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Incorporation of Aluminum in the Calcium Silicate Hydrate (C–S–H) of Hydrated Portland Cements: A High-Field ^{27}Al and ^{29}Si MAS NMR Investigation

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The calcium silicate hydrate (C–S–H) phase resulting from hydration of a white Portland cement (wPc) in water and in a 0.3 M $NaAlO_2$ solution has been investigated at 14 and 11 hydration times, respectively, ranging from 6 h to 1 year by ^{27}Al and ^{29}Si MAS NMR spectroscopy. ^{27}Al MAS NMR spectra recorded at 7.05, 9.39, 14.09, and 21.15 T have allowed a determination of the ^{27}Al isotropic chemical shift (δ_{iso}) and quadrupolar product parameter ($P_Q = C_Q\sqrt{1+\eta_Q^2/3}$) for tetrahedrally coordinated Al incorporated in the C–S–H phase and for a pentacoordinated Al site. The latter site may originate from Al^{3+} substituting for Ca^{2+} ions situated in the interlayers of the C–S–H structure. The spectral region for octahedrally coordinated Al displays resonances from ettringite, monosulfate, and a third aluminate hydrate phase ($\delta_{iso} = 5.0$ ppm and $P_Q = 1.20$ MHz). The latter phase is tentatively ascribed to a less-crystalline aluminate gel or calcium aluminate hydrate. The tetrahedral Al incorporated in the C–S–H phase has been quantitatively determined from ^{27}Al MAS spectra at 14.09 T and indirectly observed quantitatively in ^{29}Si MAS NMR spectra by the Q^2(1Al) resonance at –81.0 ppm. A linear correlation is observed between the ^{29}Si MAS NMR intensity for the Q^2(1Al) resonance and the quantity of Al incorporated in the C–S–H phase from ^{27}Al MAS NMR for the different samples of hydrated wPc. This correlation supports the assignment of the resonance at $\delta_{iso}(^{29}Si) = -81.0$ ppm to a Q^2(1Al) site in the C–S–H phase and the assignment of the ^{27}Al resonance at $\delta_{iso}(^{27}Al) = 74.6$ ppm, characterized by $P_Q(^{27}Al) = 4.5$ MHz, to tetrahedrally coordinated Al in the C–S–H. Finally, it is shown that hydration of wPc in a $NaAlO_2$ solution results in a C–S–H phase with a longer mean chain length of SiO_4 tetrahedra and an increased quantity of Al incorporated in the chain structure as compared to the C–S–H phase resulting from hydration of wPc in water.

Introduction

The principal binding phase responsible for the strength development in hydrated Portland cements is a poorly crystalline calcium silicate hydrate ($(CaO)_x(SiO_2)_y(H_2O)_z$, shorthand notation C–S–H). The C–S–H phase is formed by hydration of the calcium silicates, alite (Ca_3SiO_5) and belite (Ca_2SiO_4), which along with calcium aluminate ($Ca_3Al_2O_6$) and ferrite ($Ca_2Al_xFe_{2-x}O_5$) are the main phases in Portland cements. The structure of the C–S–H phase is difficult to study using conventional X-ray diffraction techniques as a result of the lack of long-range order and the incorporation of guest ions, (e.g., Mg^{2+}, Al^{3+}, and Fe^{3+}) in the structure.[1] From thermal analysis, microanalytical techniques (e.g., SEM, TEM, and EPMA), and ^{29}Si MAS NMR spectroscopy it is well-known that the nanostructure of the C–S–H depends strongly on the Ca/Si ratio and the water content and that domains with different structures may be present in the cement paste.[1] Furthermore, it is known that the C–S–H phase has a layer structure which ideally resembles the layer structure of the crystalline 11- and 14-Å tobermorites with the expected constitutional formulas $Ca_{4.5}Si_6O_{16}(OH)\cdot 5H_2O$[2] and $Ca_5Si_6O_{16}(OH)_2\cdot 8H_2O$,[3] respectively. Several models for the formation of the C–S–H and

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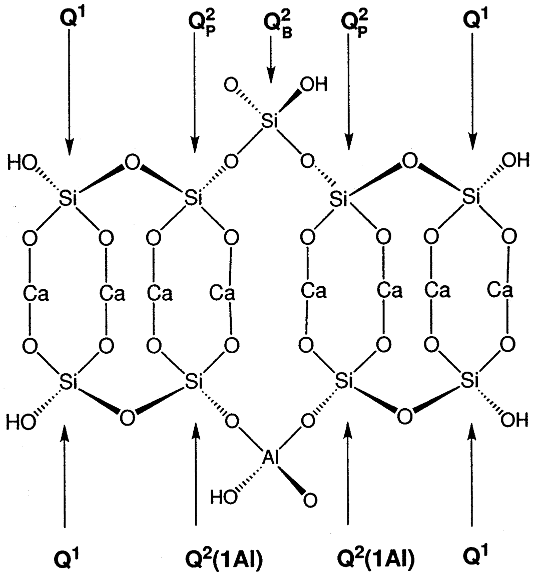

Figure 1. Schematic representation of a single layer in the crystal structure for a 14-Å tobermorite. The upper part shows a pentameric silicate chain which is a characteristic feature for the "dreierketten"-based models for the C−S−H phase. The lower part illustrates the incorporation of Al in the bridging site of the pentameric silicate chain. Interlayer water molecules and Ca^{2+} ions are not included in this representation.

its microstructure in cement pastes have been proposed.[1,4,5] Most recently, it has been suggested that a C−S−H phase with a sorosilicate-like structure (i.e., including $(Si_2O_7)^{6-}$ ions) is formed soon after setting of the cement paste and that this phase on a longer time scale becomes unstable and transforms into a tobermorite-like C−S−H structure.[4]

A common structural feature for the tobermorites is a layer structure consisting of CaO_2 layers, with 7-fold coordinated Ca^{2+} ions, where the oxygens are shared with Si^{4+} in chains of SiO_4 tetrahedra in a "dreierketten" arrangement on both sides of the CaO_2 layer[2,3,6] as illustrated in Figure 1. Water molecules and additional Ca^{2+} ions are present between these layers, which are separated by either 11 or 14 Å. The 11-Å tobermorite includes SiO_4 tetrahedra in double chains ("dreierdoppelketten", Q^2 and Q^3 units in a 2:1 ratio)[2] whereas the 14-Å tobermorite only contains SiO_4 tetrahedra in "dreierketten" chains (i.e., Q^2 units).[1] A major difference between tobermorites and the C−S−H, resulting from Portland cement hydration, is that the chains of SiO_4 tetrahedra are broken. Studies of C−S−H phases by the trimethylsilylation (TMS) technique have shown that the C−S−H contains dimeric, pentameric, and higher polymeric species of SiO_4 tetrahedra, resulting in chains of 2, 5, 8, ..., $(3n - 1)$ SiO_4 tetrahedra.[7−9] The chain of SiO_4 tetrahedra in the upper part of Figure 1 illustrates a pentameric unit where a bridging SiO_4 tetrahedron (Q_B^2) connects two dimers, resulting in two SiO_4 end-groups (Q^1) and two "paired" SiO_4 sites (Q_P^2). The presence of dimeric or end-group (Q^1) and chain (Q^2) SiO_4 tetrahedra and the absence of Q^3 SiO_4 tetrahedra (i.e., double chains of SiO_4 tetrahedra) have been demonstrated by ^{29}Si MAS NMR in a number of studies of C−S−H phases in hydrating Portland cements (see refs 10 and 11 and references therein). Although the paired and bridging SiO_4 tetrahedra have not been distinguished so far by ^{29}Si MAS NMR, this technique allows quantification of the fractions of Q^1 and Q^2 SiO_4 tetrahedra, implying that the mean chain length of SiO_4 tetrahedra in the C−S−H can be calculated.

On the basis of ^{29}Si and ^{17}O MAS NMR studies in combination with X-ray diffraction and chemical analysis of a number of synthetic (aluminum free) C−S−H phases with different Ca/Si ratios (0.41−1.85), Cong and Kirkpatrick[12−14] have proposed a defect tobermorite structural model for the C−S−H phase. This model is based on the structure of the 14-Å tobermorite but includes stacking disorder among adjacent CaO_2 layers, structural disorder within these layers, and a significant concentration of defects in the chains of SiO_4 tetrahedra. The latter types of defects are proposed to be vacancies of bridging SiO_4 tetrahedra (i.e., Q_B^2 units), resulting in many dimers in a broken chain structure of SiO_4 tetrahedra connected to the CaO_2 layer. Subsequent Ca X-ray absorption,[15] Raman,[16] and infrared[17] spectroscopic studies of the same C−S−H samples and hydrothermally prepared C−S−H phases by Kirkpatrick, Cong, and co-workers are all in overall agreement with this proposed defect tobermorite structural model.

The ^{29}Si NMR resonances originating from the Q^1 and Q^2 (i.e., Q_B^2 and Q_P^2) sites are observed as broadened resonances at about −79.5 and −84.5 ppm, respectively.[11,18−24] In a ^{29}Si MAS NMR investigation of a hydrated synthetic slag glass, Richardson et al.[23] also observed a resonance at −80.5 ppm, which they assigned to a $Q^2(1Al)$ site, i.e., a SiO_4 chain unit connected to one SiO_4 and one AlO_4 tetrahedron, employing earlier results from ^{29}Si MAS studies of Al-substituted tobermorites.[24] Moreover, they suggested that Al

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can only substitute for Si in the bridging (Q_B^2) site. The lower part of Figure 1 illustrates a pentameric unit, where Al is incorporated in the bridging site. The tetrahedral environment for aluminum in the C−S−H was supported by the observation of a broad resonance at about 70 ppm in the ^{27}Al MAS NMR spectrum of the hydrated slag glass.[23] Faucon et al. have studied the dependency of the Ca/Si ratio on the incorporation of Al in the C−S−H by ^{27}Al MAS NMR[25] and multiple-quantum (MQ) MAS NMR.[26] They proposed that aluminum preferentially substitutes a nonbridging SiO_4 tetrahedron for C−S−H phases with polymeric chains of SiO_4 tetrahedra. For a high Ca/Si ratio C−S−H, which only includes dimers of SiO_4 tetrahedra, they suggested that a limited degree of Al can substitute for Ca^{2+} ions in the interlayer or in the CaO_2 layer on the basis of the observation of resonances from pentacoordinated and octahedrally coordinated Al, respectively.[25]

This work presents the results of a ^{29}Si MAS and high-field (14.09 and 21.15 T) ^{27}Al MAS NMR investigation of the C−S−H resulting from hydration of a white Portland cement (wPc) using water and a 0.3 M aqueous solution of $NaAlO_2$. The ^{27}Al MAS spectra demonstrate that tetrahedral Al in the C−S−H can be distinguished (and quantified) from the resonances for the Al guest ions in the anhydrous alite and belite phases. Quantitative information about Al incorporated in the C−S−H is also obtained by ^{29}Si MAS NMR for the two series of hydrated wPc by the observation of the Q^2(1Al) resonance. The linear correlation between the ^{29}Si intensities for the Q^2(1Al) resonance with the quantities of tetrahedral Al in the C−S−H, observed by ^{27}Al MAS NMR, gives improved evidence for the correct assignment of these resonances in the ^{29}Si and ^{27}Al MAS NMR spectra. Furthermore, it is shown that information about ettringite, monosulfate, and a third aluminum hydrate phase, resulting from hydration of the calcium aluminate phase in the wPc, is readily achieved from high-field ^{27}Al MAS NMR spectra.

Experimental Section

Materials. The white Portland cement (wPc) was a commercial cement from Aalborg Portland A/S, Denmark, with the following metal oxide composition: 69.13 wt % CaO; 24.7 wt % SiO_2; 1.74 wt % Al_2O_3; 0.31 wt % Fe_2O_3; 0.56 wt % MgO; 1.97 wt % SO_3; Blaine fineness of 424 m^2/kg. Two series of hydrated samples were prepared using this cement. The first series corresponds to hydration of the wPc in demineralized water employing a water/cement ratio of 0.50 whereas the second series is the wPc mixed with a 0.30 M solution of $NaAlO_2$ in demineralized water using a solution/cement ratio of 1.0 to prevent “flash setting” of the cement. The wPc was added to the water/$NaAlO_2$ solution and mixed by hand for 5 min. After mixing, the cement pastes were placed in open plastic bags in a closed desiccator with a relative humidity of 100% at 20 °C. At appropriate time intervals, samples were ground to a powder and the hydration process was stopped by suspending the powder sample in acetone under stirring for about 15 min. After drying at 20 °C in a desiccator, the samples were kept in airtight containers prior to the NMR investigations to prevent atmospheric CO_2 contamination.

NMR Measurements. The solid-state ^{27}Al MAS experiments were performed on Varian INOVA-300 (7.05 T), INOVA-400 (9.39 T), and INOVA-600 (14.09 T) spectrometers using home-built CP/MAS probes for 4 and 5 mm o.d. zirconia (PSZ) rotors. The single-pulse ^{27}Al MAS experiments at 7.05 and 9.39 T used a pulse width of 1 μs for a rf field strength of $\gamma B_1/2\pi = 60$ kHz, ^{1}H decoupling with $\gamma B_2/2\pi = 75$ kHz, spinning speeds of about 10 kHz, a 2-s relaxation delay, and typically 10 000 scans. The ^{27}Al MAS spectra at 14.09 T were obtained in a similar manner for $\gamma B_1/2\pi = 50$ kHz, $\gamma B_2/2\pi = 50$ kHz, and a spinning speed of $\nu_R = 13.0$ kHz. At the three magnetic fields, the ^{27}Al MAS NMR spectrum of the probe itself including an empty zirconia rotor showed a broad resonance of very low intensity. This spectrum was subtracted from the ^{27}Al MAS NMR spectra of the cement samples prior to the quantitative evaluation of the observed intensities. The Al_2O_3 contents of the samples were determined from the ^{27}Al MAS NMR spectra recorded at 14.09 T and employed a pulse width of $\tau_p = 0.5$ μs for $\gamma B_1/2\pi = 50$ kHz (i.e., a flip angle $< \pi/6$ for ^{27}Al, $I = 5/2$, in a solid) to ensure quantitative reliability of the intensities observed for the ^{27}Al central transition for sites experiencing different quadrupole couplings. Moreover, these measurements employed weighed samples and the ^{27}Al MAS NMR spectrum of α-Al_2O_3 as an external intensity reference. A single ^{27}Al MAS NMR spectrum was obtained on a Varian INOVA-900 spectrometer (21.15 T) at Oxford Instruments, U.K., using a home-built 900 MHz CP/MAS NMR probe[27] and a pulse width of $\tau_p = 1.0$ μs for $\gamma B_1/2\pi = 60$ kHz. The solid-state ^{29}Si MAS NMR spectra were obtained on a Varian INOVA-400 (9.4 T) spectrometer using a home-built CP/MAS probe for 7 mm o.d. zirconia rotors, a spinning speed of 6.0 kHz, single-pulse excitation with a pulse width of 3 μs for a rf field strength $\gamma B_1/2\pi = 40$ kHz, a relaxation delay of 30 s, and typically 2048 scans. ^{29}Si and ^{27}Al chemical shifts are referenced to external samples of tetramethylsilane (TMS) and a 1.0 M aqueous solution of $AlCl_3 \cdot 6H_2O$, respectively. The deconvolutions were performed on a SUN Ultra 5 computer using the least-squares fitting routine of the Varian software and the method for deconvolving ^{29}Si MAS NMR spectra of anhydrous and hydrated Portland cements described elsewhere.[28,29]

Results and Discussion

High-Field ^{27}Al MAS NMR. The analysis and interpretation of ^{27}Al MAS NMR spectra of hydrated Portland cements are complicated by the second-order quadrupolar line broadening which may result in a severe overlap of broadened resonances in the case of multiple sites. A significant improvement in resolution of several resonances may be achieved by performing the MAS NMR experiments at a very high magnetic field as a result of the inverse proportionality of the second-order quadrupole interaction with the magnetic field and the increased chemical shift dispersion. Most recently, this has been demonstrated by very high-field ^{27}Al MAS NMR in the characterization of multiple aluminum

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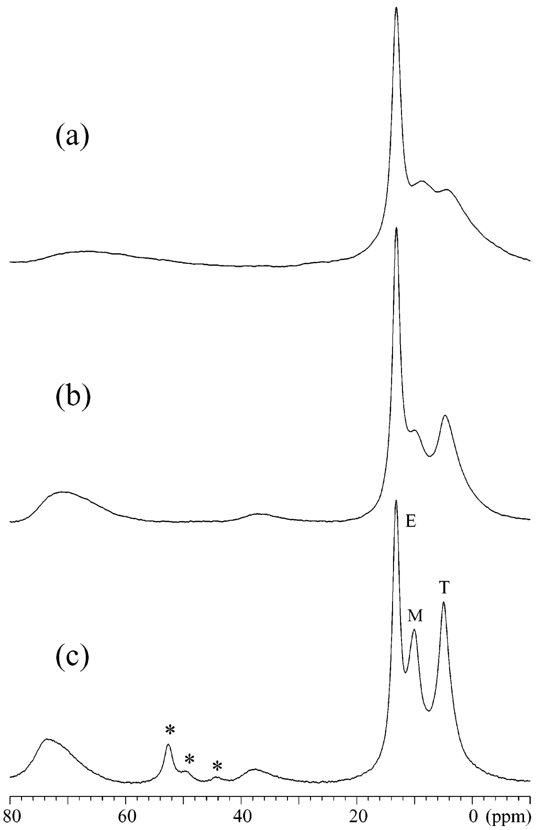

Figure 2. ^{27}Al MAS NMR spectra of the central transition for wPc hydrated for 12 weeks recorded at (a) 7.05 T, (b) 14.09 T, and (c) 21.15 T, employing ^{1}H decoupling and spinning speeds of $\nu_R = 13.0$ kHz (7.05 and 14.09 T) and $\nu_R = 9.5$ kHz (21.15 T). The asterisks indicate spinning sidebands whereas the centerbands from ettringite, monosulfate, and the third aluminate hydrate phase are indicated by E, M, and T, respectively.

environments in zeolite USY,[30] in aluminum orthovanadate,[31] and in an aluminoborate.[32] The advantages of employing very high magnetic fields in ^{27}Al MAS NMR studies of cementitious materials are illustrated in Figure 2, which compares ^{27}Al MAS NMR spectra of the central transition for the wPc hydrated for 12 weeks in water recorded at 7.05, 14.09, and 21.15 T. At 7.05 T (Figure 2a) the spectral region for octahedrally coordinated Al (20 to −10 ppm) includes a narrow centerband at 13.0 ppm and two peaks with lower intensity at 8.6 and 4.0 ppm, which arise from either a second-order quadrupolar line shape from a single ^{27}Al site or from two different Al species, possessing rather small quadrupole couplings. The ^{27}Al MAS spectra recorded at higher magnetic fields clearly demonstrate a significant increase in resolution of these two peaks, and from these spectra it is apparent that the two peaks originate from two distinct Al environments in the sample.

The centers of gravity for the central transitions reveal that the narrow centerband at 13.0 ppm and the slightly broader resonance at 9.8 ppm (14.09 T) originate from ettringite ($Ca_6[Al(OH)_6]_2(SO_4)_3 \cdot 26H_2O$) and monosulfate ($Ca_4[Al(OH)_6]_2SO_4 \cdot 6H_2O$), respectively, employing earlier reported ^{27}Al quadrupole coupling and isotropic chemical shift parameters for synthetic samples of these aluminate hydrates.[33] The centerband at lowest frequency has at the moment not been assigned to a specific type of aluminum species but arises most likely from a third aluminate hydrate phase. From the relationship[34]

$$\delta_{1/2,-1/2}{}^{cg} = \delta_{iso} - P_Q{}^2\,\frac{C_{1/2,-1/2}}{\nu_L{}^2}$$

$$C_{1/2,-1/2} = \frac{3}{40}\,\frac{I(I+1) - 3/4}{I^2(2I-1)^2} \quad (1)$$

between the center of gravity for the central transition ($\delta_{1/2,-1/2}{}^{cg}$) and the Larmor frequency (ν_L), $\delta_{iso} = 5.0 \pm 0.1$ ppm and the quadrupolar product parameter $P_Q = C_Q\sqrt{1+\eta_Q{}^2/3} = 1.20 \pm 0.10$ MHz are determined for the third aluminate hydrate phase from linear regression analysis of $\delta_{1/2,-1/2}{}^{cg}$ as a function of $\nu_L{}^{-2}$ obtained at the Larmor frequencies 78.1 MHz (7.05 T), 104.2 MHz (9.39 T), 156.3 MHz (14.05 T), and 234.5 MHz (21.15 T). For C−S−H phases synthesized in the presence of aluminum, Faucon et al.[25] observed an ^{27}Al resonance corresponding to the parameters $\delta_{iso} = 4.25$ ppm and $P_Q = 1.83$ MHz, which they assigned to Al^{3+} substituting Ca^{2+} in the CaO_2 layer of the C−S−H structure (cf. Figure 1). For synthetic Al-substituted 11-Å tobermorites, Klimesch and Ray[35] observed a resonance for octahedrally coordinated Al at approximately 3−5 ppm, which they ascribed to substitution of Al in an octahedral site of the tobermorite structure. At the moment, we believe that the low-frequency resonance in Figure 2, observed for the hydrated wPc, does not arise from Al incorporated in the C−S−H phase but more likely from a less-crystalline alumina gel or calcium aluminate hydrate phase. This belief is due to the fact that ^{27}Al{^{1}H} cross-polarization (CP) MAS NMR experiments demonstrate that Al is coordinated to a number of OH^- groups in the third aluminate hydrate phase either as $Al(OH)_6{}^{3-}$ or $O_xAl(OH)_{6-x}{}^{(3+x)-}$ octahedra. ^{27}Al{^{1}H} CP/MAS NMR spectra, recorded for an array of CP contact times or for different ^{27}Al rf field strengths with a fixed ^{1}H rf field, show very similar cross relaxation behavior for the third aluminate hydrate and monosulfate. This strongly indicates bonding of OH^- groups directly to aluminum in the third aluminate hydrate phase and most likely in the form of $Al(OH)_6{}^{3-}$ units as for monosulfate. Furthermore, ^{27}Al MAS NMR experiments for a wPc hydrated in the presence of 2−10 wt % gypsum demonstrate that an increasing quantity of gypsum results in a decrease in the quantity of the third aluminate hydrate phase and an increase in the quantity of ettringite formed after hydration for 8 weeks. It is also noted that the third aluminate hydrate phase has not been observed in an earlier ^{27}Al MAS NMR study of the hydration (10 min−28 days) of an ordinary

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Portland cement.[29] Thus, the ^{27}Al NMR resonance at $\delta_{iso} = 5.0$ ppm hardly originates from an octahedrally coordinated Al site in the C−S−H phase. Further studies aimed at elucidating the structure and composition of the third aluminate hydrate phase are in progress.

In the spectral region for tetrahedrally coordinated Al, the ^{27}Al MAS NMR spectra in Figure 2 display a rather broad resonance with the center of gravity of 69.5 and 72.3 ppm at 14.09 and 21.15 T, respectively. The line shape of this resonance indicates that it does not originate from a single well-defined aluminum environment but more likely an Al site in a less-crystalline structure. Employing eq 1, the centers of gravity for the central transition at the two magnetic fields, and the value $\delta_{1/2,-1/2}^{cg} = 63.2$ ppm determined at 9.39 T gives the parameters $\delta_{iso} = 74.6 \pm 0.2$ ppm and $P_Q = 4.5 \pm 0.2$ MHz, which should be considered mean values for ^{27}Al in this environment. Following the ^{27}Al MAS NMR studies of a hydrated synthetic slag glass[23] and of Al-substituted tobermorites,[24] this resonance is assigned to tetrahedrally coordinated Al incorporated in the C−S−H. The high-field ^{27}Al MAS NMR spectra (Figure 2b,c) allow a straightforward quantification of the intensity for this resonance and thereby of the quantity of aluminum incorporated in the C−S−H, employing the ^{27}Al MAS NMR spectrum of α-Al_2O_3 as an external intensity reference. For the wPc hydrated for 12 weeks, this procedure gives an equivalent quantity of Al_2O_3 of 0.14 wt % in the hydrated wPc, which is incorporated in the C−S−H. Finally, the high-field ^{27}Al MAS spectra recorded at 14.09 and 21.15 T also includes a minor resonance with the centers of gravity of 33.5 and 37.1 ppm, respectively. These values results in the parameters $\delta_{iso} = 39.9 \pm 0.3$ ppm and $P_Q = 5.1 \pm 0.2$ MHz. The δ_{iso} value indicates that this resonance originates from a pentacoordinated AlO_5 site, since 5-fold-coordinated Al in minerals and aluminates exhibits isotropic chemical shifts in the range 18−52 ppm.[36] A resonance from pentacoordinated Al, corresponding to the parameters $\delta_{iso} = 38.8$ ppm and $P_Q = 3.2 \pm 0.2$ MHz, has also been observed by Faucon et al.,[25] who tentatively assigned this resonance to Al^{3+} substituting for Ca^{2+} ions situated in the interlayers of the C−S−H structure.

^{27}Al MAS NMR of White Portland Cement Samples. With the aim of quantifying Al incorporated in the C−S−H phase, the samples of wPc hydrated in water and in a 0.3 M solution of $NaAlO_2$ have been investigated by ^{27}Al MAS NMR at 14.09 T. Illustrative ^{27}Al MAS NMR spectra of the wPc hydrated in water for 6 h, 1 week, and 1 year are shown in Figure 3. After hydration for 6 h, the spectral region for tetrahedrally coordinated Al displays two overlapping resonances with maximun peak intensities at 86 and 81 ppm. With employment of the results from an earlier ^{27}Al MAS study of anhydrous Portland cements,[37] these resonances are assigned to Al incorporated in the calcium silicates alite and belite (86 ppm) and Al in the impure form of calcium aluminate ($Ca_3Al_2O_6$, 81 ppm). The ^{27}Al MAS NMR spectrum of wPc after 1 week of hydration shows that nearly all Al in the calcium aluminate phase and in alite/belite have reacted and mainly formed ettringite, monosulfate, and the third aluminate hydrate phase. Thus, the centerband from Al incorporated in the C−S−H phase dominates the spectral region for tetrahedrally coordinated Al and allows a straightforward quantification of Al in the C−S−H. After hydration for 1 year, the intensity for the centerband from Al in the C−S−H has increased and the resonance from pentacoordinated Al is clearly observed.

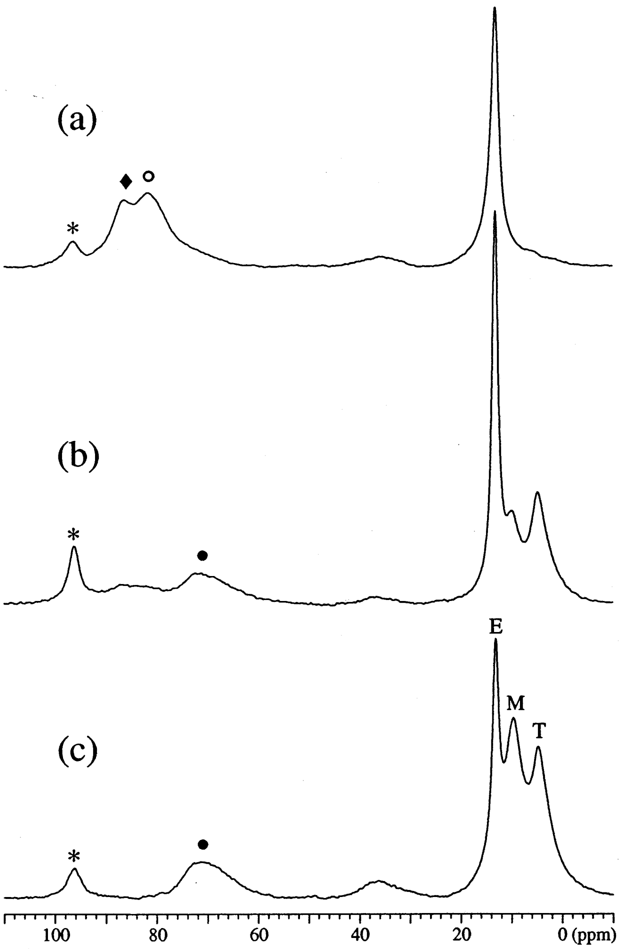

Figure 3. ^{27}Al MAS NMR spectra (14.09 T) of the central transition for the wPc hydrated in water for (a) 6 h, (b) 1 week, and (c) 1 year, obtained using ^{1}H decoupling and the spinning speed $\nu_R = 13.0$ kHz. The asterisks indicate spinning sidebands from ettringite, whereas the filled diamond and the open circle show the centerbands from Al incorporated in alite/belite and from Al in the calcium aluminate phase ($Ca_3Al_2O_6$), respectively. The filled circle indicates the centerband from Al incorporated in the C−S−H phase, while the centerbands from the hydration products ettringite, monosulfate, and the third aluminate hydrate phase are denoted by E, M, and T, respectively.

The hydration of wPc in water and 0.3 M $NaAlO_2$ solution has been studied by ^{27}Al MAS NMR at 14 and 11 different hydration times, respectively, ranging from 6 h to 1 year. From these spectra the equivalent quantities of Al_2O_3 in the hydrated wPc samples, which are incorporated in the C−S−H, are determined. Values for the different hydration times are listed in Table 1 for the two series of hydration. Figure 4 displays these quantities of Al_2O_3 in the C−S−H as a function of the hydration time for both series of hydration

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Table 1. Quantities of Al Incorporated in the C−S−H Phase and Fractions of ^{29}Si NMR Intensities for the Q^2(1Al) Resonance for 12 Hydration Times for the White Portland Cement Hydrated in Water and in a 0.3 M $NaAlO_2$ Solution

	wPc hydrated in water		wPc hydrated in 0.3 M $NaAlO_2$(aq)	
hydration time	Al_2O_3 (wt %)[a]	$I(Q^2(1Al))$ (%)[b]	Al_2O_3 (wt %)[a]	$I(Q^2(1Al))$ (%)[b]
12 h	0.02	1.8	0.09	5.2
1 day	0.05	3.1	0.12	6.5
2 days	0.05	4.4	0.13	7.4
4 days	0.07	5.0	0.14	8.2
1 week	0.09	5.1	0.16	8.8
2 weeks	0.10	5.5	0.17	9.5
4 weeks	0.12	7.1	0.19	10.1
8 weeks	0.13	7.3	0.20	11.1
12 weeks	0.14	7.5	0.21	11.3
18 weeks	0.14	7.4	0.22	11.6
30 weeks	0.13	8.0	c	11.9
1 year	0.15	8.6	0.24	13.7

[a] Equivalent quantities of Al_2O_3 in the hydrated cements which are incorporated in the C−S−H determined from ^{27}Al MAS NMR spectra of the central transition at 14.09 T, employing the ^{27}Al MAS spectrum of α-Al_2O_3 as an external intensity reference. The total quantity of Al_2O_3 in the wPc before hydration is 1.74 wt %. The error limits are estimated to ±0.02 wt % for all hydration times. [b] Relative intensity of the Q^2(1Al) resonance determined from computer deconvolutions of the ^{29}Si MAS NMR spectra. The error limits are estimated to ±0.5% for all hydration times. [c] Not determined.

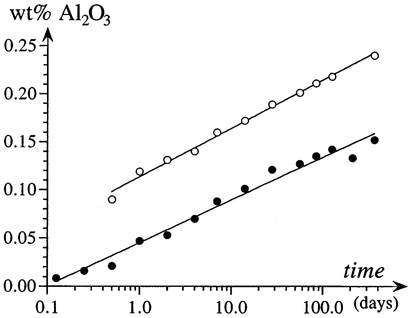

Figure 4. Graphs illustrating the equivalent quantities of Al_2O_3 (wt %) in the hydrated wPc samples which are incorporated in the C−S−H as a function of the logarithm to the hydration time for the wPc hydrated in water (filled circles) and in a 0.3 M $NaAlO_2$ solution (open circles). The quantities of Al_2O_3 in the C−S−H phase are determined from ^{27}Al MAS NMR spectra at 14.09 T by employing the ^{27}Al MAS NMR spectrum of α-Al_2O_3 as an external intensity reference (see also Table 1).

studied at 11 and 14 different hydration times. The graphs in Figure 4 clearly reveal an increasing quantity of Al incorporated in the C−S−H with increasing hydration time for both series of hydration. Furthermore, it is evident that hydration of wPc in a $NaAlO_2$ solution results in an increase in the incorporation of Al in the C−S−H.

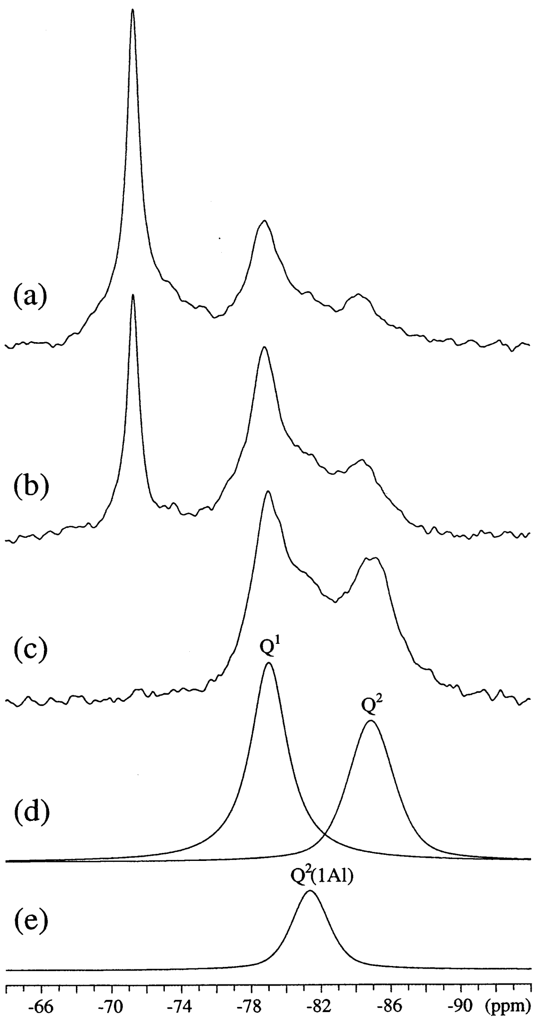

Figure 5. ^{29}Si MAS NMR spectra (9.39 T, $\nu_R = 6.0$ kHz) of wPc hydrated in a 0.3 M $NaAlO_2$ solution after (a) 1 day, (b) 2 weeks, and (c) 1 year of hydration. Parts d and e illustrate simulated resonances for the Q^1, Q^2, and Q^2(1Al) sites in the C−S−H phase, resulting from the optimized deconvolution of the spectrum after hydration for 1 year (c).

^{29}Si MAS NMR of White Portland Cement Samples. ^{29}Si MAS NMR spectra of the wPc hydrated in a 0.3 M $NaAlO_2$ solution for 1 day, 2 weeks, and 1 year are illustrated in Figure 5. In accord with earlier ^{29}Si MAS studies of anhydrous and hydrated white Portland cements,[19,21,28,29] these spectra include a narrow resonance from the unique Si environment in belite ($\delta_{iso} = -71.3$ ppm), which is superimposed on a number of broadened resonances in the range −68 to −76 ppm, originating from the monoclinic M_{III} form of alite. As the hydration proceeds, the intensities of these resonances decrease while a corresponding increase in intensity is observed for the resonances at −79 and −85 ppm, originating from the Q^1 and Q^2 (i.e., Q_B^2 and Q_P^2; cf. Figure 1) sites of the C−S−H phase, respectively. Furthermore, a low-frequency shoulder to the Q^1 resonance becomes visible, especially after prolonged hydration. This resonance, with the chemical shift $\delta_{iso} = -81.0$ ppm, is ascribed to a Q^2(1Al) site in the C−S−H, following the studies of Richardson et al.[23] With the aim of quantifying the relative intensity of this resonance, the individual ^{29}Si MAS NMR spectra of the wPc hydrated in water and in a 0.3 M $NaAlO_2$ solution have been deconvolved using the method described earlier for anhydrous and hydrated Portland cements.[28,29] This method employs separate peaks from Si in alite, belite, and the Q^1, Q^2, and Q^2(1Al) resonances from the C−S−H. Although the results from these deconvolutions contain valuable information about the hydration kinetics for alite and belite, we only focuss on the relative intensity for the Q^2(1Al) resonance in this work. Relative intensities for the Q^2(1Al) resonance are summarized in Table 1 for different times of hydration for the wPc hydrated in water and in the $NaAlO_2$ solution. These data, along with those determined for the remaining

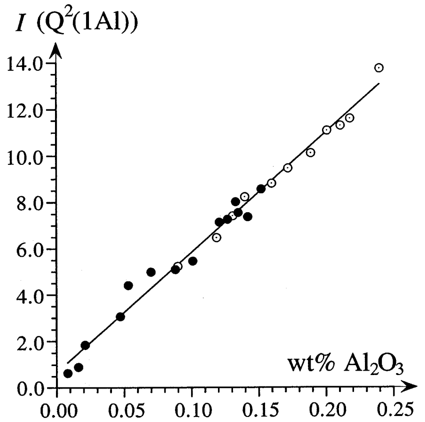

Figure 6. Graph illustrating the fraction of ^{29}Si NMR intensities for the Q^2(1Al) resonance as a function of the equivalent quantities of Al_2O_3 (wt %) in the hydrated wPc samples which are incorporated in the C−S−H phase and determined by ^{27}Al MAS NMR. The data for the white Portland cement hydrated in water and in a 0.3 M $NaAlO_2$ solution are shown by filled and open circles, respectively. Linear regression analysis of the data for both series of hydrated wPc results in eq 2.

samples in each series of hydration, reveal an increase in the relative intensity for the Q^2(1Al) resonance with increasing hydration time. Furthermore, it is apparent that hydration of wPc in a $NaAlO_2$ solution results in a higher degree of Al for Si substitution in the C−S−H phase.

Correlation between the Results from ^{27}Al and ^{29}Si MAS NMR. The fact that the quantity of Al incorporated in the C−S−H can be determined directly from the ^{27}Al MAS NMR spectra and indirectly from the intensity of the Q^2(1Al) resonance in the ^{29}Si MAS spectra points toward a correlation between the results from these two techniques. Figure 6 displays the fraction of ^{29}Si NMR intensity in the Q^2(1Al) resonance as a function of the equivalent quantity of Al_2O_3 in the wPc samples, which is incorporated in the C−S−H and measured by ^{27}Al MAS NMR. This graph demonstrates a linear relationship between the results from ^{27}Al and ^{29}Si MAS NMR where linear regression gives the equation

$$I(\mathrm{Q}^2(1\mathrm{Al})) = 51.77 \text{ wt \% } (\mathrm{Al_2O_3}) + 0.64, \quad R = 0.993 \qquad (2)$$

This linear relationship demonstrates that the ^{29}Si NMR resonance at $\delta_{\mathrm{iso}} = -80.5$ ppm is correctly assigned to a SiO_4 unit connected to an AlO_4 tetrahedron and another SiO_4 unit in the C−S−H phase, i.e., a Q^2(1Al) site. Similarly, the centerband in the ^{27}Al MAS spectrum corresponding to the mean parameters $\delta_{\mathrm{iso}} = 74.6$ ppm and $P_{\mathrm{Q}} = 4.53$ MHz is correctly assigned to tetrahedrally coordinated Al incorporated in the chains of SiO_4 tetrahedra in the C−S−H phase. Thereby, our results support the assignments of these resonances proposed by Richardson et al.[23] from ^{29}Si and ^{27}Al MAS NMR studies of a synthetic glass slag.

Table 2. Mean Chain Lengths of SiO_4 and AlO_4 Tetrahedra and Al/Si Ratios for the C−S−H Phase for 12 Hydration Times for the White Portland Cement Hydrated in Water and in a 0.3 M $NaAlO_2$ Solution

	wPc hydrated in water		wPc hydrated in 0.3 M $NaAlO_2$(aq)	
hydration time	$\overline{\mathrm{CL}}$[a]	Al/Si ratio[b]	$\overline{\mathrm{CL}}$[a]	Al/Si ratio[b]
12 h	2.67	0.043	3.19	0.084
1 day	2.95	0.045	3.28	0.068
2 days	3.08	0.050	3.16	0.065
4 days	3.03	0.048	3.23	0.064
1 week	2.91	0.044	3.27	0.065
2 weeks	3.00	0.043	3.35	0.064
4 weeks	3.10	0.048	3.31	0.062
8 weeks	3.27	0.047	3.41	0.062
12 weeks	3.35	0.047	3.50	0.061
18 weeks	3.41	0.045	3.53	0.059
30 weeks	3.49	0.045	3.80	0.061
1 year	3.49	0.046	4.07	0.069

[a] Mean chain length of SiO_4 and AlO_4 in the C−S−H phase calculated using eq 3 and the results from deconvolution of the ^{29}Si MAS NMR spectra. The error limits are estimated to ±0.15 for all hydration times. [b] Al/Si ratio for the C−S−H calculated from eq 3 using the results from deconvolution of the ^{29}Si MAS NMR spectra. The error limits are estimated to ±0.004 for all hydration times.

From Figure 6 (and Table 1) it is also apparent that hydration of wPc in a $NaAlO_2$ solution results in a larger quantity of Al incorporated in the C−S−H phase. Improved information about the C−S−H structure can be obtained from the deconvolutions of the ^{29}Si MAS NMR spectra by calculation of the mean chain length ($\overline{\mathrm{CL}}$) of SiO_4 and AlO_4 tetrahedra and the Al/Si ratio for these chains by employing the equations[38]

$$\overline{\mathrm{CL}} = \frac{2\left[Q^1 + Q^2 + \frac{3}{2}Q^2(1\mathrm{Al})\right]}{Q^1}$$

$$\mathrm{Al/Si} = \frac{\frac{1}{2}Q^2(1\mathrm{Al})}{Q^1 + Q^2 + Q^2(1\mathrm{Al})} \qquad (3)$$

where $Q^2 = Q^2(0\mathrm{Al})$. Mean chain lengths and Al/Si ratios for the hydration times, calculated using eq 3, are listed in Table 2 for the wPc hydrated in water and in a 0.3 M $NaAlO_2$ solution. These data reveal that the average chain length increases with increasing hydration time whereas the Al/Si ratios for the C−S−H phase are independent of the hydration time at least within the estimated error limits for the calculated Al/Si ratios. Furthermore, the hydration of wPc in a $NaAlO_2$ solution results in longer chains of SiO_4 and AlO_4 tetrahedra and in a larger degree of Al for Si substitution in the tetrahedral chains of the C−S−H structure as compared to the C−S−H resulting from wPc hydration in water. The mean chain lengths after prolonged hydration (Table 2) are very similar to the value $\overline{\mathrm{CL}} = 4.05$, reported for a hydrated 1/1 mixture of wPc and a blast furnace slag.[38]

Conclusions

^{27}Al MAS NMR at very high magnetic fields can advantageously be employed in studies of hydrated Portland cements, allowing detection and quantification of a number of different Al species in these materials. From such spectra the ^{27}Al isotropic chemical shift and quadrupolar product parameter (P_{Q}) have been determined for Al incorporated in the C−S−H phase, for a pentacoordinated Al site, which most likely results from Al^{3+} substituting for Ca^{2+} ions in

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(38) Richardson, I. G. Groves, G. W. *J. Mater. Sci.* **1997**, *32*, 4793.

the interlayer structure of the C−S−H, and for an unknown aluminate hydrate phase. The latter phase has been described for the first time and tentatively assigned to a less-crystalline alumina gel or calcium aluminate hydrate, which includes $Al(OH)_6^{3-}$ or $O_xAl(OH)_{6-x}^{(3+x)-}$ octahedra in its structure. Quantification of tetrahedral Al incorporated in the C−S−H phase has demonstrated that the quantity of Al in the C−S−H increases with increasing hydration time and when the white Portland cement (wPc) is hydrated in a $NaAlO_2$ solution. The tetrahedral Al sites in the C−S−H have also been observed by ^{29}Si MAS NMR, where the incorporation of Al in the C−S−H results in a resonance at −81.0 ppm from a Q^2(1Al) site. The linear correlation between the ^{29}Si NMR intensities for the Q^2(1Al) resonance and the quantities of Al incorporated in the C−S−H phase gives improved evidence for the correct assignment of the ^{29}Si NMR resonance at $\delta_{iso}(^{29}Si) = -81.0$ ppm to a Q^2(1Al) site in the C−S−H and the assignment of the ^{27}Al NMR resonance at $\delta_{iso}(^{27}Al) = 74.6$ ppm to tetrahedrally coordinated Al incorporated in the C−S−H phase. The mean chain length of SiO_4 and AlO_4 tetrahedra in the C−S−H increases with increasing hydration time. Furthermore, it has been shown that hydration of wPc in a $NaAlO_2$ solution results in a C−S−H with longer average chain lengths as compared to the C−S−H resulting from hydration of wPc in water. On the contrary, the Al/Si ratio for the chain structure of the C−S−H is independent of the hydration time for both series of hydration with a larger Al/Si ratio for wPc hydrated in 0.3 M $NaAlO_2$ solution as compared to the wPc hydrated in pure water.

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