxygen and mimic the latter labelled Q^2 . It would appear likely that organic molecules can be involved in different types of interaction with C-S-H including adsorption or grafting at sites of missing silica tetrahedra. A schematic of the C-S-H structure showing possible sites for polymer adsorption or grafts is provided in Figure 3.

X-RAY INVESTIGATION of C-S-H-HDTMA NANOSTRUCTURE.

The nanostructures of the reference C-S-H and C-S-H-based HDTMA materials were investigated using x-ray diffraction analysis. The possibility of HDMTA molecules partially penetrating the interlayer regions of C-S-H was of particular interest. The x-ray pattern of the quasicrystalline reference C-S-H (C/S = 1.6) is characterized by well-defined peaks at approximately 0.306, 0.280 and 0.182 nm. In the absence of guest molecules a (002) basal reflection at 1.25 nm is clearly detected. The pattern obtained is similar to that reported in the literature [31] for C-S-H (I). The 002 peak position will be used as a reference peak for the HDTMA modified samples. The effect of drying at 70°C on the two low angle peaks ($d=1.25$ and 4.50 nm), (curve (a), reference) and their recovery after being in contact with distilled water for 19 days and aqueous HDTMA for 24h (curves (b) and (c)) is shown in Figure 4. The recovery of the peaks is significant. The intensity of the peaks is significantly greater than that of the reference. The recovery rate was also much greater for the C-S-H treated with aqueous HDTMA solution. Drying of

C-S-H at 70°C induces collapse of interlayer space [26]. The volume change of C-S-H is also significantly reduced [32]. Although the 002 peak has not shifted following treatment with distilled water and HDTMA solution after the initial collapse of the C-S-H structure at 70°C it can be inferred (although not conclusively) that some intercalation of the polymer may be possible given the more rapid rate of recovery of the d-spacing in presence of the polymer. This, however, is not strong evidence. It has been shown in previous work that the volume stability of C-S-H immersed in distilled water is similar if drying temperatures do not exceed 50°C [26]. At more elevated temperatures the volume change is significantly reduced. Hard drying induces collapse of interlayer space. More persuasive evidence for the possibility of partial intercalation may result from examination of the basal spacing shift for C-S-H at temperatures of 50°C. The predominant mechanism contributing to the formation of the C-S-H-HDTMA nanostructure is, however, likely not intercalation but possibly surface adsorption of organic molecules at defect sites on the C-S-H surface as discussed in the previous section.

HDTMA Interaction During C-S-H Synthesis-High Speed Shear Mixing

An attempt to modify the C-S-H by interaction with HDTMA directly during synthesis of C-S-H was performed using a high-speed shear mixing method (6100 rpm for 5 min.) and reacting for up to 6 days with constant agitation and no heating. The material was designated HDTMA-C-S-H hs 6d. The evolution of the (002) peak does not fully develop until 6 days (Figure 5). There is a small shift to a higher value of the basal spacing

for these preparations compared to the synthesis procedure used previously. This is not conclusive evidence for partial intercalation but would be expected if this mechanism is operative.

SEM images of the in situ formation of HDTMA-treated C-S-H(I) are shown in Figure 6 for reaction times of 15 min., 24h, 3d (Photos (a)-(c)). A platy microstructure begins to form after 3 days reaction.

HDTMA Interaction-Effect of Na Pre-treated C-S-H

The effect of HDTMA treatment of pre-formed C-S-H (dried at temperatures below 50°C) is shown in Figure 7. The reference C-S-H03A (curve a) has a (002) reflection at $d = 1.22$ nm typical of C-S-H dried in this temperature range (i.e. 25-50°C). The HDTMA-treated C-S-H (HDTMA-C-S-H 03A) dried for 48h actually exhibits a shift in the basal spacing to a higher value than the reference i.e. $d = 1.38$ nm. This shift would be expected if intercalation were to occur (curve b) as swelling would likely occur due to the presence of the organic molecule. Prolonged drying (48h) of Na-treated C-S-H (Na-C-S-H03A) results in a shift of the basal spacing to $d = 1.01$ nm indicative of structural collapse (curve c). Peak broadening is also observed. The HDTMA- Na-treated C-S-H has a similar basal spacing ($d=1.06$ nm) but peak broadening is observed indicating some interaction of this material with HDTMA (curve d). The diffraction pattern for the HDTMA – C-S-H (*in situ* reacted) system (curve e) has a similar pattern to the Na-treated C-S-H reacted with HDTMA (curve d). The basal spacing is similar with only a slight difference in the peak broadening. It appears that a limited amount of intercalation of HDTMA in the C-S-H interlayer of both these preparations may be possible. For

example, the difference in basal spacing values between Na-C-S-H 03A (taken as a reference) and HDTMA-C-S-H 03B (curve b) is $\Delta d = 0.37$ nm. It is clear that it is important to define a reference (002) peak before making any statement of possible intercalation. Each drying condition can lead to a shift in the (002) peak.

X-ray patterns ($4^\circ < 2\theta < 85^\circ$) for C-S-H04 (Ca/Si=1.6), Na-C-S-H04 and HDTMA-Na-C-S-H04 are presented in Figure 8. There is a small amount of portlandite (CH in Fig 8) in the reference sample. The Na and HDTMA-C-S-H samples contain no portlandite. Decalcification of the latter samples is, however, indicated by the presence of calcite ($\overline{\text{CC}}$ in Fig 8). There is an indication of some calcite ($d=0.316\text{nm}$) in the Na-C-S-H sample. The shoulder on this peak is assigned to C-S-H. It has an intensity significantly greater than the corresponding peak for the control C-S-H. Further it is noted that the HDTMA treatment of the Na-C-S-H appears to increase the amount of decalcification as more intense calcite peaks are apparent. Decalcification of C-S-H generally opens up the structure. For example, it has been demonstrated to significantly increase the rate of helium inflow into the structure[33]. If intercalation of HDTMA occurs it may be facilitated by the decalcification process.

Low angle XRD Basal Spacing Analysis

A feature of all the previous XRD patterns is the presence of an additional peak at the lower angle between 1.41° and 4° 2θ ($d \cong 4.50$ nm). Analysis (after the background subtraction, curve a) of the evolution of the low angle peak after Na and HDTMA treatments (Figure 9) indicates similarities (in the increase in intensity, broadening and shifting) as observed previously with the (002) peak. C-S-H in hydrated Portland cement

products is a poorly crystalline-layered silicate [21]. Microstructural examination of the synthetic C-S-H analogues may provide evidence to support strategies for modification of C-S-H in Portland cement-based materials. The microstructures for synthetic C-S-H and HDTMA modified C-S-H are shown in Figures 10 and 11. HDTMA modified C-S-H has a microstructure consisting of a uniformly dispersed array of much smaller particles than those of the reference C-S-H. An array of smaller particles may be conducive to more efficient packing and bonding arrangements promoting improved engineering performance. These micrographs show that a simple organic molecule eg HDTMA is able to dramatically modify the texture of the material. The implication of this with respect to control of the growth and organization of C-S-H particles in cementitious materials remains to be clarified. Changes to the accessibility of helium gas into the structure will be explored in order to assess the potential for reduced ingress of destructive ions. The Na exchanged structures (not shown) are more dispersed and platy-like. The C-S-H synthesized *in situ* in presence of NaCl solution (Figure 12) also has a platy-like microstructure. The presence of water in the structure renders the surface slightly hydrophilic and the treatment with HDTMA should favor interaction with this molecule. It was concluded above that a partial intercalation of C-S-H with HDTMA maybe possible. This is a manifestation of irregular layer stratification of the C-S-H as evidenced in the SEM images (Figures 10-12). Similar observations of irregular layer stratification with serrated edges have been made for clays intercalated with organic molecules. The presence of water, its removal upon drying and the reaction temperature are critical aspects of the interaction process due to the structural changes that take place with reorganization of layers or chemical bond formation. Water molecules are most

likely bonded to Ca^{2+} ions in the interlayer. Loss of interlayer water results in formation of Ca-O-Si bonds and this next nearest neighbor effect may cause some changes in the bond angles and distances in the silica tetrahedra [34].

Summary

The XRD study has shown how the temperature can affect the structure of C-S-H and its interaction with HDTMA molecules. It has provided some evidence that the interaction of HDTMA molecules with C-S-H may include intercalation. This mechanism, however, needs further validation. The temperature effects are in agreement with the study of Cong et al. [35], that shows the inappropriateness of oven drying C-S-H at 110°C because at this temperature not only does the layered structure collapse, but the polymerization of silicate chains is also changed. In this study it has been shown that vacuum drying over 50°C and even prolonged vacuum drying at ambient temperatures have a similar effect on the C-S-H structure. It is suggested that if possible mild vacuum drying without any source of heat should be used (depending on the amount of wet sample being treated) in order to preserve the structure of the hydrate.

FTIR ANALYSIS

The infrared absorption spectra of Na – C-S-H and HDTMA – Na – C-S-H are given in Figure 13 in order to further characterize the effects of the pre-treatment of C-S-H on polymer interaction. The Na – C-S-H spectrum (curve a) shows absorption bands at 675, 877, 981, 1452, 1625 and 3460 cm^{-1} . Additional bands are observed at 1818, 2881 and

2954 cm^{-1} for HDTMA- Na – C-S-H (curve b). The 3460 cm^{-1} broad band is attributed to hydrogen-bonded surface hydroxyl stretching vibrations of H_2O molecules. The 1452 cm^{-1} and 877 cm^{-1} bands are related to carbonation of C-S-H at higher Ca/Si ratio [36] as evidenced also by the ^{13}C CP MAS. The weak broad band at 1625 cm^{-1} corresponds to the bending of the OH groups in C-S-H and water molecules in the interlayer.. The 675 cm^{-1} and 981 cm^{-1} bands are respectively attributed to bending and the asymmetric and symmetric stretching vibrations of SiO_4 [37, 38]. The bands in the range 400-500 cm^{-1} are due to deformation of SiO_4 tetrahedra. No free OH stretching absorption bands at 3600-3640 cm^{-1} , which could be attributed to less strongly hydrogen-bonded interlayer water molecules and any calcium hydroxide sites, were observed in all samples [36,37].

The additional bands at 1818, 2881 and 2954 cm^{-1} observed in treated Na – C-S-H samples with HDTMA confirm the presence of organic molecules in the C-S-H matrix. They correspond to CH_2 and CH stretching frequencies of the alkyl chain in HDTMA [39] as confirmed by the ^{13}C CP MAS NMR spectra. The 1818 cm^{-1} band is evidence of the possible presence of a carbonyl group.

Despite confirming that the organic molecules are associated with the nanostructure of C-S-H the FTIR spectra shows that only a small amount of HDTMA is retained by the solid. This observation supports the view that intercalation of HDTMA is minor if occurring at all.

THERMAL ANALYSIS

TGA

The thermogravimetric analysis provided additional evidence of the character of the polymer interaction with the C-S-H preparations.

The TGA curves of C-S-H and modified C-S-H samples (Figure 14) are similar in character up to 200°C and different above this temperature. The curve for the reference C-S-H (Figure 14) is similar to that reported in the literature [38,39] except that there are no significant weight losses in the temperature range 450 – 490°C typically associated with portlandite decomposition. The reference C-S-H continuously loses weight with increasing temperature up to about 700°C. There are 3 stages in the weight loss – temperature curve. The first stage begins at about 100°C (the specimen was vacuum dried for 14 days prior to testing). This is due to loss of adsorbed, interlayer and some compositional water. The second change beginning at about 430°C (a region of very small weight loss) is probably due to a loss of surface Si-OH groups. A small amount of free lime (if present) would also decompose in this region. The third stage beginning at about 680°C is due to the loss of compositional water and possible decomposition of any calcium carbonate that may have formed.

The HDTMA modified samples have greater weight losses than the reference C-S-H. The difference at the end of the first stage was 4.5% (at 400°C) for both HDTMA – C-S-H, HDTMA – Na – C-S-H. and can be assigned to the decomposition of surface adsorbed HDTMA. The difference (relative to the reference) at the end of the second

stage (685°C) was 6.0, 8.5, 9.5 and 12.5% weight loss. The differences at the end of the third stage (1000°C) were 10 and 7.5% of weight loss.

DTGA

The three major stages of weight loss are clearly seen in the DTGA curves, Figure 15. The peaks for the reference C-S-H are typically at 160, 430 and 675°C. There is also a shoulder at 400°C indicating there may be two decompositions occurring in this stage. A peak at about 550°C is present in all the treated C-S-H and is likely due to the decomposition of HDTMA complexes. The second peak at 430°C (for the reference) is significantly reduced (almost disappears) with HDTMA treatment although low temperature effects (at 200-300°C) are observed with HDTMA treatment of Na – C-S-H. The second major peak at 430°C is recovered. It is evident that the intercalation of HDTMA into the interlamellar space of C-S-H has dramatically altered the decomposition sequence of C-S-H. This is seen in the reduced temperatures of C-S-H dehydroxylation as well as the appearances of additional weight losses at 383, 555, 800 and 904°C. Structural reorganization occurs above 830°C and up to 914°C for the analyzed samples. The structural collapse followed by the complete dehydroxylation of the C-S-H itself appears to cause the residual interlayer carbonaceous material to be trapped within a meta – C-S-H like matrix, forming a carbon-calcium silicate nanocomposite material. Some of this carbonaceous material may be released once the material undergoes this structural reorganization between 800-1000°C. Combustion in air occurs relatively fast and a weight loss not normally associated with a structural reorganization is observed [12].

CONCLUSIONS

The present study has shown how the temperature and drying conditions affect the structure and ability of C-S-H to interact with HDTMA molecules. The results show that vacuum drying over 50°C and even prolonged vacuum drying at 25°C lead to a collapse of the interlayer space of the C-S-H structure. It is suggested that mild vacuum drying without any source of heat be used in order to preserve the structure of the hydrate. The study has also shown that depending on the drying conditions, intercalation of HDTMA into the C-S-H interlayer space can not be completely ruled out. It needs additional validation to confirm its role. The importance of defining a 002 peak reference position (XRD) before making any assessment of possible interlayer penetration is recommended.

The present study has provided evidence (based on TGA) that the interaction of C-S-H surfaces with HDTMA molecules can dramatically alter the decomposition behavior of C-S-H. This was reflected in the reduced temperatures of C-S-H (I) dehydroxylation as well as the appearances of additional weight losses at 383, 555, 800 and 904°C. Structural reorganization occurs above 830°C and up to 914°C for analyzed samples with weight loss thought to be the result of the release of carbonaceous materials trapped within a meta-C-S-H-like matrix. All data are consistent with the structural integrity of C-S-H being maintained after organic modification. It can be inferred from this study that the curing temperature, the degree of hydration, and the presence of chemical and mineral admixtures in Portland cement-based materials can significantly influence the nature of the C-S-H composition, nanostructure, and morphology. An understanding of these processes could have meaningful impact on the long-term durability of concrete

structures. Further, it is suggested that tailoring the nanostructure of C-S-H-based materials offers a potential route for the realization of durability strategies.

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FIGURE CAPTIONS

- Fig. 1 ^{13}C CP MAS NMR spectra of HDTMA-C-S-H: (a) regular CP MAS spectra; (b) dipolar dephasing spectra.
- Fig. 2 ^{29}Si CP MAS NMR spectra of: (a) C-S-H04; (b) Na-C-S-H04; (c) HDTMA-C-S-H04. C-S-H designations are described in detail in Table 1.
- Fig. 3 A schematic of C-S-H nanostructure showing possible sites for polymer graft
- Fig. 4 The effect of C-S-H drying condition on the position of the 002 XRD peak and its recovery following immersion in distilled water (19d) and HDTMA solution (24h). Curves: (a) C-S-H02, vacuum dried 12h at 70°C; (b) C-S-H02-DW immersed in DW 19d and vacuum dried 12h at 25°C; (c) HDTMA-C-S-H02 immersed in aqueous HDTMA for 24h and vacuum dried at 25°C. C-S-H designations are described in detail in Table 1.
- Fig.5 Evolution of the XRD (002 peak development during synthesis of *in situ* HDTMA treated C-S-H employing high speed shear mixing (6100 rpm for 5 min.). Hydration time: 15 min. to 6 d.
- Fig.6 Scanning electron micrographs of *in situ* HDTMA treated C-S-H (HDTMA-C-S-Hhs) prepared using high speed shear mixing (6100 rpm for 5 min.). Slurry was hydrated for (a) 15 min.; (b) 24h; (c) 3d; (d) 6d.

Fig.7 The effect of HDTMA treatment of C-S-H and Na – C-S-H on the XRD 002 peak position. XRD curves: (a) C-S-H03A (vacuum dried 12 h at 47-50°C); (b) HDTMA-C-S-H03A (immersed in aqueous HDTMA solution and vacuum dried 48h at 25°C); (c) Na-C-S-H03A (C-S-H03A immersed in NaCl solution for 24h and vacuum dried 12h at 47-50°C); (d) HDTMA-Na-C-S-H03A (immersed in aqueous HDTMA solution and vacuum dried 48h at 25°C); (e) HDTMA-C-S-H hs bd vacuum dried at 25°C). C-S-H designations are described in detail in Table 1. Numbers in brackets indicate 2θ angle and d-spacing (nm).

Fig. 8 XRD patterns ($4^\circ < 2\theta < 85^\circ$) for C-S-H04 (Ca/Si = 1.6), Na-C-S-H04 and HDTMA-Na-C-S-H04. $\overline{\text{CC}}=\text{CaCO}_3$; $\text{CH}=\text{Ca}(\text{OH})_2$.

Fig. 9 Evolution of low angle XRD peak (about $2.15^\circ 2\theta$) for Na, HDTMA and PEG polymer treated C-S-H. XRD curves: (a) background; (b) C-S-H03B (vacuum dried at 60-65°C for 12h); (c) Na-C-S-H03B (vacuum dried at 50-60°C); (d) HDTMA-Na-C-S-H03B (vacuum dried at 25°C for 12h). C-S-H designations are described in detail in Table 1.

Fig. 10 SEM micrographs of C-S-H04 (C-S-H vacuum dried at 25°C for 12h).

Fig. 11 SEM micrographs of HDTMA treated C-S-H (HDTMA-C-S-H04). See Table 1 for details.

Fig. 12 SEM micrograph of C-S-H synthesized in a saturated NaCl solution i.e. insitu formation using a high-speed shear mixing procedure.

Fig.13 FTIR patterns for: (a) Na-C-S-H03B; (b) HDTMA-Na-C-S-H03B

Fig. 14 TGA curves illustrating the effects of Na and HDTMA pretreatment of C-S-H. C-S-H designations are described in detail in Table 1.

Fig. 15 DTGA curves for Na and HDTMA modified C-S-H. C-S-H designations are described in detail in Table 1.

Table 1 – Designations for C-S-H Preparations

Designation	Description
C-S-H01	Vacuum dried at 65-70°C for 12h
C-S-H02	Vacuum dried at 70-75°C for 12h
C-S-H03A	Vacuum dried at 47-50°C for 12h
C-S-H03B	Vacuum dried at 50-60°C for 12 h
C-S-H04	Vacuum dried at 25°C for 12h
Na-C-S-H03B1	C-S-H immersed in NaCℓ solution (20 g/L) for 24 h and vacuum dried for 12h at 50-60°C
Na-C-S-H03B2	C-S-H immersed in NaCℓ solution (saturated) for 24h and vacuum dried at 50-60°C for 12h
Na-C-S-H hs6d	NaCℓ solution (20 g/L) used during synthesis of C-S-H. High speed shearing (hs) for 5 min. was used (see text) with a 6 day reaction time
HDTMA-C-S-H	C-S-H immersed in 0.01M HDTMA-Br for 24h and vacuum dried for 12h at 25°C
HDTMA-Na-C-S-H	Na-C-S-H 03B1 or B2 immersed in 0.01M HDTMA-Br for 24h and vacuum dried for 12h
HDTMA-C-S-H hs 15 min	HDTMA solution used during synthesis of C-S-H. High speed shearing (hs) for 5 min. was used with a 15 min. reaction time
HDTMA-C-S-H hs 24 h	Same as above with 24h reaction time
HDTMA-C-S-H hs 3d	Same as above with 3d reaction time
HDTMA-C-S-H hs 6 d	Same as above with 6d reaction time

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9

Figure 10

Figure 11

Figure 12

Figure 13

Figure 14

Figure 15