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Understanding hydrogen bonding in calcium silicate hydrate combining solid-state NMR and first principle calculations

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HIGHLIGHTS

- Mechanisms of hydrogen bonding and molecular structure in the C-S-H are revealed.
- Strong hydrogen bonds are favored to form in C-S-H with high Ca/Si molar ratios.
- The hydrogen bonding in terminal silicate sites is stronger than those in the paring or bridging silicate sites.

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ABSTRACT

Mechanisms of hydrogen bonding and molecular structure in the C-S-H are investigated by combining results of ²⁹Si, ¹H solid SSNMR analysis and first principle calculations. First principle calculations for ¹H chemical shifts are used to correlate the observed ¹H SSNMR spectra with the underlying structure of various hydrogen bonds between different silicon moieties and hydrogen groups in the C-S-H gels. The results show that strong hydrogen bonds are formed between water and terminal silicate sites or silanols, between adjacent terminal silanols and terminal silicate sites, between water or terminal silanols and hydroxyl groups bonded with interlayer calcium ions. Strong hydrogen bonds are favored to form in C-S-H with high Ca/Si molar ratios. The hydrogen bonding in terminal silicate sites is stronger than those in the paring or bridging silicate sites. New insights into the changes of basal spacing, Ca/Si ratio and H₂O/Si ratio of in the molecular structure of C-S-H are presented based on the mechanism of hydrogen bonding.

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1. Introduction

Hydrated Portland cement paste is a porous matrix consisting of crystals embedded in a poorly crystalline phase, the calcium-silicate-hydrate (C-S-H) gel [1,2]. C-S-H gel is the most abundant hydration product of Portland cement, accounting for about 50–60% by volume of hardened cement paste and making it one of the most common substances of the modern world [3]. It is also the primary binding component in cementitious materials.

Various technologies have been extensively used to characterize the composition and structure of C-S-H gels in different scales, including X-ray diffraction (XRD) for analyzing the crystalline structure, infrared and Raman spectroscopies for detection of chemical bonding of groups, and more recently advanced Magic

Angle Spinning Solid-state Nuclear Magnetic Resonance (MAS SSNMR) spectroscopy to probe the local chemical environments and atomic arrangements in C-S-H gel [4–6].

C-S-H gel has a layered structure and shows similarities to 14 Å tobermorite (Ca₅Si₆O₁₆(OH)₂·4H₂O) in which the Ca/Si molar ratio (Ca/Si ratio) is 0.83. Tobermorite contains layers of calcium ions linked on both sides to linear silicate chains in the 'dreierkette' form in such a way as to repeat a kinked pattern after every three tetrahedra [7,8]. Two of the three tetrahedra, named pairing tetrahedra (Q₂²), are linked together and share O-O edges with the central Ca-O part of the layer. The third tetrahedron, named bridging tetrahedron (Q₂³), shares an oxygen atom at the pyramidal apex of a calcium polyhedron and connects the dimers of pairing tetrahedra [5].

The Ca/Si ratio of C-S-H varies between 0.66 and 2.0. The variation in stoichiometry of C-S-H is caused in two ways including the disappearance of bridging tetrahedra in the dreierketten silicate chains, and the coexistence with amorphous Ca(OH)₂ phase [7].

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The nanocrystalline $\text{Ca}(\text{OH})_2$ exists in bulk form occupying the gel pores in the C-S-H or as chemically distinct ribbons or sheets interwoven within C-S-H [9].

The basal spacing of C-S-H varies between 10 and 14 Å [5,10]. The basal spacing of C-S-H is affected by the coordination requirement of the interlayer calcium atom and decreases with increasing Ca/Si ratios [10]. Variation in basal spacing of C-S-H is caused by the change of water molecules and the coordination state of calcium ions in the interlayers [10].

SSNMR spectroscopy is extensively used to probe the local chemical environments and atomic arrangements in C-S-H gel [5,7]. The SSNMR peaks are assigned with the assumption that ^{29}Si chemical shifts decrease with the condensation degree of (SiO_4) units, structures of which transform from isolated monomers to tetrahedrally coordinated chains [11]. Results of SSNMR analysis show that C-S-H gel contains silicate chains with a chain length sequence of a 2, 5, 8... $(3n-1)$ ($n = 1, 2, \dots$) [2]. Models for C-S-H with different mean chain lengths are developed using crystal-chemical and geometrical reasoning based on experimental observations, including variations in Ca/Si ratio, basal spacing and silicate chain length [10].

Hydrogen atoms in C-S-H exist in the form of silanols, hydroxyl groups and water molecule which play an important role in atomic interactions between protons and silicate chains with hydrogen bonding. Hydrogen bonding is a special type of atomic interactions between a hydrogen atom covalently bonded to an electronegative atom such as a N, O, or F atom and another electronegative atom, whose strength ranges from 4 to 50 kJ per mole of hydrogen bonds [12]. The hydrogen bonding between hydrogen-containing species and oxygen atoms has a wide range of bond length and bond strength which contributes to the internal cohesion in the C-S-H [13].

The mechanisms of hydrogen bonding in C-S-H gel or hydrated cements are not sufficiently clarified, yet. Efforts have been made to study the hydrogen bonding and interactions between different silicate and hydrogen-containing species in cement hydrates or synthetic C-S-H gels [14–16]. ^{29}Si Homonuclear and ^1H - ^{29}Si Heteronuclear SSNMR are used to study the molecular structure of synthetic C-S-H gels [14], and the results support the model of tobermorite. The different silicate and aluminate molecular species during the clinker hydration are studied and the molecular structures of hydrated white Portland cements and gray oil well cements are established with one and two dimensional (2D) SSNMR [16]. The results from 2D ^{29}Si $\{^1\text{H}\}$ HETCOR nuclear chemical shift correlation establish strong interactions of the Q^1 species with water molecule. The 2D ^{29}Si $\{^1\text{H}\}$ HETCOR nuclear test provides information about the distance of protons to silicon atoms and interactions between protons and silicate moieties. However, the information on the chemical environment of hydrogen bonds involving a hydrogen-containing group and an oxygen atom is lacking because the abundance of ^{17}O is low and signals from the ^{17}O SSNMR tests are weak.

Classical molecular simulation is a useful method to study the hydrogen bonds in C-S-H gel. The nanopore space in the C-S-H gel is hydrophilic because the oxygen atoms on the disordered silicate chains serve as hydrogen-bond acceptor sites [17]. Glassy nature of hydrogen bonds between interlayer water and silicate chains is demonstrated because of the heterogeneity in the distribution of hydrogen bond strengths and multi-range structure [17].

A method combining advanced SSNMR and first principle calculation to reveal the chemical environment of hydrogen bonds is proposed in C-S-H gel [15] and in Maltose Anomers [18]. The strong hydrogen bonding is responsible for stabilizing the structure of C-S-H at high Ca/Si ratios [15].

First principle calculations based on the Density Functional Theory (DFT) with the Gauge Including Projector Augmented Wave

(GIPAW) algorithm enable the calculation of chemical shielding, which establishes a clear link between the observed spectra and underlying atomic structure [19]. The mechanisms of hydrogen bonding between various silicate moieties and hydrogen groups in C-S-H can be determined by using combination of ^1H SSNMR and first principle calculations.

Understanding the mechanisms of hydrogen bonding provides great possibilities for developing C-S-H gel with strong cohesive performance [13,20] and thermodynamic stability [15]. In this paper, three types of C-S-H gels with Ca/Si ratios of 1.0, 1.4 and 1.5 are synthesized. First principle calculations for ^1H chemical shifts are used to correlate the observed ^1H SSNMR spectra with underlying structure of various hydrogen bonding between different silicon moieties and hydrogen groups in the C-S-H gels. The effect of Ca/Si ratios on the chemical environment of hydrogen bonds is studied together the atomic interactions of C-S-H gel with different drying condition. New insights into the changes of basal spacing, Ca/Si ratio and $\text{H}_2\text{O}/\text{Si}$ ratio of in the molecular structure of C-S-H are presented based on the mechanism of hydrogen bonding.

2. Experiments

2.1. Experiments

C-S-H gels are synthesized by using pozzolanic reaction between calcium oxide and amorphous silica fume [21]. No alkaline solution is used in the experiments to avoid the impact of alkaline solution on the chain length of C-S-H, which is different from the method used in the study of [15]. Alkaline solution is used in preparation of C-S-H gels to elevate the pH values of the reactant solution [15]. However, the high concentration of alkali ions lowers the mean chain length and polymerization degree of C-S-H gels [8], or forms a secondary Ca-containing N-S-H gel [19].

C-S-H gels with Ca/Si molar ratios of 1.0, 1.4 and 1.5 are synthesized according to the mix designs in Table 1. Calcium oxide is prepared with decomposition of calcium carbonate (AR grade, Sinopharm) at 1000 °C for 10 h. Amorphous silica fume (99.6% SiO_2 , Shenzhen Annisco) with a specific area of 250 m^2/g is used as silicon sources. Deionized water is mixed with calcium oxide and silica fume and the water/powder mass ratio is 50. The resulting slurry is stirred under nitrogen protection for 7d at 30 °C followed by filtration. The filtrates are analyzed with Inductively Coupled Plasma (ICP, Model Optima 4300DV) to determine the Ca/Si molar ratio of the filtrate. Each test is performed three times with test error smaller than 0.01 mM and the mean value of the results is recorded.

Table 1
Mix design for synthesizing C-S-H and compositions of C-S-H gels.

Numbering	C-S-H1.0	C-S-H1.4	C-S-H1.5
Mix design			
CaO	4.96	4.14	3.31
SiO_2	5.04	6	6.69
Water (ml)	500		
Analysis of filtrate (volume 500 ml)*			
Ca in filtrate (mM)	6.7	14.6	22.4
Si in filtrate (mM)	0.08	0.01	0.01
Composition of C-S-H			
Calculated Ca/Si ratio [§]	0.98	1.42	1.57
Measured Ca/Si ratio [*]	0.98	1.44	1.52
Measured $\text{H}_2\text{O}/\text{Si}$ ratio	1.66	1.83	2.08

Note: * Determined with ICP-OES.

[§]Calculated from the moles of Ca and Si in the filtrates.

^{*}Determined with XRF of the powders.

The powders are washed with deionized water. No portlandite is detected in X-ray diffraction pattern (XRD, Model Rigaku Mini-Flex600, Cu K α = 1.5406 Å, step size of 0.02° from 5° to 50°) after three times washing. The XRD patterns of the C-S-H gels are analyzed.

The Ca/Si ratio in C-S-H is determined in two ways, including calculations from the elemental concentrations of calcium and silicon in the filtrate and measurements with X fluorescence spectrometer (XRF, Model Axios Advanced) of the C-S-H solids. The H₂O/Si molar ratios are calculated with the weight loss after calcination 1000 °C for 12 h. The results of Ca/Si ratios and H₂O/Si molar ratios are listed in Table 1.

Two types of drying methods including vacuum drying and freeze-vacuum drying are used in the research. 2 g of C-S-H1.5 gels are stored in a container under vacuum conditions at 0.10 Torr for 7 days (labeled as C-S-H1.5VD), which is expected to remove the free water [21,22]. Other C-S-H gels are freeze dried under vacuum at 0.10 Torr to remove the water for 24 h and labeled as C-S-H1.0FD, C-S-H1.4FD and C-S-H1.5FD, which is expected to remove both the free water and partially gel water [22].

High resolution Transmission Electron Microscope (TEM) and electron diffraction are performed with JEM-1400Plus electron microscope with an acceleration voltage of 120 kV and electron beam size about 4 nm. One drop of C-S-H (about 0.1 ml) slurry are mixed with 20 ml deionized water by stirring for 30 s followed by ultrasonic dispersion for one minute. The diluted suspension of cement slurry is deposited on a copper holder for TEM imaging.

²⁹Si and ¹H MAS SSNMR spectra are recorded on an Agilent 600 DD2 spectrometer, equipped with a 14.1 T magnet, operating at a Larmor frequency of 600 MHz. A 7 mm probe is used for ²⁹Si SSNMR with a spinning speed of 6.0 kHz, a $\pi/2$ pulse length of 5 ms, a relaxation delay of 30 s and 2200 scans. A 4.0 mm probe is used for ¹H SSNMR with a spinning speed of 25.0 kHz, a $\pi/2$ pulse length of 5 ms, a relaxation delay of 20 s and 200 scans. Tetramethylsilane is used as the reference for ²⁹Si and ¹H tests.

During the deconvolution of ²⁹Si SSNMR spectra, the peak shapes are constrained with Voigt function in which the Lorentzian/Gaussian ratio is constrained to 0.5 [23]. The position, Lorentzian width and Gaussian width of each peak are constant during the deconvolution of three spectra. The detailed parameters used in the deconvolution are shown in Table 2. And the fraction of Q₂² sites is fixed to two times of the fraction of Q₂³.

2.2. First principles calculation

The first principle calculations on SSNMR results are performed with CASTEP (Accelrys, Material Studio17.2) using DFT theory [19]. The calculation is executed in three steps, including geometry optimization, energy calculation and chemical shielding calculation. Geometry optimization and energy calculation are carried out within CASTEP using a k point grid of $4 \times 2 \times 1$ equal to 0.04 1/Å and cut off energy of 400 eV. The core-valence interactions are described with ultrasoft pseudopotentials. Little changes of unit cell and atomic positions are allowed during geometry optimization. ¹H chemical shielding calculation is performed in the crystal frame. All-electron wave function in the presence of a magnetic field is reconstructed with the gauge including projector

augmented wave (GIPAW) algorithm [19]. The “on the fly” pseudopotentials are used in the ¹H chemical shielding calculation. A k point grid of $4 \times 2 \times 1$ equal to 0.04 1/Å is employed. Cut off energy of 300, 400, 500 and 600 eV are selected in the ¹H chemical shielding calculation of C-S-H gel. Variations of ¹H chemical shielding lower than 0.1 ppm are obtained when the cut off energy is 400, 500 and 600 eV. The chemical shifts δ_{cal} are obtained from chemical shielding σ_{cal} with the relation

$$\delta_{cal} = \sigma_{ref} - \sigma_{cal} \quad (1)$$

where σ_{ref} is 30.09 ppm.

3. Results

3.1. XRD analysis and morphologies of C-S-H gels

The XRD patterns of the three types of C-S-H gels are shown in Fig. 1, which shows a typical tobermorite-like structure. Poorly resolved XRD patterns demonstrate the prominent features of heavy defects and poor long range order in C-S-H structures. No secondary calcic phases such as portlandite, calcite and monocarboaluminate (Ca₄Al₂(OH)₁₂CO₃·5H₂O) [5] are observed in all C-S-H gels, indicating that crystalline portlandite is sufficiently removed by washing with deionized water.

The position of the first diffraction peak ((0 2 0) about 2 θ = 7°) shows the basal spacing of the tobermorite-like structure. The basal spacing of C-S-H1.0 is about 13 Å (2 θ = 6.78°), while the basal spacing decreases to 11.3 Å (2 θ = 7.81°) and 11 Å (2 θ = 8.02°) for C-S-H1.4 and C-S-H1.5, respectively (Fig. 2). The change of basal spacing with Ca/Si ratio of C-S-H observed in the experiments agrees with the findings in the study of Renaudin et al. [5] corresponding to about 20% contraction of the unit cell volume. The basal spacing is determined by the amount of water and the coordination requirements of the interlayer calcium ions. Removal of interlayer water and calcium ions will thus decrease the basal spacing of C-S-H. According to model proposed by Richardson, C-S-H gels with Ca/Si ratio greater than 1.4 consist of C-S-H(I) with constant basal spacing and a Ca-rich phase intermixed with C-S-H(I) [10].

High resolution TEM images of the C-S-H gels shown in Fig. 3. Nanofoils and nanofibrous morphologies are observed in C-S-H. The C-S-H gel with a Ca/Si ratio of 1.0 shows a nanofoil-like morphology with sizes about 200 nm. The morphology of synthetic C-S-H is similar to C-S-H in hydration products of Portland cement paste with a high alkali content [2], though the sizes of the foils are

Fig. 1. XRD patterns of three types of C-S-H gels after freeze drying.

Table 2
Parameters used in the deconvolution of ²⁹Si SSNMR spectra.

Silicate sites	Chemical shift	Lorentzian width	Gaussian width
Q ¹	-79	3.0	1.5
Q _B ²	-82	2.6	1.3
Q _B ³	-85	3.2	1.6

Fig. 2. Relationship between basal spacing and Ca/Si ratio of freeze dried C-S-H gel plotted together with the results of (5).

much greater in the synthetic C-S-H. Nanofibers with sizes up to several nanometers are observed in C-S-H gels with Ca/Si ratios of 1.4 and 1.5. All the C-S-H gels are amorphous at less than a 16 nm^2 size because no obvious diffraction rings are observed in the electron diffraction patterns.

3.2. Molecular structure of C-S-H

The ^{29}Si MAS SSNMR spectra of freeze-dried C-S-H gels are shown in Fig. 4 which show two distinct peaks. The sample is dried [24] before 1D MAS SSNMR because free water can be separated from the sample by high speed centrifugation and damage the probe or equipment when the water content is too high. The end of the silicate chain (Q^1) is bonded to silanols or calcium ions forming the major defects in structure of C-S-H gels. The peaks at -79 and -85 ppm correspond to Q^1 and Q^2 sites, respectively. The peak of Q^2 site is about -82 ppm [11,23].

Deconvolution the ^{29}Si SSNMR spectra of C-S-H gels are shown in Fig. 5, and results of the quantitative analysis of different silicate sites are listed in Table 3. The deconvolution is performed with the condition that the fraction of Q^2 sites is two times of that of the Q^1 sites according to the “dreierketten” structures. The decrease of Q^2 and Q^3 sites, and increase of Q^1 sites in C-S-H gels with increasing Ca/Si ratio suggests lowered degree of polymerization of silicate chains, which agrees with the observation in previous studies [24,25]. About half of the sites are Q^1 sites in C-S-H gels with a Ca/Si ratio of 1.4 or 1.5.

The relationships between the Ca/Si ratio and ratio of Q^1 to ($\text{Q}^1 + \text{Q}^2$) ($\text{Q}^1/(\text{Q}^1 + \text{Q}^2)$) ratio) are plotted with the results [15,24,26] in Fig. 6, which agrees with the calculated linear correlation between Ca/Si ratio and $\text{Q}^1/(\text{Q}^1 + \text{Q}^2)$ ratio proposed by Cong

Fig. 4. ^{29}Si SSNMR spectra for C-S-H gels.

and Kirkpatrick based on the tobermorite model [25]. C-S-H with a Ca/Si ratio greater than 0.83, which is the ratio in tobermorite ($\text{Ca}_5\text{Si}_6\text{O}_{16}(\text{OH})_2 \cdot 4\text{H}_2\text{O}$) with infinite silicate chain, has Q^1 sites that is charge compensated and connected to calcium atoms. Removal of Q^2 sites in the silicate chain forms Q^1 sites that is associated with Ca^{2+} and CaOH^+ to compensate the local charge balance. Removal of Q^2 sites in the silicate chain decreases its polymerization degree as well, and dimers consisting of two tetrahedral silicates and pentamers dominate the silicate chains. Dimers generated in the process of removing Q^2 sites in the silicate chain of C-S-H have a general formula of $\text{Ca}_2\text{Si}_2\text{O}_5(\text{OH})_2$ if the unbalanced charges are compensated with protons. The general formula changes to $\text{Ca}_3\text{Si}_2\text{O}_7$ if the unbalanced charge of the two resultant Q^1 sites are compensated with a Ca ion. Similarly, pentamers have a general formula of $\text{Ca}_5\text{Si}_5\text{O}_{14}(\text{OH})_2$ if the unbalanced charges are compensated with protons, while the general formula changes to $\text{Ca}_6\text{Si}_5\text{O}_{16}$ if the two Q^1 sites are connected with a calcium ion.

Information obtained in the ^1H SSNMR analysis helps probing the molecular structure of C-S-H gels and the atomic interactions between hydrogen groups and silicate moieties. The C-S-H gels are dried to facilitate sample preparation of the ^1H SSNMR tests. Drying of the gels affects its water content, molecular structure and atomic interactions between hydrogen groups and silicate moieties. Excessive drying of the C-S-H gel decreases the basal spacing of C-S-H due to removal of interlayer water, from $14 \text{ \AA}$ to $9 \text{ \AA}$ for C-S-H with a Ca/Si ratio of 1.2 [5]. Nanosheets of portlandite precipitate in C-S-H gels after excessive drying as well [4]. The effect of drying condition on the molecular structure of C-S-H gel and the hydrogen bonds needs further studies.

The ^1H SSNMR spectra of freeze-dried C-S-H are compared with those of gels with vacuum-drying in order to clarify the effect of drying condition on the atomic interactions between hydrogen

Fig. 3. High-resolution TEM image and electron diffraction pattern of C-S-H gels. (a) C-S-H1.0, (b) C-S-H1.4, (c) C-S-H1.5.

Fig. 5. Deconvolution of ^{29}Si SSNMR spectra of C-S-H gels. (a) C-S-H1.0FD, (b) C-S-H1.4FD, (c) C-S-H1.5FD.

Table 3

Quantities of different silicate sites in C-S-H gels obtained with deconvolution of ^{29}Si SSNMR spectra.

Numbering	Q^1	Q^2_B	Q^2_P
	-79 ppm	-82 ppm	-85 ppm
C-S-H1.0FD (%)	35	22	43
C-S-H1.4FD (%)	54	15	31
C-S-H1.5FD (%)	66	13	21

Fig. 6. Relationships between Ca/Si ratios and $Q^1/(Q^1 + Q^2)$ ratios of freeze dried C-S-H gel plotted together with the results of (15, 24, 26).

groups and silicate moieties (Fig. 7). Five distinct peaks of protons are observed in the ^1H MAS SSNMR spectra of C-S-H gels. The first peak at about -0.3 ppm corresponding to the hydroxyl proton in the ^1H MAS SSNMR spectra suggests the formation of portlandite in C-S-H with a Ca/Si ratio of 1.4 or 1.5. It is previously reported

Fig. 7. ^1H SSNMR spectra of C-S-H gels.

that portlandite is formed after excessive drying of C-S-H gels with Ca/Si ratios up to 1.5 [9]. No peaks of crystalline portlandite in the XRD patterns of C-S-H are observed (Fig. 1). The hydroxyl protons identified in ^1H MAS SSNMR spectra in C-S-H gels with Ca/Si ratios of 1.4 and 1.5 exist most likely in portlandite in an amorphous state. Amorphous portlandite in C-S-H gels is also traced in other studies by using nanoindentation and high energy X-ray tests [9,27,28].

The chemical shifts of proton species in Ca-OH, and Al-OH are between 0 and 3 ppm, and those of the protons in water are between 3 and 6 ppm, based on ^1H SSNMR studies on crystalline silicates and aluminosilicate minerals [29]. The chemical shifts of protons in Si-OH groups of silicates extend to the range between

6 and 18 ppm. High chemical shifts of Si-OH groups between 10 and 18 ppm correspond to strongly hydrogen-bonded protons in silicates [16].

The ^1H SSNMR spectrum of vacuum dried C-S-H (C-S-H1.5VD) shows the resonance peak of strong hydrogen bonded proton at about 16.7 ppm, whereas this peak disappears after freeze-drying for 24 h. Other resonance peaks of protons in absorbed water, Si-OH and Ca-OH show little changes after freeze-drying.

The ^1H SSNMR spectrum of C-S-H gel with the Ca/Si ratio of 1.0 shows a sharp resonance peak at 4.4 ppm, indicating that most protons exist as absorbed water in the interlayer, which is consistent with the observation of tobermorite. A broad and overlapped peak shifts to 5.2 and 5.6 ppm in the ^1H SSNMR spectra of C-S-H gels with Ca/Si ratios of 1.4 and 1.5, respectively, which indicates that the protons in these C-S-H gels exist in more complex environment than those in C-S-H with a Ca/Si ratio of 1.0. Resonance peaks of the Si-OH groups between 6 and 10 ppm are observed in the C-S-H gels with Ca/Si ratio of 1.4 and 1.5, whereas the peaks are absent in C-S-H gels with a Ca/Si ratio of 1.0.

The deconvolution of ^1H SSNMR spectra of C-S-H gels with different Ca/Si ratios based on the assignment of the peaks described above is shown in Fig. 8 and Table 4. Portlandite is not listed in Table 4 since it is considered as a second phase. The resonance peak assigned to absorbed water represents about 40–80% of the total ^1H population in all C-S-H gels with different Ca/Si ratio, which decreases with increasing Ca/Si ratio. The resonance peaks of Si-OH groups between 6 and 10 ppm and Ca-OH in the C-S-H at about 2.5 ppm is observed in C-S-H gels with Ca/Si ratios higher

Table 4

Quantitative results of fractions of hydrogen groups obtained via deconvolution of ^1H SSNMR spectra.

Numbering	Si-OH	H ₂ O	Ca-OH in C-S-H gel
	6–15 ppm	3–6 ppm	0–3 ppm
C-S-H1.0FD (%)	13.8	84	3.2
C-S-H1.4FD (%)	23	52	25
C-S-H1.5FD (%)	33	38	29

than 1.0. The relative fractions of Si-OH groups and Ca-OH in the C-S-H increase with the Ca/Si ratio.

3.3. First principle calculation of ^1H chemical shifts

The mechanism of hydrogen bonding especially the chemical environment of protons and the interactions between hydrogen containing groups and silicate chains are not known, yet. The chemical environment of protons and the distribution of hydrogen bonding between hydrogen containing groups and silicate chains are essential for establishing the structural model of C-S-H. The observed ^1H SSNMR results are linked to the underlying structure of hydrogen bonds with the help of first principle calculation rooting in DFT-GIPAW methods, with which the mechanism of hydrogen bonding are investigated and the changes of basal spacing, fractions of different protons with Ca/Si ratio, the effect of drying condition on the hydrogen bonds are interpreted.

Combining the results of the SSNMR analysis and well defined values of atomic bond distances/angles, coordination state, and

Fig. 8. Deconvolution of ^1H SSNMR spectra of C-S-H gels. (a) C-S-H1.0FD, (b) C-S-H1.4FD, (c) C-S-H1.5FD.

Table 5

Geometrical parameters of defined C-S-H models in this study.

	Ca-O (Å)	Coordination Number of Ca	O-H (Å)	OH...O (Å)
C _{1.2} SH _{1.8}	2.3 ± 0.3	6	1.0	1.5 ~ 3.0

local charge balance (Table 5) [15,30], a structural model of C-S-H is developed using first principle calculation with which the mechanism of hydrogen bonding can be revealed. The structural model of C-S-H gel used in calculating the chemical shifts of protons is based on tobermorite-14 Å provided by Crystallography Open Database (as shown in Fig. 9a). The protons in the tobermorite-14 Å exist in the interlayer water and silanols bonded with bridging tetrahedral silicates (Q_B²-OH).

A structural model of C-S-H gel consisting of dimers and pentamers is constructed by modifying the infinite silicate chain model following the literature [11,25]. The dimers and pentamers are obtained by removing some bridging tetrahedral silicates (Q_B²-OH) in the infinite chains in the structure of tobermorite. The local negative charge is compensated with H⁺, Ca²⁺ or Ca(OH)⁺ ions, forming the defective sites and increasing the Ca/Si ratios [11,15]. After removing a bridging silicate tetrahedron, the unbalanced charge is compensated by either adding two protons forming two silanols bonded with terminal tetrahedral silicates or adding a bridging Ca²⁺ to connect terminal tetrahedral silicates. Additional interlayer water molecular, interlayer Ca(OH)⁺ ions and Ca(OH)₂ are used to connect the defect sites through the interlayer spaces. Three types of calcium ions are distinguished in the model of C-S-H as calcium ions in mainlayer (Ca_M), calcium ions in interlayer (Ca_I) and calcium ions in bridging sites (Ca_B). Four proton environments are distinguished as interlayer water molecular (H₂O), silanols bonded with bridging tetrahedral silicates (Q_B²-OH), silanols bonded with terminal tetrahedron silicates (Q¹-OH) and hydroxyl associated with Ca ions (OH⁻). The constructed structure are geometry and energy optimized with CASTEP based on DFT theory. The optimized structure of the C-S-H model with the mean chemical formula of C_{1.2}SH_{1.8} and various proton environments are shown in Fig. 9b.

Protons in different chemical environments exist in the structure of tobermorite-14 Å and constructed model of C-S-H gel. The hydrogen bonds are classified into three types according to the donors in the bond. Three different structure units containing protons and oxygen atoms are labeled as TH (silanols bonded with tetrahedral silicates (T)), W (water molecular) and OH (hydroxyl groups bonded with calcium ions). Nine different hydrogen bonds involving the different donors and acceptors are named as W---W, W---T(Q²) and W---T(TH)(Q¹) etc. (Table 6). W---OH (white triangle) indicates that water molecule donate a proton to form hydrogen bonds with hydroxyl groups who are acceptor, while OH---W (black diamond) water molecule act as acceptor. The observed NMR chemical shifts are compared with the calculated values, aiming to correlate the underlying structure of hydrogen containing groups which are shown in the C-S-H model to the observed spectra. Hydrogen bonds affect greatly the isotropic ¹H chemical shifts. A well-established linear relationship between ¹H isotropic chemical shifts and distance of O-H...O ($d_{(O-H...O)}$) has been reported by experiment if the proton is bonded to oxygen atoms [6,26]. The accurate values of $d_{(O-H...O)}$ are calculated from the C-S-H model used in the calculation, with which the correlation between ¹H isotropic chemical shifts and hydrogen bonds are established. The linear relationship between the calculated ¹H chemical shift and values of $d_{(O-H...O)}$ is shown in Fig. 10. The chemical shifts of protons in water molecule vary from 4 to 10 ppm because of different strength of hydrogen bonds.

Fig. 9. Optimized geometry structures of tobermorite-14 Å minerals and C_{1.2}SH_{1.8} gel. (a) tobermorite-14 Å and various proton environments, (b) C_{1.2}SH_{1.8} gel and various proton environments.

The comparison between the observed ¹H chemical shifts and the calculated values shows much higher overlapped ranges of protons in water and silanols groups than that indicated from the literatures [29]. Protons in water molecule resonate from 3 to 11 ppm, while peaks of protons in silanols bonded with tetrahedral silicates ranges between 10 and 14 ppm, leading to broaden and overlapped peaks observed in the ¹H SSNMR spectra of C-S-H gels with the Ca/Si ratio of 1.4 and 1.5 (as shown in Fig. 7). The highly overlapped ranges of protons are due to the different distance and strength of hydrogen bonds which influence shielded effect to protons. Thus, the hydrogen bonds should be taken into consideration to reasonably analyze the ¹H SSNMR of C-S-H or cement based materials.

There is a linear correlation between the calculated ¹H chemical shift and the values of $d_{(O-H...O)}$: $\delta_{iso} = 28.587 - 10.10 d_{(O-H...O)}$, with δ_{iso} in ppm and $d_{(O-H...O)}$ in Å (Fig. 10). The protons in Ca-OH involved in the hydrogen bond labeled as OH---W resonate at about 2.5 ppm, suggesting an average $d_{(O-H...O)}$ value of about 2.7 Å and rather weak hydrogen bonds. Protons in hydroxyl groups

Table 6
Schematic diagram of three types of hydrogen bonds.

Type 1 W---O(T,TH,W,OH) W---W	Type 2 TH---O(T,TH,W) (Q ¹)TH---W	Type 3 OH---O(W)

Fig. 10. Relationship between calculated ¹H chemical shift and value of $d_{(O-H...O)}$ (HBs: Hydrogen Bonds).

serves as a weak donator in hydrogen bonds. Most protons in C-S-H gels exit in water involving Type 1 hydrogen bonds whose ¹H chemical shifts spread in a wide range and has various values of $d_{O-H...O}$. The protons resonating at 4.6 ppm is involved in hydrogen bond named as W---W and have an average $d_{(O-H...O)}$ value of 2.37 Å, which is the dominant chemical environment of protons in C-S-H with Ca/Si ratio of 1.0. The protons in water forming the hydrogen bonds with Q¹ sites (W---T(TH) (Q¹)) show higher chemical shifts at 10 ppm than those with Q² sites (W---T (Q²)) and have an average value of $d_{(O-H...O)}$ about 1.84 Å. The observation suggests stronger hydrogen bonding between water and Q¹ sites than those with Q² site in the silicate chains, which agrees with the ranking of strength of hydrogen bonds proposed in the literature [17]. Non-bridging oxygen atoms in Q¹ sites serve as stronger hydrogen-bond acceptor sites than bridging oxygen atoms in Q² sites [17]. The protons in forming hydrogen bonds with water show similar observation that hydrogen bonding between Si-OH groups in Q¹ sites and water ((Q¹)TH---W) are stronger than those between Si-OH groups in Q² sites ((Q²)TH---W) with water. In conclusion,

the Q¹ sites enhance the internal cohesions with water and hydrophilicity of the silicate main chain.

Hydrogen bonds whose average value of $d_{(O-H...O)}$ are lower than 1.8 Å are defined as strong hydrogen bonds (shown in Fig. 10). The strong hydrogen bonding are dominated by (Q¹)T-H---T(Q¹), (Q¹)T-H---W, W---OH, W---T(Q¹) and (Q¹)TH---OH. Strong hydrogen bonding between terminal silanol and terminal silicate sites shows the internal cohesions between the parallel chains, which are present in the minerals suolunite and acts as the major interactions between dimers in the structure [31]. The hydroxyl groups bonded with calcium ions serve as strong acceptors for hydrogen bonds, which forms the strong bonding with water (W---OH) and terminal silanol ((Q¹)TH---OH). The strong hydrogen bonding between water and hydroxyl are reported to stabilize Ca_B ions and increase Ca/Si ratios in C-S-H [15], while the strong hydrogen bonding between terminal silanol and hydroxyl acts as the interlayer affinity in the structure of C-S-H gel.

4. Discussions

The observed ¹H SSNMR spectra are correlated with the local environment of protons and hydrogen bonding in the structure of C-S-H gel with the first principle calculations. The ¹H chemical shifts ranges from 5 to 16 ppm are observed in the C-S-H gel with the Ca/Si ratio of 1.4 and 1.5 (Fig. 8), indicating the fractions of protons in hydroxyl groups and silanol increase with the increasing Ca/Si ratio, as well as the hydrogen bonding between protons containing groups and silicate chains.

Amorphous portlandite is observed using ¹H SSNMR in C-S-H gels with high Ca/Si ratios, which is an interpretation for the varied Ca/Si ratio of C-S-H gel especially for the Ca/Si ratio which is higher than 1.4. The calcium ions in the interlayer space either connect the terminal silicate chains as bridging sites or compensate the unbalanced charge induced by removal of Q_B² sites are another interpretation for the varied Ca/Si ratio of C-S-H gel. The strong

Fig. 11. Relationships between H_2O/Si ratios and $Q^1/(Q^1 + Q^2)$ ratios C-S-H gel plotted together with the results of (15, 24, 26).

hydrogen bonding between water and hydroxyl are observed in this study, which is reported to stabilize Ca_B ions and increase Ca/Si ratios in C-S-H.

The relationship of H_2O/Si ratios and $Q^1/(Q^1 + Q^2)$ ratios is shown in Fig. 11. The H_2O/Si ratios increase with the increasing $Q^1/(Q^1 + Q^2)$ ratios. Q^1 sites become the dominant silicate species when the Ca/Si ratio increase to higher than 1.0 (Fig. 6), thereby protons in water and silanols are mostly associated with Q^1 sites. Enhanced hydrogen bonding with water and hydrophilicity of Q^1 sites is concluded from the results in this study. Moreover, the hydroxyl groups bonded with calcium ions serve as strong acceptors for hydrogen bonds with water. The observation of increased H_2O/Si ratios of C-S-H with increasing $Q^1/(Q^1 + Q^2)$ ratios are interpreted with strong interaction between water and Q^1 or hydroxyl groups bonded with interlayer calcium ions.

The basal spacing of C-S-H varies between 10 and 14 Å and decrease with the increasing Ca/Si ratio. The reason for the variation in basal spacing of C-S-H is reported to be the change of water molecules and the coordination state of calcium ions in the interlayers [10]. The strong hydrogen bonding between terminal silanol and hydroxyl bonded with calcium ions in C-S-H gel with high Ca/Si ratio is observed in our study, which acts as the affinity in the interlayer space of C-S-H gel. To the author's knowledge, the decrease of basal spacing is caused by the absence of bridging silicate tetrahedra. The strong hydrogen bonding in the interlayer is thought to be another cause of the decrease of basal spacing with increasing Ca/Si ratio in our study.

The peak of protons in strong hydrogen bonds of C-S-H1.5 with vacuum drying is absent after freeze-drying, indicating the strong hydrogen bonds disappear after excessive drying. The strong hydrogen bonds observed here is mostly assigned to hydrogen bonding between water and terminal silicate sites. And the water which are far away from the silicate chains with weak hydrogen bonds is firstly removed during the drying process. The water which forms strong hydrogen bonds with silicate chains is removed by continuous drying.

5. Conclusion

The atomic structures and mechanism of hydrogen bonding in C-S-H gels are investigated by combining ^{29}Si , 1H solid SSNMR and first principle calculation. The observed 1H SSNMR results are correlated with the underlying structure of hydrogen bonds, aiming to reveal the mechanism of hydrogen bonding and provide the interpretation for the changes of basal spacing, fractions of different protons with Ca/Si ratio, the effect of drying condition

on the hydrogen bonds. The main conclusions can be drawn as followings.

1. Amorphous portlandite exists in C-S-H gels with high Ca/Si ratios.
2. Chemical shifts of protons in C-S-H gel are affected greatly by the hydrogen bonds. Protons in water and silanol resonate in a highly overlapped range. Hydrogen bonds should be taken into consideration to reasonably analyze the 1H SSNMR of C-S-H or cement based materials.
3. Strong hydrogen bonding between water and terminal silicate sites or silanol are revealed, which enhance the hydrophilicity of silicate chains in the C-S-H gel. The strong hydrogen bonding between water and Q^1 or hydroxyl groups bonded with interlayer calcium ions is the reason for increased H_2O/Si ratios of C-S-H with increasing $Q^1/(Q^1 + Q^2)$ ratios.
4. The strong hydrogen bonding between terminal silanol and hydroxyl bonded with calcium ions in C-S-H gel with high Ca/Si ratio is observed, which acts as the affinity in the interlayer space of C-S-H gel, and consequently decreased basal spacing with increasing Ca/Si ratio.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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