Ca–OH Bonding in the C–S–H Gel Phase of Tricalcium Silicate and White Portland Cement Pastes Measured by Inelastic Neutron Scattering

Jeffrey J. Thomas,[*,†] Jeffrey J. Chen,[‡] and Hamlin M. Jennings[†,‡]

Departments of Civil and Environmental Engineering and Materials Science and Engineering, Northwestern University, Evanston, Illinois 60208

Dan A. Neumann

NIST Center for Neutron Research, National Institute of Standards and Technology Gaithersburg, Maryland 20899

Inelastic neutron spectroscopy (INS) was used to determine the content of Ca–OH bonds in a series of mature tricalcium silicate ($3CaO \cdot SiO_2$) and white portland cement (WPC) pastes that were decalcified to calcium/silicon molar ratios (Ca/Si) as low as 1. These measurements indicate that the band in the INS data at 41 meV, which originates from lattice modes involving the translational oscillations of OH groups attached to Ca, has intensity contributions from both $Ca(OH)_2$ and C–S–H gel, the main hydration product of cement paste. Quantitative analysis of the INS spectra show that ~23% of the Ca in C–S–H gel with Ca/Si = 1.7 is charge-balanced by OH groups, with the remainder charge-balanced by silicate groups. This substantial concentration of Ca–OH bonds supports the hypothesis that C–S–H gel has a local structure resembling a disordered form of the mineral jennite. On decalcification, the concentration of Ca–OH bonds in C–S–H gel decreases and is eliminated at Ca/Si ratios slightly above 1. The observed trend is shown to be consistent with charge balance calculations and interpretations of recent phase equilibrium findings.

1. Introduction

The hydration of Portland cement is a complex process involving several simultaneous reactions. The most important of these reactions is the hydration of tricalcium silicate ($3CaO \cdot SiO_2$) to form a poorly crystalline calcium–silicate–hydrate (C–S–H[1]) gel and calcium hydroxide, $Ca(OH)_2$. C–S–H gel is responsible for most of the important engineering properties of concrete, including strength and permeability. The $Ca(OH)_2$ forms as both hexagonal micrometer-sized crystals that yield sharp X-ray peaks and as finer, possibly amorphous grains that are intimately mixed with the C–S–H gel due to the simultaneous precipitation of these two phases out of the pore solution. The molar calcium-to-silicon ratio (Ca/Si) of the C–S–H phase can be measured accurately using TEM microanalysis, a technique with sufficient resolution to allow the C–S–H to be analyzed free of admixture with other phases.[2,3] These studies have shown that the C–S–H gel in hardened paste has a distribution of Ca/Si with an average value close to 1.7, and a value of 1.7 is also supported by the

weight of the evidence from other types of measurements.[4]

Determination of the nanostructure of C–S–H gel is difficult due to the lack of long-range order and a high propensity for structural variations. There is, however, a definite short-range order that combines features of the crystal structures of the minerals 1.4-nm tobermorite ($Ca_5Si_6O_{16}(OH)_2 \cdot 8H_2O$)[5] and jennite ($Ca_9(Si_6O_{18})(OH)_6 \cdot 8H_2O$).[6] Both minerals are based on a composite layer structure composed of a central Ca–O layer ribbed on either side with continuous chains of silicate tetrahedra. These silicate chains have a "dreierketten" structure that repeats at an interval of every three tetrahedra. The first two tetrahedra share two of their O atoms with the main Ca–O layer, while the third shares only one.[5] In 1.4-nm tobermorite, all O atoms in the main Ca–O layer are shared with silicate tetrahedra, whereas in jennite half is shared with tetrahedra and the remainder exist in Ca–OH groups. Thus, a key difference between jennite and 1.4-nm tobermorite is the presence of Ca–OH bonds in jennite.

Because of the difficulty in isolating the C–S–H gel from $Ca(OH)_2$ in a hardened paste, analytical studies are often performed on phase-pure "synthetic" C–S–H

(1) The term "C–S–H" is based on cement chemistry notation (e.g., C=CaO, S=SiO_2, H=H_2O), and the dashes indicate that the composition is not fixed.
(2) Richardson, I. G.; Groves, G. W. *J. Mater. Sci.* **1993**, *28*, 265.
(3) Richardson, I. G. *Cem. Concr. Res.* **1999**, *29*, 1131.
(4) Taylor, H. F. W. *Cement Chemistry*, 2nd ed.; Thomas Telford: London, 1997.
(5) Merlino, S.; Bonaccorsi, E. In *Applied Mineralogy*; Rammlmair, D., Mederer, J., Oberthür, T., Heimann, R. B., Pentinghaus, H., Eds.; Balkema: Rotterdam, 2000; p 859.
(6) Bonaccorsi, E.; Merlino, S.; Taylor, H. F. W. Work in preparation.

formed by precipitation or reaction in solutions much more dilute than those present in a hydrating paste. Techniques such as ^{17}O magic-angle spinning (MAS) NMR,[7,8] infrared spectroscopy,[9] and multipulse spectroscopy (CRAMPS)[10] have shown that C–S–H with a Ca/Si greater than ~1.2 contains Ca–OH bonds and that the amount of Ca–OH bonding increases with Ca/Si up to Ca/Si = ~1.54. The structure of such synthetic C–S–H has been studied in detail and can be described as an imperfect analogue of 1.4-nm tobermorite.[7,9,11] However, C–S–H gel that forms in hardened pastes is believed to have a different structure, as evidenced in part by its higher Ca/Si of 1.7. On the basis of a variety of evidence including silicate chain length, water content, density, thermogravimetric data, and analytical electron microscopy analysis, Taylor[12] proposed that the structure of the C–S–H gel in mature cementitious pastes resembles that of jennite more closely than that of 1.4-nm tobermorite. His model thus implicitly assumes that the C–S–H gel has a substantial Ca–OH content, and this accounts for its higher Ca/Si.

A recent study[13] showed that variations in the equilibrium aqueous solubility of different C–S–H preparations were related to differences in the mean silicate chain length and Ca–OH content and concluded that C–S–H gel generally has a greater Ca–OH content, at a given Ca/Si, than do synthetic C–S–H preparations. In that study, the content of Ca–OH bonds was deduced from charge balance calculations but was not measured directly.

Inelastic neutron spectroscopy (INS) is a valuable quantitative probe of the content of Ca–OH bonds in cementitious materials because hydrogen has a much higher cross section for neutron scattering than any other element in cement, and the energy lost when a neutron scatters from a hydrogen nucleus depends strongly on the bonding environment of the hydrogen atom. A plot of scattered neutron intensity vs neutron energy loss will thus exhibit peaks corresponding to various vibrational modes that involve motions of the protons. When INS is applied to a cement or $3CaO \cdot SiO_2$ paste, the dominant signal below 60 meV is a well-defined band at 41 meV (331 cm^{-1}) that is also seen in specimens of pure $Ca(OH)_2$ powder.[14] This peak arises from lattice modes involving the translational oscillations of the hydroxyl group attached to Ca in Ca–OH bonds.[15] Like infrared or Raman spectroscopy, INS probes the local structural environment of protons and is thus equally sensitive to Ca–OH bonds within crystalline and amorphous regions of the specimen. A previous study[14] used INS to monitor the Ca–OH

content of a $3CaO \cdot SiO_2$ paste during the early stages of hydration; the kinetics of hydration were seen clearly, but individual contributions to the signal from $Ca(OH)_2$ and C–S–H gel were not considered.

In this study, mature tricalcium silicate ($3CaO \cdot SiO_2$) and white portland cement pastes were decalcified by leaching in strong ammonium nitrate solutions to form specimens with a range of Ca/Si values. The Ca–OH content of the leached samples was then measured by INS. Quantitative analysis shows that an appreciable concentration of Ca–OH is present in C–S–H gel at Ca/Si = 1.7 and that Ca–OH bonding is eliminated when the Ca/Si is reduced to near 1. These trends agree well with charge balance calculations and interpretations of recent phase equilibrium results presented in another study.[13]

2. Experimental Section

Experiments were performed using pastes made from both white Portland cement (WPC, US Gypsum Corp.[16]) and $3CaO \cdot SiO_2$. The mineral composition of the WPC is 72% $3CaO \cdot SiO_2$, 17% $2CaO \cdot SiO_2$, 5% $3CaO \cdot Al_2O_3$, 1% $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$, and 0.7% alkalis. Pure triclinic $3CaO \cdot SiO_2$ powder was made by repeatedly calcining a 3:1 mixture of CaO and SiO_2 powder at 1430 °C and then grinding the resulting product in a mortar and pestle. X-ray analysis indicated no unreacted CaO. The WPC and $3CaO \cdot SiO_2$ powders were mixed at a water-to-solids ratio of 0.5 by weight and sealed into plastic containers for 24 h to harden. The pastes were then demolded and further cured under a saturated CaO solution for 8 months. XRD analysis of the $3CaO \cdot SiO_2$ paste detected no residual unhydrated $3CaO \cdot SiO_2$. A few days before the INS measurement the hardened pastes were cut into 0.8-mm-thick disks using a water-lubricated wafering saw. Decalcification was then performed by placing the disks into a 6 mol/L aqueous solution of NH_4NO_3, a method that has been shown to give results similar to that of leaching in water or dilute acid while requiring a fraction of the time.[17,18] Due to the small thickness of the specimens and the extremely high solubility of calcium in NH_4NO_3, decalcification required <1 h in all cases. The mass loss during leaching was monitored by removing and weighing the saturated specimens at regular intervals. Specimens were removed and rinsed when they reached a preselected mass loss value.

Immediately following the leaching treatment, specimens were vacuum-dried through a reservoir of ice maintained at −78 °C (D-drying) for several days and were then stored in tightly sealed nitrogen-filled plastic containers until the neutron spectroscopy analysis. Removal of liquid H_2O decreased the background scattering during the INS measurement, increasing the sensitivity to the remaining bound hydrogen. The mass loss from the saturated state to the dried state was measured. The original unleached mass of any specimen (dry or saturated) could therefore be calculated from its dry leached mass and its Ca/Si.

To determine accurately the Ca/Si of the pastes, ~0.1 g of each decalcified specimen was interground with $LiBO_3$ flux and heated to 1000 °C in a graphite crucible [see ref 19], vitrifying the sample so that it would dissolve easily in dilute HCl. The elemental Ca and Si concentrations in the resulting aqueous solutions were measured using ICP-AES, using appropriate standard reference solutions. Tests conducted using a standard OPC in our laboratory have shown that this

(7) Cong, X.; Kirkpatrick, R. J. *J. Am. Ceram. Soc.* **1996**, *79*, 1585.

(8) Cong, X.; Kirkpatrick, R. J. *Cem. Concr. Res.* **1993**, *23*, 1065.

(9) Yu, P.; Kirkpatrick, R. J.; Poe, B.; McMillan, P. F.; Cong, X. *J. Am. Ceram. Soc.* **1999**, *82*, 742.

(10) Klur, I.; Pollet, B.; Virlet, J.; Nonat, A. In *Nuclear Magnetic Resonance Spectroscopy of Cement-Based Materials*; Colombet, P., Grimmer, A.-R., Zanni, H., Sozzani, P., Eds.; Springer: Berlin, 1998; p 119.

(11) Cong, X.; Kirkpatrick, R. J. *Adv. Cem. Based Mater.* **1996**, *3*, 144.

(12) Taylor, H. F. W. *J. Am. Ceram. Soc.* **1986**, *69*, 464.

(13) Chen, J. J.; Thomas, J. J.; Jennings, H. M.; Taylor, H. F. W. *Cem. Concr. Res.*, submitted for publication.

(14) FitzGerald, S. A.; Neumann, D. A.; Rush, J. J.; Kirkpatrick, R. J.; Cong, X.; Livingston, R. A. *J. Mater. Res.* **1999**, *14*, 1160.

(15) Baddour-Hadjean, R.; Fillaux, F.; Floquet, N.; Belushkin, S.; Natkaniec, I.; Desgranges, L.; Grebille, D. *Chem. Phys.* **1995**, *197*, 81.

(16) Information on commercial products is given for completeness and does not constitute or imply their endorsement by the National Institute of Standards and Technology.

(17) Carde, C.; Escadeillas, G.; Francois, R. *Magn. Concr. Res.* **1997**, *49*, 295.

(18) Heukamp, F. H.; Ulm, F. J.; Germaine, J. T. *Cem. Concr. Res.* **2001**, *31*, 767.

(19) Farinas, J. C.; Ortega, P. *Analusis* **1992**, *20*, 221.
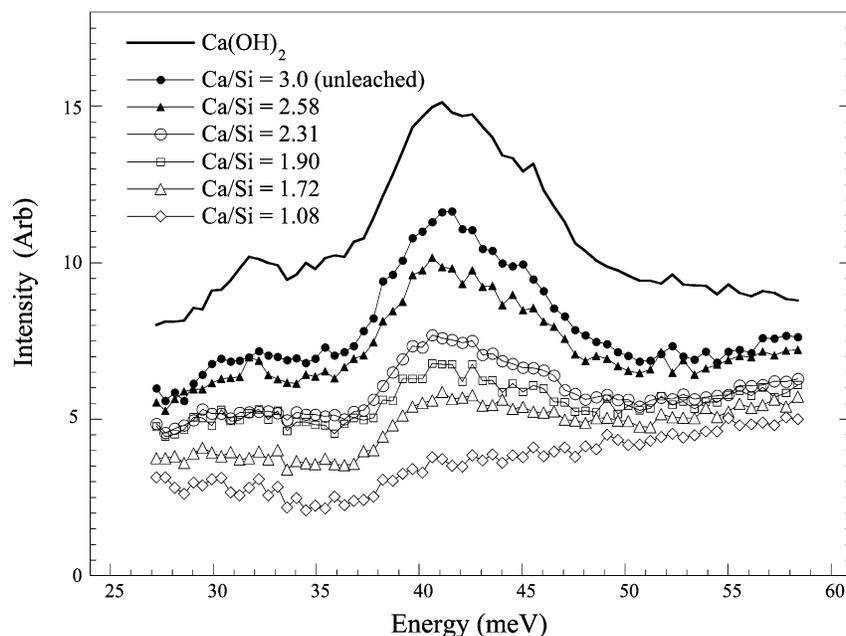
Figure 1. Energy loss spectra as measured by inelastic neutron scattering of pure $Ca(OH)_2$ powder (top curve) and $3CaO \cdot SiO_2$ pastes decalcified to various Ca/Si ratios. The broad peak centered near 41 meV arises from hydrogen in Ca−OH bonds. Spectra from $3CaO \cdot SiO_2$ pastes are normalized to the original sample mass before decalcification.

procedure is accurate to within 2%.[13] The bound water content of the vacuum-dried specimens was also determined by measuring the mass loss on ignition to 1000 °C.

$Ca(OH)_2$ is more soluble than C−S−H, and under equilibrium conditions the $Ca(OH)_2$ in a hydrated paste will be completely removed before the C−S−H gel begins to decalcify. However, gradients in Ca/Si across the sample thickness are inevitable and thus C−S−H near the specimen surface will begin to decalcify before the $Ca(OH)_2$ at the center has been fully extracted. To account for this effect, quantitative X-ray diffraction (QXRD) was used to measure the $Ca(OH)_2$ content of a parallel series of leached $3CaO \cdot SiO_2$ pastes, using corundum as an internal standard. The Ca/Si of the C−S−H in these specimens was then computed from the measured $Ca(OH)_2$ content and the bulk Ca/Si of the leached paste. These results, which indicated that the $Ca(OH)_2$ was fully removed from the paste at a bulk Ca/Si of ~1.4, were used to estimate the Ca/Si of the C−S−H gel in the specimens analyzed with INS. The present findings indicate that it is difficult to remove all of the $Ca(OH)_2$ from a paste without also removing some Ca−OH from the C−S−H gel. This may explain why measurements of the $Ca(OH)_2$ content of pastes based on chemical extraction methods are higher than those based on other techniques.[4]

The INS experiments were performed at the NIST Center for Neutron Research in Gaithersburg, MD, using the filter analyzer neutron spectrometer (FANS) located at instrument position BT4.[20] A Cu(220) crystal was used to produce the monochromatic beam that was incident on the sample. Collimations of 60′ and 40′ were used before and after the monochromator, respectively, yielding an overall energy resolution of ~1.2 meV at an energy transfer of 45 meV. Data were collected by varying the initial energy of the neutrons while the final neutron energy was fixed at 1.2 meV by the filter. For each point in the scan, neutrons were counted until an instrument monitor reached a preselected value, providing an initial normalization of the spectral intensities. Just before the INS measurement, ~1 g of specimen was placed into a flat, rectangular aluminum sample cell with an interior thickness of 1 mm and sealed to prevent moisture and CO_2 from interacting with the specimen during the measurement. One spectrum was obtained using an empty sample cell to allow

background scattering to be subtracted, and reference spectra of pure reagent-grade calcium hydroxide powder were also obtained to provide a calibration of the amount of Ca−OH bonds in the decalcified pastes. Measurements were performed at room temperature, and counting times ranged from 4 to 6 h.

3. Results and Discussion

Figure 1 shows the inelastic neutron scattering spectra for the $Ca(OH)_2$ reference material (top curve) and for the $3CaO \cdot SiO_2$ pastes. The intensity of the leached $3CaO \cdot SiO_2$ pastes were normalized to the original unleached, saturated mass of the specimen, and the intensity of the $Ca(OH)_2$ spectrum was normalized to the mass of powder. In the energy range studied, INS bands at 32 meV (moderate), 41 meV(strong), and 46 meV (shoulder) were observed in the $Ca(OH)_2$ powder. These three bands could also be distinguished in the leached $3CaO \cdot SiO_2$ pastes with Ca/Si > 1.7 during the fitting procedure, although only the strong band at 41 meV is obvious to the eye. All of the above bands have been observed in other INS studies[15] of $Ca(OH)_2$ and have been assigned to lattice translational modes of the crystal.

For the leached pastes, the intensity of the bands, most notably that of the strong band at 41 meV, decreases with the bulk Ca/Si of the paste, indicating a decreasing concentration of Ca−OH bonds in the samples. This trend is expected since $Ca(OH)_2$ is the primary phase initially leached from the paste. At Ca/Si = 1.72 significant intensity in the band at 41 meV still remains, even though almost all of the calcium hydroxide in the paste has been removed. This suggests that Ca−OH bonding is present in the C−S−H gel. At the lowest Ca/Si of 1.0, the peak has disappeared, indicating that the Ca−OH bonds in the C−S−H have been removed. Results for WPC paste were similar.

The spectra shown in Figure 1 were fit using two Gaussian peaks representing the main peak centered

(20) Copley, J. R. D.; Neumann, D. A.; Kamitakahara, W. A. *Can. J. Phys.* **1995**, *73*, 763.

Table 1. Calculation of the Ca−OH Bond Content of C−S−H Gel in 3CaO·SiO$_2$ Pastes as a Function of Ca/Si

1 Ca/Si of paste (mol/mol)	2 Ca/Si of C−S−H (mol/mol)	3 H$_2$O/Si of C−S−H[b] (mol/mol)	4 wt. Ca(OH)$_2$/ wt. paste[c] (g/g)	5 Ca−OH in Ca(OH)$_2$/ wt. paste[d] (mmol/g)	6 Ca−OH/ wt. paste[e] (mmol/g)	7 Ca−OH in C−S−H/ wt. paste[f] (mmol/g)	8 (Ca−OH−Ca) in C−S−H (mol/mol)	9 (Ca−OH/Si) in C−S−H (mol/mol)	10 fraction of Ca in C−S−H balanced by OH
3.00	1.70	1.34	0.349	9.43	12.23	2.81	0.46	0.77	0.23
2.58	1.65[a]	1.31	0.281	7.59	10.52	2.93	0.44	0.72	0.22
2.31	1.60[a]	1.28	0.233	6.30	8.71	2.41	0.34	0.54	0.17
1.90	1.45[a]	1.19	0.170	4.59	6.96	2.38	0.32	0.47	0.16
1.72	1.40[a]	1.15	0.130	3.50	5.96	2.47	0.32	0.45	0.16
1.08	1.08	0.95	0.000	0.00	0.97	0.97	0.12	0.13	0.06

[a] Estimated from QXRD data of a parallel set of leached 3CaO·SiO$_2$ samples. [b] H$_2$O content of C−S−H equilibrated to the D-dry state (see text). [c] Calculated from the mass of the paste and columns 1−3. [d] Calculated from column 4 using 2 mol of Ca−OH/mol of Ca(OH)$_2$. [e] Based on the INS results (see text and Figure 2). [f] Equals column 6 − column 5.
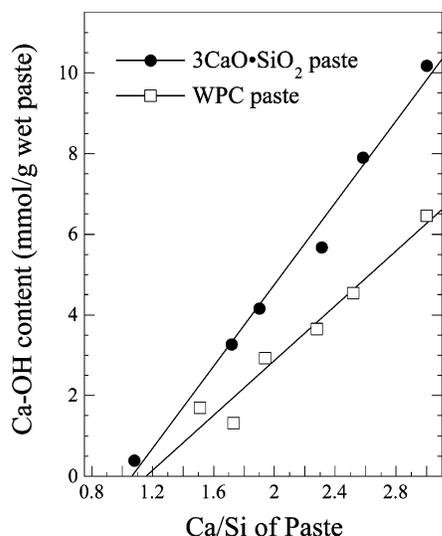

Figure 2. Ca−OH bond content in decalcified CaO·SiO$_2$ and WPC pastes as measured by inelastic neutron spectroscopy. The lines are linear fits to the data. The Ca−OH contents are normalized to the original saturated mass of the specimens before decalcification.

at ~41 meV and the shoulder at ~46 meV, and a linearly varying background. The ratio of the intensities of the two Gaussian peaks was found to be sample-independent. For the leached pastes, the intensity of the bands, most notably that of the strong band at 41 meV, decreases with the bulk Ca/Si of the paste, indicating a decreasing concentration and was therefore held constant for the final fits. The Ca−OH bond content of the paste specimens was then calculated using the fitted intensity from the Ca(OH)$_2$ powder specimen and the known Ca−OH bond content of Ca(OH)$_2$. Figure 2 shows the Ca−OH bond content of the 3CaO·SiO$_2$ and WPC pastes plotted against the total Ca/Si of the paste. The Ca/Si of the paste includes both the C−S−H gel and the Ca(OH)$_2$ phase, when present. For both types of paste, the Ca−OH content decreases with Ca/Si and extrapolates to zero at a Ca/Si slightly greater than 1.0. Since QXRD results indicated that crystalline Ca(OH)$_2$ was fully removed from the leached pastes by Ca/Si = 1.4, this shows that Ca−OH bonds are present in C−S−H gel for Ca/Si greater than about 1. The Ca−OH content, normalized to the mass of paste, is significantly higher in the 3CaO·SiO$_2$ paste than in the WPC paste at a given Ca/Si. This is expected, as cement phases other than 3CaO·SiO$_2$ do not form significant amounts of Ca(OH)$_2$ on hydration.

Quantitative calculation of the Ca−OH content of the C−S−H gel in the leached 3CaO·SiO$_2$ pastes is shown in Table 1. The Ca/Si ratios of the paste (column 1) were determined using ICP-AES, and the Ca/Si ratios of C−S−H (column 2) and the H$_2$O/Si ratios of C−S−H (column 3) were estimated from measurements on parallel specimens using QXRD and loss-on-ignition from the D-dry state, respectively. Values from columns 1−3 were used to calculate the mass of Ca(OH)$_2$ in the pastes (column 4), which were then converted to the number of Ca−OH bonds within Ca(OH)$_2$ in each paste (column 5). Finally, the Ca−OH bond content of the C−S−H phase in each paste (column 7) was calculated by subtracting the quantity of Ca−OH bonds contributed by Ca(OH)$_2$ (column 5) from the total Ca−OH content measured by INS (column 6). The results are renormalized in three ways: as moles of Ca−OH bonds per mole of Ca in C−S−H (column 8), as moles of Ca−OH bonds per mole of Si in C−S−H (column 9), and as the fraction of the Ca atoms in C−S−H balanced by OH (column 10).

As shown by columns 7−10 in Table 1, the C−S−H gel contains a significant proportion of Ca−OH bonds at high Ca/Si, and the amount of Ca−OH bonds decreases with decreasing Ca/Si, nearing zero by Ca/Si = 1.08. The complete removal of Ca−OH at this composition is consistent with recent phase equilibrium evidence[13] that Ca−OH bonds are absent in C−S−H gel formed from 3CaO·SiO$_2$ at Ca/Si < 1.2, and similar conclusions have been reached for synthetic preparations of C−S−H.[9,11] For the unleached specimen (first row of Table 1), there are 0.45 mol of Ca−OH bonds per mole of Ca in C−S−H. Since two Ca−OH bonds are required to charge balance one Ca atom, ~23% of the Ca in C−S−H at Ca/Si = 1.7 is effectively charge-balanced by OH groups rather than by silicate anions (see column 10). In the mineral jennite, this value is 33%,[6] while for 1.4-nm tobermorite the value is zero (no Ca−OH bonds). The present analysis thus suggests that the local structure of C−S−H gel with Ca/Si = ~1.7 produced by the hydration of 3CaO·SiO$_2$ resembles that of jennite more closely than that of 1.4 nm tobermorite. This presumes that the Ca−OH bonds in the C−S−H gel occur within the main Ca−O sheet as is the case with jennite; this is a reasonable assumption given the high Ca−OH content.

The Ca−OH content of a C−S−H specimen with Ca/Si > 1 can be calculated from the mean silicate chain length if an assumption is made about the bonding. We assumed here that all of the silicate groups in the
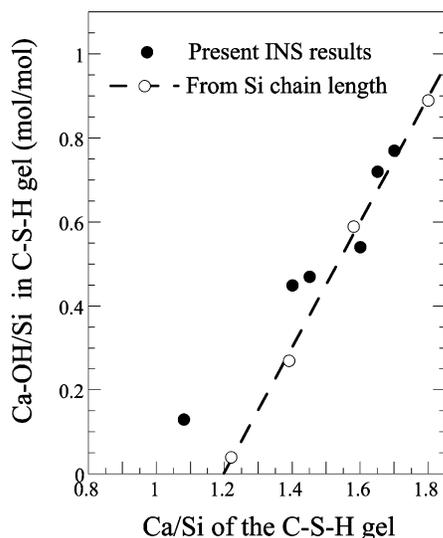
Figure 3. Mole ratio of Ca−OH bonds to Si atoms in the C−S−H gel, as a function of the Ca/Si ratio of the C−S−H gel. Note the difference with Figure 2, which is plotted against the total Ca/Si ratios of the paste. Values determined from the INS data are compared with charge balance calculations based on ^{29}Si MAS NMR data[13] (see text).

C−S−H structure are preferentially charge-balanced by calcium ions. Thus, the Ca−OH content is simply assumed to be the amount of calcium in the C−S−H in excess of that required to charge balance the silicate structure. However, if some silicate anions are charge-balanced by hydrogen (Si−OH bonds), then the actual Ca−OH content would be correspondingly higher. The average chain length of a parallel series of mature 3CaO·SiO$_2$ pastes was measured as a function of Ca/Si using ^{29}Si MAS NMR and reported in a separate study.[13] The calculated Ca−OH content of those specimens is plotted in Figure 3 along with the values from the present study. The agreement is good at high Ca/Si, but at lower Ca/Si the Ca−OH content measured by INS is

higher than the value calculated from the chain length. The apparent deviation in the Ca−OH content at lower Ca/Si may indicate the coexistence of Si−OH and Ca−OH groups, as has been postulated for synthetic C−S−H preparations.[7,11] However, more data in this composition range are required to reach a firm conclusion.

4. Conclusions

Inelastic neutron spectroscopy (INS) was used to determine the content of Ca−OH bonds in mature tricalcium silicate (3CaO·SiO$_2$) and white Portland cement (WPC) paste specimens that were decalcified to various degrees by a chemical leaching process. The Ca−OH content in both types of paste as measured by INS decreased with decalcification, reaching zero at Ca/Si ∼ 1. Quantitative analysis of the INS data for the 3CaO·SiO$_2$ pastes indicate that approximately 23% of the Ca in undecalcified C−S−H gel with Ca/Si = 1.7 exists in Ca−OH groups. This significant proportion of Ca−OH bonding suggests that the local structure of C−S−H gel resembles that of jennite (which has 33% Ca−OH) more closely than that of 1.4-nm tobermorite (which has no Ca−OH bonding). The measured Ca−OH content at high Ca/Si is in good agreement with charge balance calculations based on the mean silicate chain length of a parallel set of 3CaO·SiO$_2$ paste specimens and the assumption that Si−OH bonding is not present. At lower Ca/Si close to 1, the Ca−OH content measured in the present study is higher than the value calculated by charge balance, indicating that a small concentration of Si−OH groups may be present in this composition range.

CM034227F