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Characterization of white Portland cement hydration and the C-S-H structure in the presence of sodium aluminate by ^{27}Al and ^{29}Si MAS NMR spectroscopy

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Abstract

The effects of hydrating a white Portland cement (wPc) in 0.30 and 0.50 M solutions of sodium aluminate ($NaAlO_2$) at 5 and 20 °C are investigated by ^{27}Al and ^{29}Si magic-angle spinning (MAS) NMR spectroscopy. It is demonstrated that $NaAlO_2$ accelerates the hydration of alite and belite and results in calcium-silicate-hydrate (C-S-H) phases with longer average chain lengths of SiO_4/AlO_4 tetrahedra. The C-S-H phases are investigated in detail and it is shown that the Al/Si ratio for the chains of tetrahedra is quite constant during the time studied for the hydration (6 h to 2 years) but increases for higher concentration of the $NaAlO_2$ solution. The average chain lengths of "pure" silicate and SiO_4/AlO_4 tetrahedra demonstrate that Al acts as a linker for the silicate chains, thereby producing aluminosilicate chains with longer average chain lengths. Finally, it is shown that $NaAlO_2$ reduces the quantity of ettringite and results in larger quantities of monosulfate and a calcium aluminate hydrate phase.

Keywords: Portland cement; Admixture; Acceleration; Spectroscopy; Calcium-silicate-hydrate

1. Introduction

It is a well-known fact that the hydration kinetics for the calcium silicate and calcium aluminate phases in Portland cements can be modified using a variety of additives. For example, in the cementing of gas and oil wells, where the hydration of the clinker minerals take place at elevated temperatures and pressures, it is often of interest to retard the hydration reactions to obtain workable thickening and setting times. Typical admixtures are sucrose and other sugars as well as hydroxy carboxylic acids, which retard the setting by adsorption on either the clinker minerals or the hydration products [1,2]. Moreover, the hydroxy carboxylic acids are strong calcium binding agents, which lead to a lowering of the Ca/Si ratio in the pore solution, resulting in a thicker protective coating of the cement grains [3]. Under cold conditions (e.g., cementing in arctic regions), the hydration reactions are slowed down and accelerating admixtures may be required for constructional applications where high strength must be obtained in a decent time. Alkaline and alkaline-earth salts (e.g., $CaCl_2{\cdot}2H_2O$ and $SrCl_2$) may act as accelerators because they increase the heat evolution during the early hydration [4–7]. For these salts, it has been shown that both cations and anions contribute to the accelerating effect and that the effect tends to increase with increasing charge and decreasing size of the ions [7]. An acceleration of the hydration of the calcium silicate phases can also be achieved using admixtures with very small particle sizes such as silica fume [8–11] and clay minerals [12]. The mechanism for this kind of acceleration is ascribed to the very small particles acting as nucleation agents for the formation of the calcium-silicate-hydrate (C-S-H) phase.

To accelerate the hydration of an oil well cement for its potential use in cementing under cold conditions, Lota et al. [13] have investigated the effect of sodium aluminate ($NaAlO_2$) on the hydration of a class G oil well cement. They found that hydration of this cement in 0.1–1.0 M aqueous solutions of $NaAlO_2$ accelerates the hydration in a different manner as compared with other accelerating admixtures because $NaAlO_2$ prevents the formation of a hydration shell boundary, which completely surrounds the cement grains. Furthermore, they observed that the alumi-

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nate ions in the solution react rapidly with the calcium ions released by the dissolution of the calcium silicate phases and form calcium aluminate hydrates [13].

In this work, we investigate the accelerating effect of aqueous $NaAlO_2$ solutions on the hydration of a white Portland cement (wPc) using ^{27}Al and ^{29}Si magic-angle spinning (MAS) NMR spectroscopy. These studies utilize the fact that ^{29}Si MAS NMR allows quantification of alite and belite in anhydrous as well as hydrated Portland cements [8,14,15] and thereby kinetic studies of the hydration of these calcium silicates. Furthermore, ^{27}Al MAS NMR allows investigations of the low Al content in wPc, thereby providing information about (1) the calcium aluminate phase (C_3A) [16], (2) the Al incorporated in alite and belite [17] and in the C-S-H phase [18,19] and (3) the hydration products ettringite, monosulfate and other C-A-H phases [16,19].

A second task of the present work is a quantitative study of the incorporation of Al in the C-S-H phase and the effect of $NaAlO_2$ solutions on this process. The incorporation of Al in the C-S-H phase can be detected by ^{29}Si MAS NMR by the observation of a separate resonance from SiO_4 tetrahedra bonded to an AlO_4 tetrahedron or by ^{27}Al MAS NMR where the AlO_4 tetrahedra in the C-S-H structure are observed directly [18,19]. Recent NMR studies [19] of the C-S-H phase in hydrated wPc samples support the model proposed by Richardson et al. [28] and Richardson [20] where Al is solely incorporated in the bridging sites of the C-S-H structure. These sites are illustrated in Fig. 1, which shows a schematic model of the SiO_4 and AlO_4 tetrahedra in the C-S-H phase in accordance with the model by Richardson et al. [18] and Richardson [20] and the defect tobermorite structural model proposed by Cong and Kirkpatrick [21,22]. It is generally accepted that the C-S-H phase has a tobermorite-like structure, which includes CaO_2 layers with sevenfold coordinated Ca^{2+} ions, where the oxygen are shared with Si^{4+} in chains of SiO_4 tetrahedra in a "dreierketten" arrangement on both sides of the CaO_2 layer. The chain of SiO_4 tetrahedra in the upper part of Fig. 1 illustrates an octameric unit where two bridging SiO_4 tetrahedra (Q^2_B) connect three dimers, resulting in two SiO_4 end groups (Q^1) and four paired SiO_4 sites (Q^2_P). The lower part of Fig. 1 shows the incorporation of Al in a bridging site and the corresponding two Q^2(1Al) sites (i.e., a SiO_4 chain unit connected to one SiO_4 and one AlO_4 tetrahedron). Moreover, a defect in the tobermorite structure is illustrated by a missing bridging tetrahedron in the lower part of Fig. 1, which results in two neighboring Q^1 sites.

2. Experimental

2.1. Materials and sample preparation

The wPc was a commercial cement from Aalborg Portland (Denmark) with the following metal oxide composition: 69.13 wt.% CaO, 24.70 wt.% SiO_2, 1.74 wt.% Al_2O_3, 0.31 wt.% Fe_2O_3, 0.56 wt.% MgO, 1.97 wt.% SO_3 and a blaine fineness of 424 m^2/kg. The $NaAlO_2$ additive (99.9%

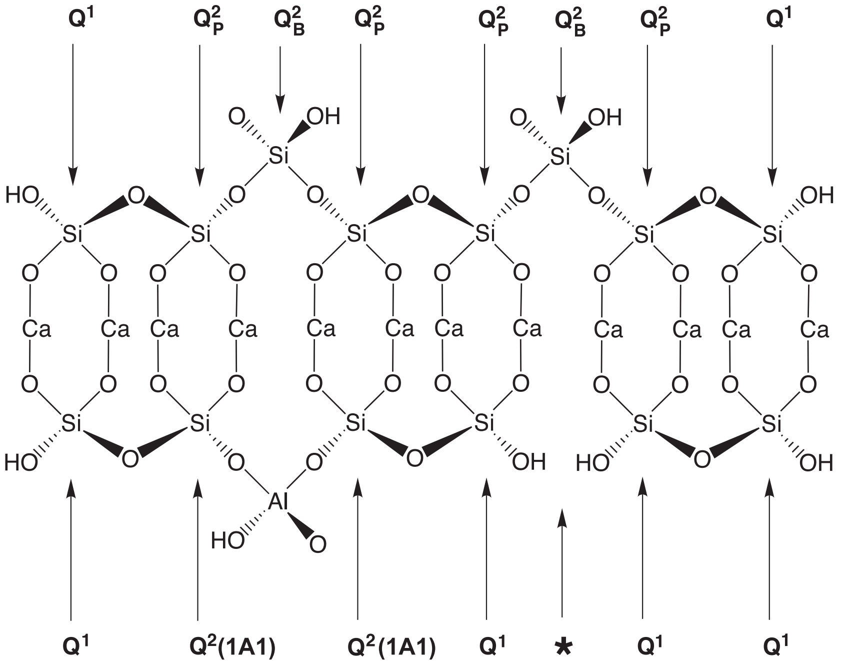

Fig. 1. Schematic representation of a single layer in the crystal structure for a 14 Å tobermorite. The upper part shows an octameric silicate chain with the characteristic features of the "dreierketten"-based models for the C-S-H phase. The lower part illustrates the incorporation of Al in a bridging site of the silicate chain and a defect site (*) in the chain structure. Thus, the lower part shows a pentameric chain and a dimer of SiO_4 tetrahedra. Interlayer Ca^{2+} ions and water molecules are not included in this representation.

purity) was obtained from Strem Chemicals (Newburyport, MA) and contained 8 wt.% water.

Five series of hydrated samples were prepared using the wPc. The first series (C1_H) was wPc hydrated in demineralized water, employing the water–cement ratio (w/c) = 0.5, and stored at 20 °C. The second (C2_3NA) and third (C3_5NA) series correspond to wPc hydrated in 0.30 and 0.50 M solutions of $NaAlO_2$ in demineralized water, respectively, and used a solution–cement ratio (s/c) = 1.0 (to prevent “flash setting” of the cement pastes) and were stored at 20 °C. The last two series were stored at 5 °C and correspond to wPc hydrated in demineralized water (w/c = 0.5, C4_H_5) and in a 0.30 M $NaAlO_2$ solution (s/c = 1.0, C5_3NA_5). The wPc and water/$NaAlO_2$ solutions were mixed by hand for about 5 min. Subsequently, the samples were placed in open plastic bags in a desiccator with a relative humidity of 100% at either 5 or 20 °C. At specific curing times, a part of the pastes was ground to a fine powder and the hydration process was stopped by stirring the samples in acetone for 15 min. After drying the powdered samples in a desiccator over silica gel at room temperature, the samples were kept in airtight containers to prevent contamination from atmospheric CO_2. The quantity of Al_2O_3 in the hydrated samples is 1.16 wt.% for the C1_H and C4_H_5 series, 1.63 wt.% for the C2_3NA and C5_3NA_5 series and 2.14 wt.% for the C3_5NA series.

2.2. NMR measurements

Solid-state ^{29}Si MAS NMR spectra were recorded at 79.4 MHz on a Varian INOVA-400 (9.4 T) spectrometer using a home-built CP/MAS probe for 7 mm o.d. zirconia (PSZ) rotors (220 μl sample volume) and a spinning speed of $\nu_R = 6.0$ kHz. The ^{29}Si MAS experiments employed a RF field strength of $\gamma B_1/2\pi = 40$ kHz, a pulse width of 3 μs, a relaxation delay of 30 s and typically 2048 scans. These conditions were found to give quantitative reliable intensities in the ^{29}Si MAS NMR spectra. The solid-state ^{27}Al MAS experiments were performed at 156.3 MHz on a Varian INOVA-600 (14.1 T) spectrometer using a home-built CP/MAS probe for 4 mm o.d. PSZ rotors and a spinning speed of $\nu_R = 13.0$ kHz. The ^{27}Al MAS NMR spectra were acquired with a pulse width of 0.5 μs for a RF field strength of $\gamma B_1/2\pi = 50$ 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, the experiments employed ^{1}H decoupling ($\gamma B_2/2\pi = 50$ kHz) during acquisition, a relaxation delay of 2 s and typically 8192 scans. An ^{27}Al MAS NMR spectrum of the probe itself with an empty spinning ($\nu_R = 13.0$ kHz) PSZ 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 quantities of the different aluminate phases were determined from the ^{27}Al MAS NMR spectra using weighed samples and the ^{27}Al MAS NMR spectrum of a weighed α-Al_2O_3 sample, which served as an external intensity reference. ^{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. Simulations and deconvolutions of the solid-state NMR spectra were performed on a SUN ULTRA 5 workstation using the STARS solid-state NMR software package, developed earlier [23], for analysis of the ^{27}Al MAS NMR spectra and the least-squares fitting routine of the Varian Vnmr software for deconvolving the ^{29}Si MAS spectra.

3. Results and discussion

3.1. Hydration kinetics for alite and belite in the presence of $NaAlO_2$ at 20 °C

^{29}Si MAS NMR spectra following the hydration of wPc at 20 °C in (1) water (C1_H), (2) 0.3 M $NaAlO_2$ solution (C2_3NA) and (3) 0.5 M $NaAlO_2$ solution (C3_5NA) for 1 day, 2 weeks and 1 year are shown in Fig. 2. In accord with earlier ^{29}Si MAS NMR studies of Portland cement hydration [8,14,15,24], the spectra after hydration for 1 day exhibit the characteristic broadened line shape, resulting from the inequivalent SiO_4 tetrahedra in the monoclinic M_{III} form of alite (chemical shift range $-66 \text{ ppm} \le \delta_{iso} \le -78$ ppm) and a narrow resonance from the unique Si site in the β-form of belite ($\delta_{iso} = -71.3$ ppm). As the hydration proceeds, the intensities of these resonances decrease and result in an increase of the intensities for the resonances from the C-S-H phase. These resonances originate from end groups of SiO_4 tetrahedra (Q^1 sites, $\delta_{iso} = -78$ ppm), middle and bridging SiO_4 tetrahedra (Q_P^2 and Q_B^2 sites, $\delta_{iso} = -85$

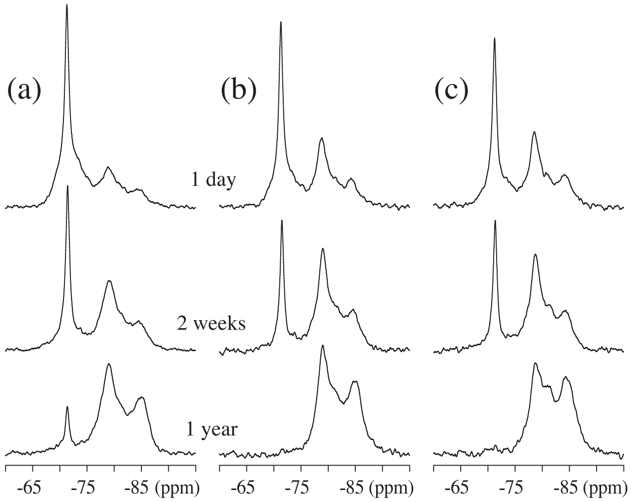

Fig. 2. ^{29}Si MAS NMR spectra (9.4 T, $\nu_R = 6.0$ kHz) of wPc hydrated at 20 °C in (a) water (C1_H), (b) a 0.3 M $NaAlO_2$ solution (C2_3NA) and (c) a 0.5 M $NaAlO_2$ solution (C3_5NA). The spectra are obtained for samples hydrated for 1 day, 2 weeks and 1 year.

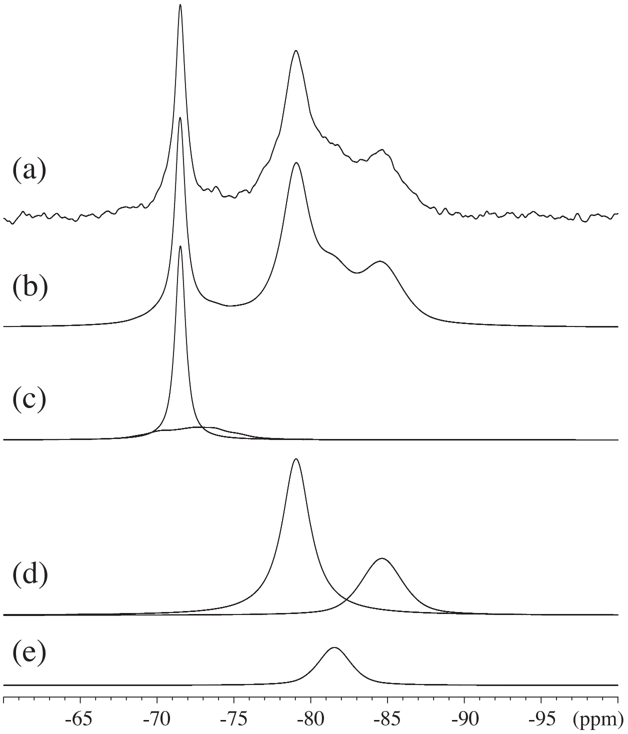

Fig. 3. (a) ^{29}Si MAS NMR spectrum (9.4 T, $\nu_R = 6.0$ kHz) of wPc hydrated in a 0.3 M $NaAlO_2$ solution at 20 °C for 2 weeks. (b) Optimized deconvolution of the experimental spectrum in (a) employing subspectra for the (c) alite and belite, (d) Q^1 and Q^2 sites of the C-S-H phase and (e) Q^2(1Al) site of the C-S-H phase.

ppm) and SiO_4 tetrahedra with an AlO_4 tetrahedron as nearest neighbor (Q^2(1Al) sites, $\delta_{iso} = -81$ ppm). The resonance at -81 ppm was originally assigned to a Q^2(1Al) site by Richardson et al. [18] in a ^{29}Si MAS NMR investigation of a hydrated synthetic slag glass. This assignment has recently been supported by a high-field ^{27}Al and ^{29}Si MAS NMR study of the C-S-H phase in hydrated wPc samples [19]. In that work, a linear correlation has been observed between the ^{29}Si NMR intensities of the Q^2(1Al) resonance and the quantity of tetrahedrally coordinated Al incorporated in the C-S-H phase determined by ^{27}Al MAS NMR. A comparison of the ^{29}Si spectra in Fig. 2 clearly reveals that hydration of wPc in the $NaAlO_2$ solutions accelerates the hydration of alite and belite and results in an increased quantity of Al incorporated in the C-S-H phase. The latter is apparent from the increased intensity observed for the Q^2(1Al) resonance for the C2_3NA and C3_5NA series as compared with the C1_H series. Following 1 year of hydration, the alite and belite phases are completely consumed for both series while a minor quantity of belite (~3.3 wt.% C_2S) is still present in the C1_H paste. Furthermore, significant differences in the intensities for the ^{29}Si resonances from the C-S-H phase are observed among the three series of wPc hydration.

Quantification of the relative intensities for the resonances in the ^{29}Si MAS spectra is achieved by computer deconvolutions using the method described earlier for anhydrous and hydrated Portland cements [14,15]. As an example, Fig. 3 illustrates the deconvolution, resulting from least-squares analysis of the ^{29}Si MAS spectrum of the C2_3NA paste hydrated for 2 weeks, and the corresponding ^{29}Si subspectra of belite, alite and the Q^1, Q^2 and Q^2(1Al) sites for the C-S-H phase. The fact that the Q^2(1Al) resonance is only partly resolved from the Q^1 peak complicates the determination of the line width for this resonance in the deconvolutions. Analysis of different samples after prolonged hydration gives a line width of 200 Hz with a Lorentzian/Gaussian line shape fraction of 0.5 for the Q^2(1Al) peak. Thus, this line width and line shape have been used as fixed values for the Q^2(1Al) resonance in the deconvolutions of all ^{29}Si MAS NMR spectra. The quantities of alite and belite, resulting from these deconvolutions, for the three series stored at 20 °C and following the hydration from 1 h to 2 years are illustrated in Fig. 4. These graphs demonstrate that the addition of $NaAlO_2$ to the cement–water mixture result in a significant acceleration of the hydration of alite. This effect increases with the concentration of $NaAlO_2$ and it is observed that the high concentration of $NaAlO_2$ (C3_5NA) leads to a significant reduction of the dormant period for the hydration of alite (Fig. 4a). After 1 year of hydration, there is virtually no alite

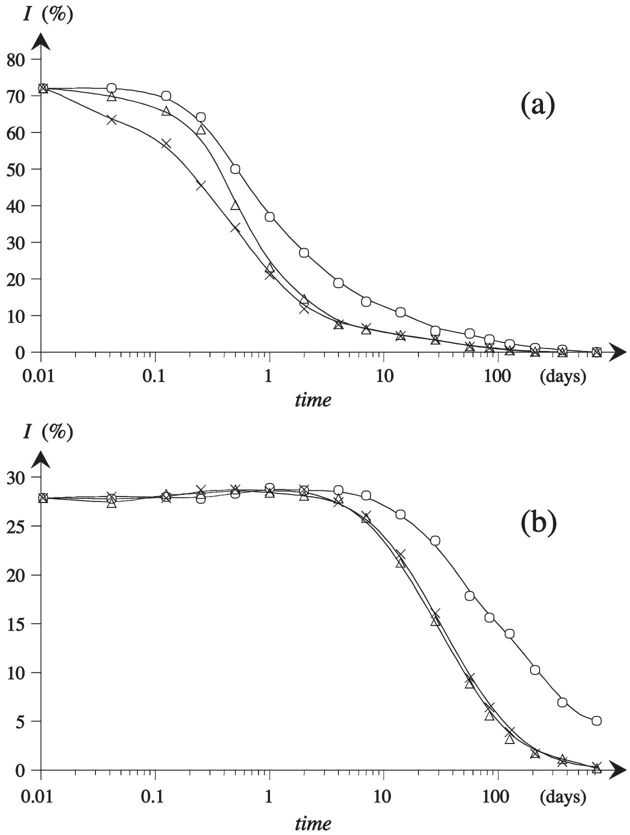

Fig. 4. Relative ^{29}Si MAS NMR intensities for (a) alite and (b) belite as a function of the hydration time for the three series hydrated at 20 °C. ○, wPc hydrated in water (C1_H); △, wPc hydrated in a 0.3 M $NaAlO_2$ solution (C2_3NA); ×, wPc hydrated in a 0.5 M $NaAlO_2$ solution (C3_5NA).

left in the three series. The graphs for belite as a function of the hydration time (Fig. 4b) show that this phase is not consumed during the first 4 days of hydration for any of the three series, in agreement with similar observations in earlier studies [8,12,15]. After 4 days of hydration, the addition of $NaAlO_2$ results in an accelerated hydration for belite and very similar rates of hydration in the subsequent period for belite in the two cement pastes containing $NaAlO_2$. This observation contrasts the kinetics for alite, which depends strongly on the concentration of $NaAlO_2$ for the first 28 days of hydration. The accelerating effect on the hydration for alite and belite agrees well with the results reported by Lota et al. [13] from thermal analysis, SEM and IR for the hydration of an oil well cement in the presence of $NaAlO_2$. These authors propose that the accelerating effect is a result of the absence of a hydration shell, which completely surrounds the anhydrous cement grains as normally observed for hydrated cements [25]. This results in a rapid and less controlled hydration as compared with cement hydration in the absence of $NaAlO_2$ [13].

3.2. Effects of lowering the temperature on the hydration for alite and belite

The effect of lowering the temperature on the hydration kinetics for alite and belite in the wPc is investigated for the C4_H_5 and C5_3NA_5 series, which have been stored at 5 °C during hydration. ^{29}Si MAS NMR spectra following hydration for 12 h, 2 days and 4 weeks are compared in Fig. 5 for these series with the corresponding series at 20 °C (i.e., C1_H and C2_3NA). As expected, these spectra indicate that a lowering of the temperature retards the hydration for alite and belite in water as well as in the 0.3 M $NaAlO_2$ solution, especially during the early hydration. From Fig. 5, it is apparent that the presence of $NaAlO_2$ also accelerates the hydration of alite and belite at 5 °C. Deconvolving the ^{29}Si MAS NMR spectra results in the quantities of alite and belite as a function of the hydration time shown in Fig. 6 for the C4_H_5 and C5_3NA_5 series. The graphs demonstrate that a lowering of the hydration temperature from 20 to 5 °C extends the dormant period for alite from about 3 to 12 h. After this period, the hydration of alite is initiated and it is observed that $NaAlO_2$ accelerates this process. After more than 2 days of hydration, the quantity of alite is smaller for the C5_3NA_5 samples (5 °C) as compared with the corresponding quantities of alite in the wPc hydrated at 20 °C. A similar effect on lowering the temperature is apparent for belite in the wPc samples hydrated in water because no hydration of this phase occurs for the first 14 days of hydration at 5 °C, whereas the hydration of belite is initiated after about 7 days for the sample stored at 20 °C. Moreover, it is observed that $NaAlO_2$ also accelerates the hydration of belite at 5 °C.

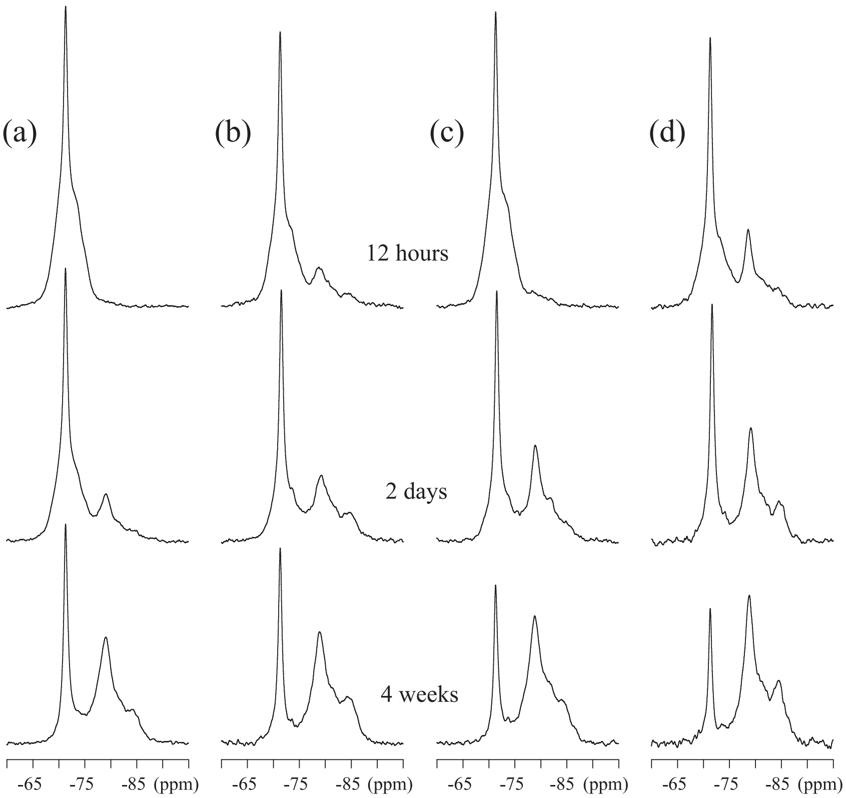

Fig. 5. ^{29}Si MAS NMR spectra (9.4 T, $\nu_R = 6.0$ kHz) of wPc hydrated in (a) water at 5 °C (C4_H_5), (b) a 0.3 M $NaAlO_2$ solution at 5 °C (C5_3NA_5), (c) water at 20 °C (C1_H) and (d) a 0.3 M $NaAlO_2$ solution at 20 °C (C2_3NA). The spectra are obtained for samples hydrated for 12 h, 2 days and 4 weeks.

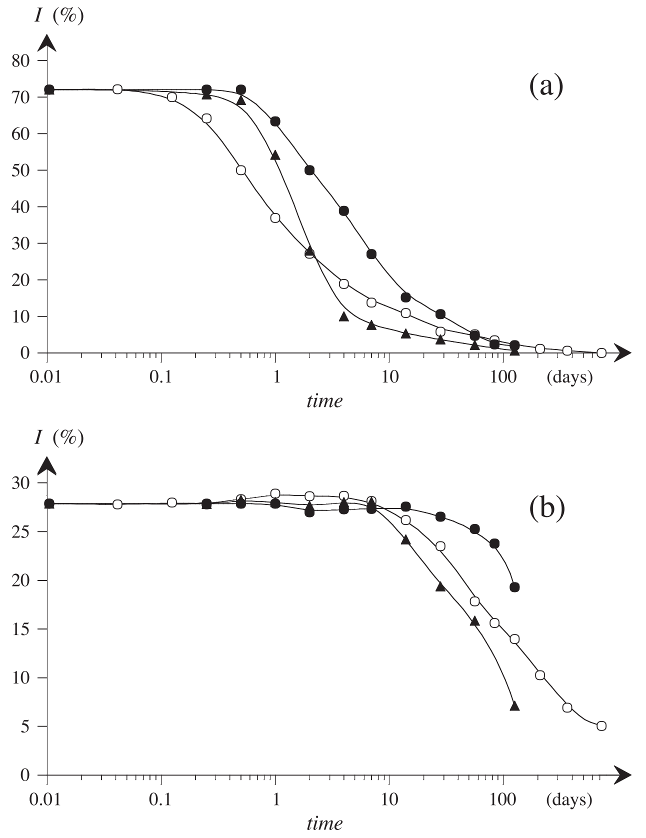

Fig. 6. Relative ^{29}Si MAS NMR intensities for (a) alite and (b) belite as a function of the hydration time for the two series hydrated at 5 °C and for the wPc hydrated in water at 20 °C (C1_H, ○). The filled circles (●) correspond to the wPc hydrated in water at 5 °C (C4_H_5); ▲, wPc hydrated in a 0.3 M $NaAlO_2$ solution at 5 °C (C5_3NA_5).

3.3. The effect of $NaAlO_2$ on the structure of the C-S-H phase

The time evolutions for the Q^1, Q^2 and $Q^2(1Al)$ species in the C-S-H phase are compared in Fig. 7 for the three series of wPc hydrated at 20 °C. Overall, these data illustrate that the increased rate of hydration for alite and belite in the C2_3NA and C3_5NA series results in increased quantities of the Q^1, Q^2 and $Q^2(1Al)$ SiO_4 species in the C-S-H phase as compared with the data for the C-S-H resulting from hydration of the C1_H series. Furthermore, this effect is most significant for the C3_5NA series in accordance with the observation of an increased acceleration of the hydration for alite and belite with increasing concentration of the $NaAlO_2$ solution (cf. Fig. 4). However, the time evolution for the Q^1 units (Fig. 7a) shows that the quantity of these species starts to decrease after ∼ 8 weeks (56 days) of hydration for the series with the highest concentration of $NaAlO_2$. This decrease is compensated by a similar increase in Q^2 units (Fig. 7b), indicating that dimers of SiO_4 tetrahedra or pentameric SiO_4 units polymerize and form pentamers and higher polymeric chains of SiO_4 tetrahedra. A decrease in the Q^1 units with increasing hydration time is in qualitative agreement with the model of formation for the C-S-H recently proposed by Grutzeck [26] who suggested that 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 structure. The time evolution for the $Q^2(1Al)$ units (Fig. 7c) reveals a continuous increase in the quantities of these species with increasing hydration time and with increasing concentration of $NaAlO_2$. The increase in the degree of Al for Si substitution in the bridging sites of the C-S-H with increas-

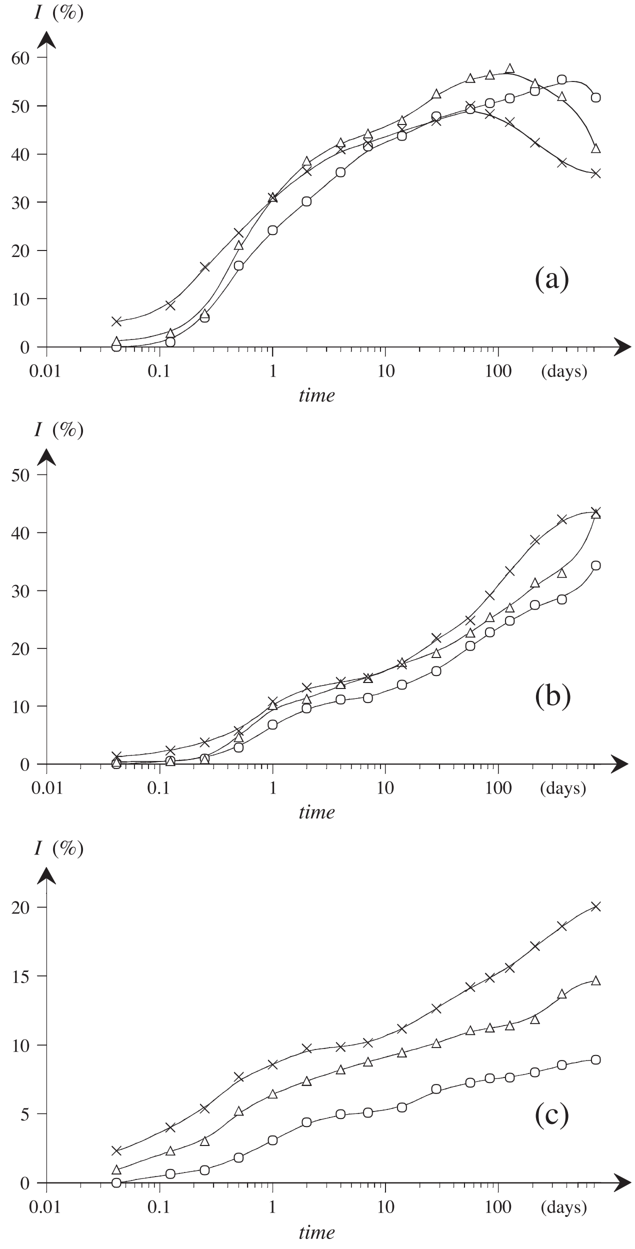

Fig. 7. Relative ^{29}Si MAS NMR intensities for (a) the Q^1 sites, (b) the Q^2 sites and (c) the $Q^2(1Al)$ sites of the C-S-H phases for the three series hydrated at 20 °C. ○, wPc hydrated in water (C1_H); △, wPc hydrated in a 0.3 M $NaAlO_2$ solution (C2_3NA); ×, wPc hydrated in a 0.5 M $NaAlO_2$ solution (C3_5NA).

ing $NaAlO_2$ concentration may partly be a result of the accelerated hydration rate of alite and belite. However, from the graph in Fig. 7c, it is clearly evident that the main effect of the $NaAlO_2$ admixture is a larger quantity of Al incorporated in the C-S-H structure.

Considering the structure of the 14 Å tobermorite as the idealized model for the connectivities of SiO_4 and AlO_4 tetrahedra in the C-S-H phase (cf. Fig. 1), the average chain length ($\overline{\mathrm{CL}}$) of SiO_4/AlO_4 tetrahedra and the Al_{IV}/Si ratio for the C-S-H (i.e., the AlO_4/SiO_4 ratio in the chains of tetrahedra) can be estimated [27] from the relative fractions of the different Q-species using the following equations:

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

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

These chain lengths and Al_{IV}/Si ratios are calculated (Table 1) using the data resulting from the deconvolutions of the ^{29}Si MAS NMR spectra for the three cement series hydrated at 20 °C for 13 different hydration times. These data reveal that the average chain length increases with increasing hydration time and that an increase in concentration of $NaAlO_2$ results in significantly longer average chain lengths. On the contrary, the Al_{IV}/Si ratios are approximately constant for the time of hydration studied for each of the three series. However, the Al_{IV}/Si ratio increases from ~ 0.045 for C1_H to 0.065 and 0.080 for C2_3NA and C3_5NA, respectively, in agreement with the increase in Al incorporated in the C-S-H observed by the relative fraction of $Q^2(1Al)$ sites (Fig. 7c). Thus, the addition of $NaAlO_2$ to the cement paste not only increases the rate of hydration for alite and belite but also results in an increase for the average SiO_4/AlO_4 chain lengths and a larger quantity of Al incorporated in the C-S-H structure. The mean Al_{IV}/Si ratios for the C1_H series (Table 1) are somewhat smaller than the mean Al/Si ratios (0.095–0.129) determined by energy dispersive X-ray spectroscopy (EDS) microanalysis for the C-S-H in mortars prepared using an ordinary Portland cement (2.2 wt.% Al_2O_3) and hydrated for 28 and 300 days [28]. However, these ratios were determined specifically for the "inner" C-S-H [28], which is formed within the original boundaries of the cement grains [4], whereas the Al_{IV}/Si ratios from ^{29}Si MAS NMR (only including tetrahedral Al sites) are mean values for the "inner" C-S-H and the "outer" C-S-H, the latter being formed in the initially water-filled spaces [4].

Further insight into the role of Al on the formation of the chains of SiO_4/AlO_4 tetrahedra may be achieved by evaluating the average chain length of "pure" SiO_4 tetrahedra ($\overline{\mathrm{CL}}_{\mathrm{Si}}$), which can be calculated from the equation

$$\overline{\mathrm{CL}}_{\mathrm{Si}} = \frac{\mathrm{Q}^1+\mathrm{Q}^2+\mathrm{Q}^2(1\mathrm{Al})}{\frac{1}{2}(\mathrm{Q}^1+\mathrm{Q}^2(1\mathrm{Al}))} \qquad (2)$$

using the results from the deconvolutions of the ^{29}Si MAS NMR spectra. The average chain lengths of SiO_4 tetrahedra are summarized in Table 1 for the C1_H, C2_3NA and C3_5NA series, while Fig. 8 compares the evolution of average chain lengths of SiO_4/AlO_4 tetrahedra ($\overline{\mathrm{CL}}$) and of silicate tetrahedra ($\overline{\mathrm{CL}}_{\mathrm{Si}}$) for these series. These plots reveal that the $\overline{\mathrm{CL}}$ chain lengths increase with increasing concentration of Al_2O_3 in the hydrated samples while the $\overline{\mathrm{CL}}_{\mathrm{Si}}$ chain lengths are quite similar for the three series with different Al_2O_3 content. These observations suggest that Al links together already existing silicate chains or $Si_2O_7^{6-}$ dimers, thereby producing aluminosilicate chains with lon-

Table 1
Average chain lengths of SiO_4/AlO_4 tetrahedra ($\overline{\mathrm{CL}}$) and SiO_4 tetrahedra ($\overline{\mathrm{CL}}_{\mathrm{Si}}$) and Al_{IV}/Si ratios for the C-S-H phase for 13 hydration times for the wPc hydrated in water and in 0.3 and 0.5 M $NaAlO_2$ solutions

Hydration time	wPc hydrated in water			wPc hydrated in 0.3 M $NaAlO_2$			wPc hydrated in 0.5 M $NaAlO_2$		
	$\overline{\mathrm{CL}}$[a]	$\overline{\mathrm{CL}}_{\mathrm{Si}}$[a]	Al/Si ratio[b]	$\overline{\mathrm{CL}}$[a]	$\overline{\mathrm{CL}}_{\mathrm{Si}}$[a]	Al/Si ratio[b]	$\overline{\mathrm{CL}}$[a]	$\overline{\mathrm{CL}}_{\mathrm{Si}}$[a]	Al/Si ratio[b]
12 h	2.67	2.31	0.043	3.19	2.35	0.084	3.46	2.37	0.104
1 day	2.95	2.50	0.045	3.28	2.55	0.068	3.53	2.55	0.085
2 days	3.08	2.56	0.050	3.16	2.49	0.065	3.53	2.57	0.082
4 days	3.03	2.54	0.048	3.23	2.55	0.064	3.42	2.56	0.076
1 week	2.91	2.49	0.044	3.27	2.56	0.065	3.43	2.57	0.075
2 weeks	3.00	2.56	0.043	3.35	2.62	0.064	3.51	2.61	0.076
4 weeks	3.10	2.59	0.048	3.31	2.61	0.062	3.74	2.73	0.078
8 weeks	3.27	2.72	0.047	3.41	2.68	0.062	3.85	2.77	0.080
12 weeks	3.35	2.78	0.047	3.50	2.75	0.061	4.13	2.92	0.080
18 weeks	3.41	2.84	0.045	3.53	2.78	0.059	4.44	3.07	0.082
30 weeks	3.49	2.90	0.045	3.80	2.94	0.061	5.05	3.30	0.087
1 year	3.49	2.89	0.046	4.07	3.00	0.069	5.68	3.49	0.094
2 years	3.85	3.13	0.047	5.17	3.55	0.074	6.09	3.56	0.101

[a] Mean chain length of AlO_4/SiO_4 and SiO_4 tetrahedra in the C-S-H phase calculated using Eqs. (1) and (2) and the results from the deconvolutions of the ^{29}Si MAS NMR spectra. The error limits are estimated to ± 0.15 for all hydration times.

[b] Al_{IV}/Si ratio for the C-S-H phase calculated from Eq. (1) using the results from the deconvolutions of the ^{29}Si MAS NMR spectra. The error limits are estimated to ± 0.004 for all hydration times.

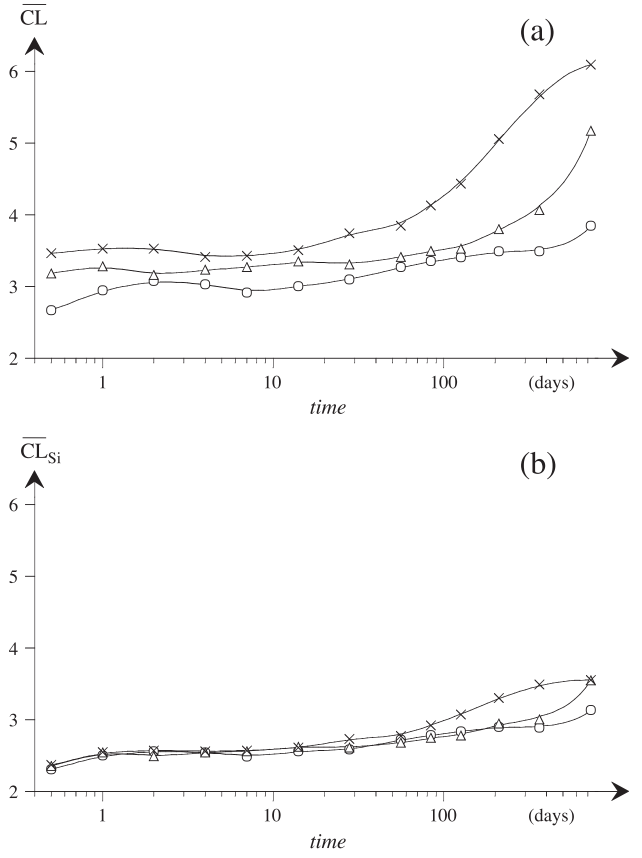

Fig. 8. Graphs illustrating the average chain lengths of (a) SiO_4/AlO_4 tetrahedra ($\overline{CL}$) and (b) SiO_4 tetrahedra ($\overline{CL}_{Si}$) of the C-S-H phase as a function of the hydration time for the three series hydrated at 20 °C. The average chain lengths are calculated from Eqs. (1) and (2) using the results from the deconvolutions of the ^{29}Si MAS NMR spectra. ○, wPc hydrated in water (C1_H); △, wPc hydrated in a 0.3 M $NaAlO_2$ solution (C2_3NA); ×, wPc hydrated in a 0.5 M $NaAlO_2$ solution (C3_5NA).

ger average chain lengths. This finding agrees well with the suggestion by Richardson et al. [18] that Al only substitutes for Si in bridging sites (Q_B^2) of the silicate chain structure (cf. Fig. 1). However, for a synthetic C-S-H phase with a high average Al_{IV}/Si ratio of 0.32 and prepared in the presence of NaOH, Faucon et al. [29] observed two distinct resonances with quite different intensities from Al in tetrahedral coordination by ^{27}Al MQMAS NMR. These resonances were assigned to Al substituting for Si in bridging (Q_B^2) and nonbridging (Q_P^2) sites with a preferential substitution into the bridging (Q_B^2) sites. For a similar C-S-H sample, prepared without addition of NaOH and with an Al_{IV}/Si ratio of 0.19, they observed only a single Al resonance from Al in tetrahedral coordination, which they assigned to Al incorporated in the bridging (Q_B^2) sites of the silicate chains. It is noted that the Al_{IV}/Si ratios of the C-S-H samples studied by Faucon et al. [29] are significantly higher than those observed for the C-S-H phases in this work, indicating that substitution of Al into the nonbridging sites (Q_P^2) is only plausible for synthetic C-S-H phases with very high Al_{IV}/Si ratios. Moreover, employing trimethylsilylation for a range of KOH-activated slag cement pastes with Al_{IV}/Si ratios in the range 0.10–0.34, Richardson [20] observed that Al substitutes for Si solely in the bridging (Q_B^2) sites.

3.4. High-field ^{27}Al MAS NMR

Recently, we have demonstrated that significant improvements in resolution of the resonances from the different Al species in Portland cements may be achieved by performing the experiments at a high magnetic field [19]. This is due to the increased chemical shift dispersion with increasing magnetic field (B_0) and the fact that the second-order quadrupole interaction scales inversely with B_0. The ^{27}Al MAS NMR spectra, following the hydration for the C1_H and C2_3NA series from 6 h to 1 year, have been recorded at a magnetic field of $B_0 = 14.1$ T and the interpretation of these spectra follows closely the analysis of similar spectra reported in our recent investigation of Portland cement hydration [19]. Illustrative ^{27}Al MAS NMR spectra following the hydration of wPc in water and in the 0.3 M $NaAlO_2$ solution are shown in Fig. 9. After 12 h of hydration, the spectral region for tetrahedrally coordinated Al (50 ppm ≤ δ_{iso} ≤ 100 ppm) displays resonances from Al incorporated in alite and belite ($\delta_{1/2,-1/2}^{cg} \approx 86$ ppm [17]) and from Al in an impure form of tricalcium aluminate ($\delta_{1/2,-1/2}^{cg} \approx 81$ ppm [16]). Moreover, for the C2_3NA sample, a center band at $\delta_{1/2,-1/2}^{cg} \approx 72$ ppm, corresponding to the parameters $\delta_{iso} = 74.6$ ppm and $P_Q = C_Q(1+\eta_Q^2/3)^{1/2} = 4.5$ MHz [19], is observed which originates from tetrahedrally coordinated Al incorporated in the C-S-H phase. A comparison of the intensities for this resonance in the spectra of Fig. 9 clearly reveals that hydration in a $NaAlO_2$ solution results in an increased quantity of Al incorporated in the C-S-H structure. Furthermore, the ^{27}Al MAS NMR spectra display a resonance with the center of gravity at 33.5 ppm ($\delta_{iso} = 39.9$ ppm and $P_Q = 5.1$ MHz [19]), which increases in intensity with increasing hydration time. The chemical shift indicates that this resonance originates from a penta-coordinated AlO_5 site. Faucon et al. [30] have observed a similar resonance and assigned this resonance to Al^{3+} substituting for Ca^{2+} ions in the interlayers of the C-S-H structure. For the wPc hydrated in water, the spectral region for octahedrally coordinated Al displays separate resonances from ettringite ($\delta_{iso} = 13.1$ ppm [16]), monosulfate ($\delta_{iso} = 11.8$ ppm [16]) and a third aluminate hydrate phase ($\delta_{iso} = 5.0$ ppm and $P_Q = 1.20$ MHz [19]). An ^{27}Al resonance in the same spectral region as observed for the third aluminate hydrate phase has also been reported by Faucon et al. [30] and by Klimesch and Ray [31] for C-S-H synthesized in the presence of Al. These authors assigned this resonance to the substitution of Al in an octahedral site of the C-S-H structure. As discussed elsewhere [19], we believe that this resonance originates from a separate phase, most likely a less crystalline alumina phase or a calcium aluminate hydrate including $Al(OH)_6^{3-}$ or $O_xAl(OH)_{6-x}^{(3+x)-}$ octahedra. The spectral region for octahedrally coordinated Al (−10

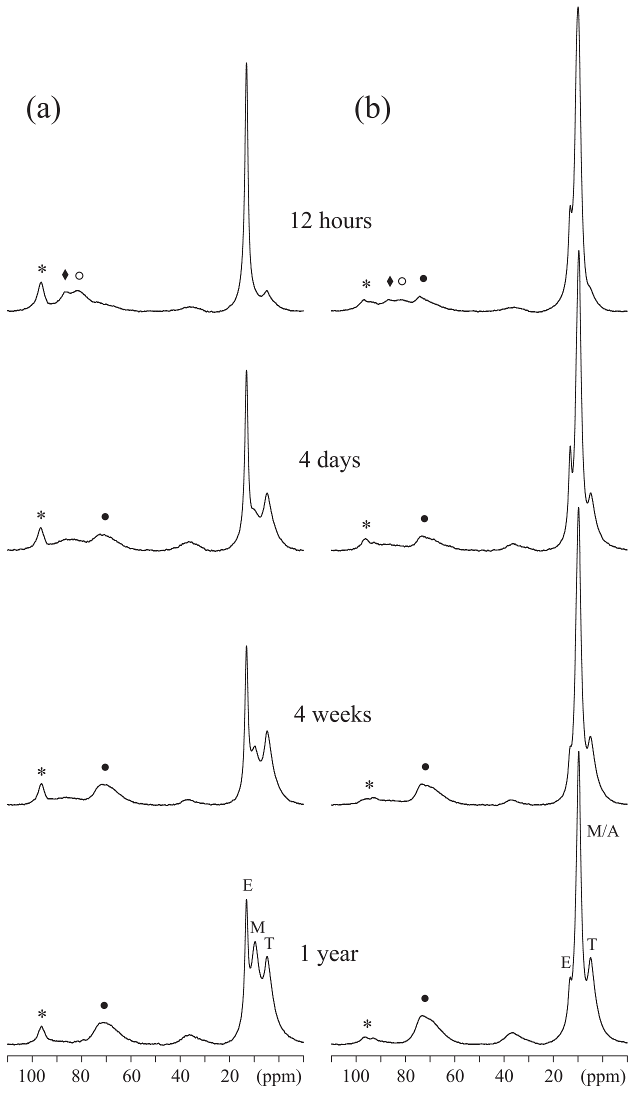

Fig. 9. ^{27}Al MAS NMR spectra (14.1 T, $\nu_R = 13.0$ kHz) obtained with high-power ^{1}H decoupling of the central transition for the wPc hydrated in (a) water at 20 °C (C1_H) and (b) a 0.3 M $NaAlO_2$ solution at 20 °C (C2_3NA). The spectra are obtained for samples hydrated for 12 h, 4 days, 4 weeks and 1 year. *, spinning side bands; ♦ and ○, center bands from Al incorporated in alite/belite and from Al in the calcium aluminate phase $Ca_3Al_2O_6$, respectively. ●, center band for tetrahedral Al incorporated in the C-S-H phase. Center bands from the hydration products ettringite, monosulfate, calcium aluminate hydrate and third aluminate hydrate phase are denoted by E, M, A and T, respectively.

ppm $\leq \delta_{iso} \leq$ 20 ppm) in the spectra of the C2_3NA samples is dominated by a center band with the center of gravity $\delta_{1/2,-1/2}^{cg} = 9.4$ ppm, which most likely arises from a calcium aluminate hydrate, formed by reaction of the $Al(OH)_4^-$ ions of the $NaAlO_2$ solution with Ca^{2+} ions released from alite, belite or $Ca(OH)_2$ during hydration. Unfortunately, this center band overlaps with the resonance from monosulfate, preventing a quantification of monosulfate and this calcium aluminate hydrate from the present spectra.

The hydration for the C1_H and C2_3NA series were examined for 14 different hydration times, ranging from 6 h to 1 year. From these spectra, the equivalent quantities of Al_2O_3 (wt.%) in the different aluminate phases have been quantified using ^{27}Al MAS NMR spectra of α-Al_2O_3 as an external intensity reference, and the results are illustrated in Figs. 10 and 11. Fig. 10a shows that the quantity of Al guest ions in alite and belite decreases with increasing hydration time and thereby that these Al^{3+} ions are released when the anhydrous calcium silicates are consumed. Furthermore, it is apparent that this release of Al^{3+} ions proceeds faster for the C2_3NA series in agreement with the results from ^{29}Si

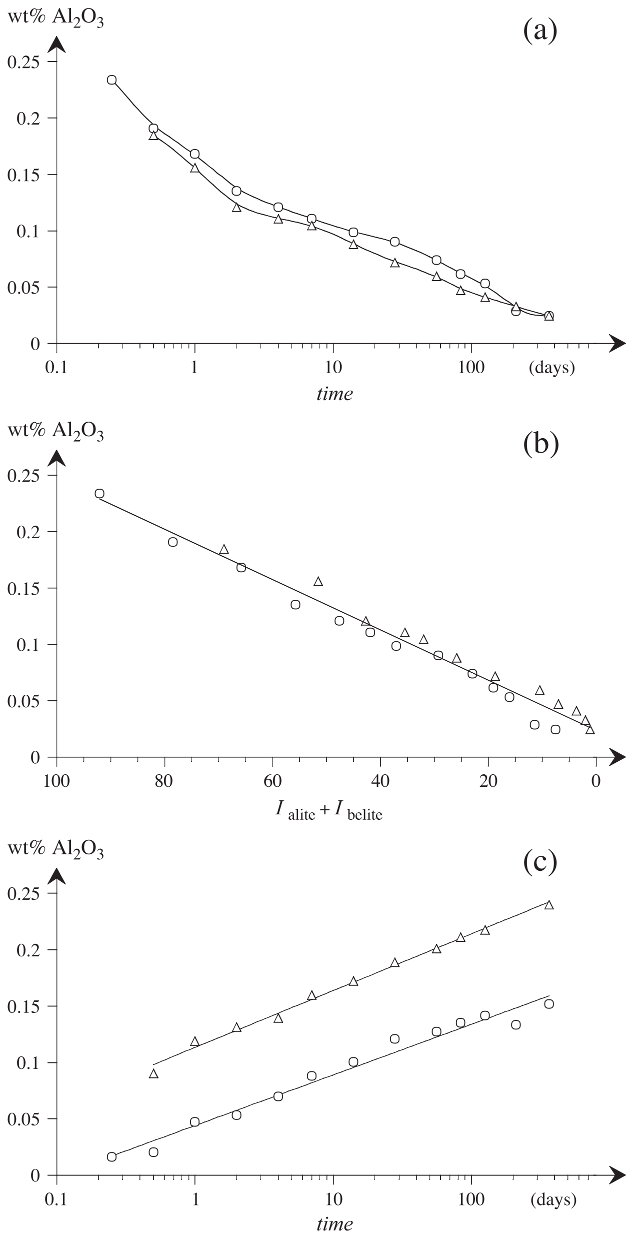

Fig. 10. Equivalent quantities of Al_2O_3 (wt.%) in the wPc samples hydrated at 20 °C in water (C1_H, ○) and a 0.3 M $NaAlO_2$ solution (C2_3NA, △) for the (a) Al guest ions in alite and belite and (c) tetrahedral Al incorporated in the C-S-H phase as a function of the hydration time. (b) Equivalent quantities of Al_2O_3 present as guest ions in alite and belite as a function of the sum of ^{29}Si intensities for alite and belite obtained from the corresponding ^{29}Si MAS NMR spectra. The quantities of Al_2O_3 are determined from the ^{27}Al MAS NMR spectra recorded at 14.1 T.

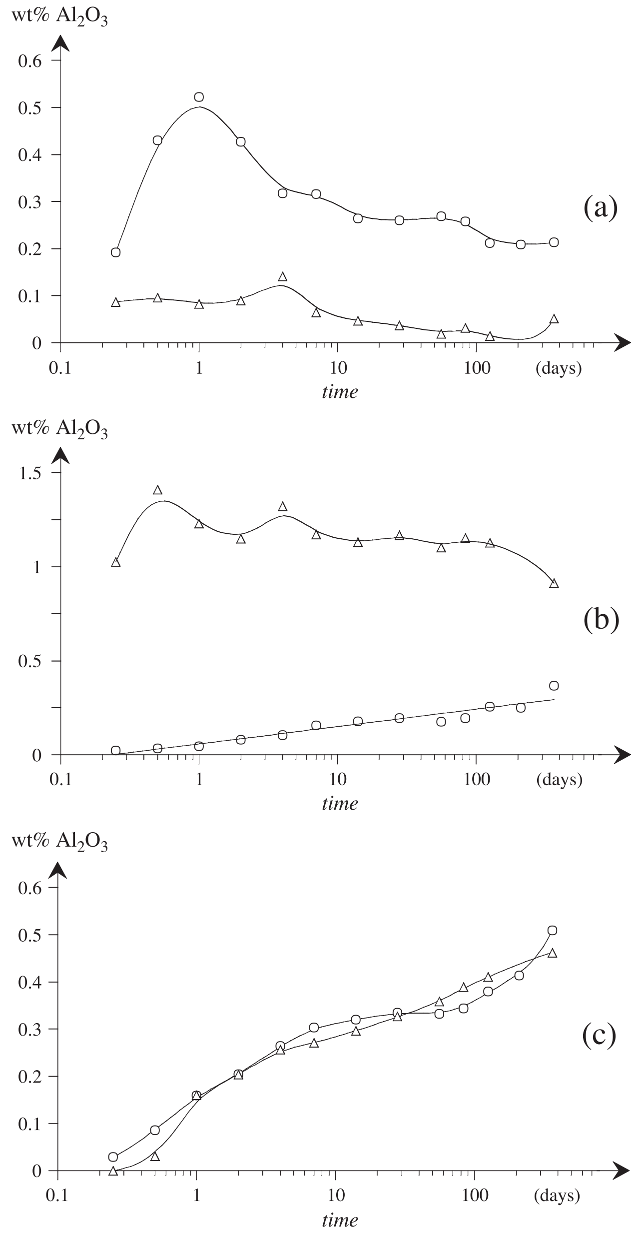

Fig. 11. Graphs illustrating the equivalent quantities of Al_2O_3 (wt.%) in the aluminate hydration products as a function of the hydration time for (a) ettringite, (b) monosulfate (○) and the sum of monosulfate and the calcium aluminate hydrate (△) and (c) the third aluminate hydrate phase. ○, wPc hydrated in water at 20 °C (C1_H); △, wPc hydrated in a 0.3 M $NaAlO_2$ solution at 20 °C (C2_3NA). The quantities of Al_2O_3 are determined from the ^{27}Al MAS NMR spectra recorded at 14.1 T.

MAS NMR where it was observed that $NaAlO_2$ accelerates the hydration for alite and belite. Thus, the quantities of Al guest ions in alite/belite determined from ^{27}Al MAS NMR correlate well with the results from ^{29}Si MAS NMR (Fig. 4). This is further supported by the plot in Fig. 10b, which shows a straight line when the quantities of Al guest ions in alite and belite at different hydration times for the two series are plotted as a function of the sum of ^{29}Si intensities for alite and belite, obtained from the corresponding ^{29}Si MAS NMR spectra. This observation of a straight line strongly supports the assignment of the ^{27}Al resonance at 86 ppm in the ^{27}Al MAS NMR spectra (Fig. 9) to Al guest ions in alite and belite. A quantitative analysis of the resonance from Al^{3+} ions incorporated in the C-S-H phase (Fig. 10c) results in a nearly logarithmic increase in the number of these sites with increasing hydration time for both series. This is in accord with the similar increase in intensity for the Q^2(1Al) resonance observed in the ^{29}Si MAS NMR spectra (cf. Fig. 7c). Furthermore, the graphs in Fig. 10c clearly reveal that hydration of wPc in a $NaAlO_2$ solution results in an increased quantity of Al sites in the chains of tetrahedra in the C-S-H structure and thereby supports the results obtained from ^{29}Si MAS NMR.

The quantities of Al_2O_3 in the aluminate hydration products are shown as a function of the hydration time in Fig. 11. For the wPc hydrated in water (C1_H), the largest quantity of ettringite (Fig. 11a) is observed after hydration for 1 day, where the equivalent amount of Al_2O_3 (0.52 wt.%) corresponds to 6.3 wt.% ettringite, assuming a stoichiometric composition for ettringite ($Ca_6[Al(OH)_6]_2(SO_4)_3{\cdot}26H_2O$). The quantity of ettringite decreases from 1 to 14 days of hydration for the C1_H series, and after this period, its remains almost invariant for the hydration period from 14 days to 1 year. On the contrary, the quantities of monosulfate (Fig. 11b) and the third aluminate hydrate phase (Fig. 11c) increase slowly but continuously over the studied period of hydration for the C1_H series. This indicates that ettringite is transformed into monosulfate as well as the third aluminate hydrate phase during the early hydration and that the Al^{3+} ions, released during prolonged hydration of alite and belite, also contribute to the formation of these two phases. The time evolution for the formation of ettringite is quite different for the C2_3NA series because the quantity of ettringite in these samples is significantly smaller than those observed for the C1_H series. Once ettringite is formed during the early hydration, the quantity of this phase decreases only slowly from about 1 day to 1 year. The hydration of wPc in a $NaAlO_2$ solution increases the ratio of $Al(OH)_4^-/SO_4^{2-}$ ions in the pore solution. Thus, the lower quantity of ettringite, observed for the C2_3NA series, indicates that the increase in this ratio favors the formation of monosulfate, as expected from the composition of ettringite ($Ca_6[Al(OH)_6]_2(SO_4)_3{\cdot}26H_2O$) and monosulfate ($Ca_4[Al(OH)_6]_2SO_4{\cdot}6H_2O$). Unfortunately, the resonances from monosulfate and the calcium aluminate hydrate, which results from the reaction of the $Al(OH)_4^-$ ions of $NaAlO_2$ with Ca^{2+} ions and water, cannot be distinguished in the ^{27}Al MAS NMR spectra. The total quantity of Al_2O_3 in these two phases (Fig. 11b) indicates that a significant amount of the calcium aluminate hydrate is formed during the initial hydration for the C2_3NA series, when the total quantities of SO_4^{2-} ions and of Al_2O_3 (1.63 wt.%) in the wPc-0.3 M $NaAlO_2$ system are considered. Although the quantity of Al_2O_3 in monosulfate and the calcium aluminate hydrate phase decreases slowly after the initial hydration period, this decrease does not result in an increased quantity of the third aluminate hydrate phase (Fig.

10c) because the time evolution for this phase is very similar for the C1_H and C2_3NA series. Thus, the formation of the third aluminate hydrate phase appears to be independent of an increased amount of $Al(OH)_4^-$ ions present in the pore solution during hydration. Further studies aimed at elucidating the structure and composition of the third aluminate hydrate phase are in progress.

4. Conclusions

^{29}Si and ^{27}Al MAS NMR spectroscopies are valuable tools in structural and kinetic studies of Portland cement hydration. The ^{29}Si MAS NMR investigation of wPc hydrated in water and in $NaAlO_2$ solutions at 5 and 20 °C have shown that $NaAlO_2$ accelerates the hydration of alite and belite at both temperatures, indicating that $NaAlO_2$ can be used as an accelerator in cementing under cold conditions. The relative fraction of Al incorporated in the C-S-H phase (i.e., the Al_{IV}/Si ratio) and the average chain length of SiO_4/AlO_4 tetrahedra of the C-S-H have been found to increase with increasing concentration of the $NaAlO_2$ solution. However, the Al_{IV}/Si ratio for the chain structure of the C-S-H is almost independent of the hydration time for wPc hydrated in water and in the $NaAlO_2$ solutions. Combining this result with an evaluation of the average length of "pure" silicate tetrahedra of the C-S-H phases has shown that Al primarily links together already existing chains or dimers of SiO_4 tetrahedra, thereby forming a chain structure that has a longer average chain length of SiO_4/AlO_4 tetrahedra. Overall, the results from ^{27}Al and ^{29}Si MAS NMR in this work on the C-S-H structure agree with a defect tobermorite structural model for the C-S-H phase where tetrahedrally coordinated Al only occupies the bridging sites in the "dreierketten" silicate chain structure. The high-field ^{27}Al MAS NMR spectra have allowed quantification of the (1) Al guest ions in alite and belite, (2) tetrahedral Al incorporated in the C-S-H phase and (3) Al in the hydration products ettringite, monosulfate and a third aluminate hydrate phase. The latter phase has been tentatively assigned to a less crystalline alumina phase or a calcium aluminate hydrate including $Al(OH)_6^{3-}$ or $O_xAl(OH)_{6-x}^{(3+x)-}$ octahedra in its structure. The ^{27}Al MAS NMR spectra of the wPc-$NaAlO_2$ mixtures have shown that $NaAlO_2$ reduces the quantity of ettringite formed during hydration and gives larger quantities of monosulfate and a calcium aluminate hydrate. The latter phase is formed during the early hydration by the reaction of the $Al(OH)_4^-$ ions from the $NaAlO_2$ solution with water and Ca^{2+} ions released during the dissolution of alite and belite.

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