Cement & Concrete Composites 25 (2003) 823–829

Cement & Concrete Composites

www.elsevier.com/locate/cemconcomp

^{29}Si cross-polarization magic-angle spinning NMR spectroscopy—an efficient tool for quantification of thaumasite in cement-based materials

Jørgen Skibsted [a,*], Søren Rasmussen [b], Duncan Herfort [b], Hans J. Jakobsen [a]

[a] *Instrument Centre for Solid-State NMR Spectroscopy, Department of Chemistry, University of Aarhus, Langelandsgade 140, DK-8000 Århus C, Denmark*

[b] *Aalborg Portland A/S, P.O. Box 165, DK-9100 Aalborg, Denmark*

Abstract

^{29}Si{^{1}H} cross-polarization (CP) magic-angle spinning (MAS) NMR spectroscopy is a powerful and reliable tool for the quantification of thaumasite in cement-based materials. The most efficient method for quantifying thaumasite from ^{29}Si{^{1}H} CP/MAS NMR spectra is described and it is shown that the method allows detection of thaumasite contents below approximately 10 wt.% with a relative precision of 15% and contents above 10 wt.% with a relative precision of 10%. The applicability of ^{29}Si{^{1}H} CP/MAS NMR for quantification of thaumasite is demonstrated for different Portland cement pastes and shows that thaumasite contents as low as 0.2–0.5 wt.% can be detected in cementitious systems with low concentrations of paramagnetic impurities. For a Portland cement containing various amounts of limestone dust and stored at 5 °C in a $MgSO_4$ solution, large quantities of thaumasite have been detected. Furthermore, the quantity of thaumasite is found to be less sensitive to the amount of added limestone dust. For samples of a Portland cement with a fixed content of limestone dust but different quantities of added gypsum, the increased contents of gypsum are observed to result in larger quantities of thaumasite after prolonged hydration.

Keywords: Thaumasite quantification; ^{29}Si{^{1}H} CP/MAS NMR spectroscopy; Limestone-filler cement; Cement-based materials

1. Introduction

The reaction of sulfate ions with cement minerals in concrete is a well-known problem which has a major impact on the lifetime of concrete structures. The sulfate ions react with the calcium aluminate phases and form gypsum and ettringite, which may result in cracking of the concrete caused by the increase in volume associated with this reaction. For sulfate-resisting Portland cements the low content of calcium aluminate phases limits the risk for significant expansion. Another form of sulfate attack is the reaction of sulfate and carbonate ions with the calcium–silicate–hydrate (C–S–H) phase to form thaumasite. Because thaumasite is formed at the expense of the main binding phase in hardened cements, the presence of a continuous supply of sulfate and carbonate ions may result in the formation of large quantities of thaumasite which can cause severe softening or cracking of the concrete [1].

The crystal structure and morphology of ettringite ($Ca_6[Al(OH)_6]_2(SO_4)_3 \cdot 26H_2O$) [2] and thaumasite ($Ca_6[Si(OH)_6]_2(CO_3)_2(SO_4)_2 \cdot 24H_2O$) [3] are strongly related since ettringite consists of columns with the composition $[Ca_3Al(OH)_6 \cdot 12H_2O]^{3+}$ and with sulfate ions between the columns while thaumasite is built up of $[Ca_3Si(OH)_6 \cdot 12H_2O]^{4+}$ units with both sulfate and carbonate ions in between the columns. Although powder X-ray diffraction is the most commonly used method for detection of thaumasite [4], this phase is very difficult to distinguish and quantify from ettringite because of the close similarity in unit cells and low-angle, high-intensity reflections for ettringite and thaumasite. An unambiguous detection of thaumasite is also difficult to obtain by thermal analysis and infrared spectroscopy [5], again as a result of the strong similarities between ettringite and thaumasite. Raman spectroscopy has earlier been used in studies of pure calcium silicates and white Portland cements [6]. Most recently, the Raman

---

[*] Corresponding author. Tel.: +45-8942-3900; fax: +45-8619-6199. *E-mail address:* jskib@chem.au.dk (J. Skibsted).

doi:10.1016/S0958-9465(03)00108-2

microprobe technique has shown its potential for a rapid identification of veins of thaumasite in specimens of field concrete [7]. Furthermore, low-vacuum scanning electron microscopy (SEM) may be used to identify thaumasite and distinguish between thaumasite and ettringite in field concretes [8]. However, this method requires several steps of preparation of the samples before the actual investigation can be performed.

Solid-state nuclear magnetic resonance (NMR) spectroscopy is a powerful research tool for characterization and structural analysis of cement pastes and cement-based materials [9]. Especially ^{29}Si magic-angle spinning (MAS) NMR has become a popular technique for cement chemists since the ^{29}Si isotropic chemical shift reveals the degree of condensation of SiO_4 tetrahedra in silicate minerals [10] including calcium silicates and the amorphous C–S–H phase produced by Portland cement hydration. The vast majority of silicate minerals contain silicon in tetrahedral coordination while only a few compounds are known to have silicon in an octahedral environment. Thaumasite belongs to the latter type of silicates and it is the only mineral in cementitious systems that contains Si in octahedral coordination. This fact can be utilized to detect thaumasite by ^{29}Si MAS NMR spectroscopy [11], since tetrahedrally coordinated SiO_4 units have a chemical shift range from about −65 to −120 ppm whereas ^{29}Si in SiO_6 groups resonates from −170 to −220 ppm. Furthermore, the coordination of Si with six OH^- ions in thaumasite can be utilized in the ^{29}Si{^{1}H} cross-polarization (CP) MAS NMR experiment where magnetization is transferred from ^{1}H to ^{29}Si. This method results in a significant gain in sensitivity with a simultaneous reduction in instrument time by up to a factor of 1000 as compared to standard ^{29}Si MAS NMR [11]. In this work we focus on the aspects of ^{29}Si{^{1}H} CP/MAS NMR spectroscopy for detection and quantification of small quantities of thaumasite in cement-based materials and demonstrate the applicability of the method for a series of hydrated Portland cements containing limestone dust (i.e., a raw feed precipitator dust—RFPD) as additive and stored in a 0.25 M solution of $MgSO_4$. Furthermore, we investigate the formation of thaumasite during hydration at 5 °C of a Portland cement–RFPD blend containing up to 10 wt.% SO_3 in the form of gypsum as an additive.

2. Experimental

2.1. NMR spectroscopy

The solid-state ^{29}Si{^{1}H} CP/MAS and MAS NMR experiments were performed on a Varian INOVA-400 (9.4 T) spectrometer using a home-built CP/MAS probe for 7 mm o.d. rotors (225 μl sample volume). Because the spinning speed (ν_R) affects the ^{29}Si{^{1}H} CP efficiency for weakly dipolar coupled spins (e.g. for Si–OH groups), all ^{29}Si{^{1}H} CP/MAS experiments were performed with a moderate spinning speed ($\nu_R = 3.0$ kHz). The Hartmann–Hahn match ($\gamma_{Si}B_{1Si}/2\pi = \gamma_H B_{2H}/2\pi$, where B_{1Si} and B_{2H} are the radio frequency (RF) field strengths and γ_{Si} and γ_H the gyromagnetic ratios for ^{29}Si and ^{1}H, respectively) was determined using a mineral sample of thaumasite (Sulitjelma, Sweden) while the initial 90° ^{1}H pulse and the ^{1}H decoupling RF field strength during acquisition of the free induction decay (FID) were calibrated using a sample of sodium 3-(trimethylsilyl)-propane-1-sulfonate. The resulting parameters were $\gamma_{Si}B_{1Si}/2\pi = \gamma_H B_{2H}/2\pi = 32$ kHz for the Hartmann-Hahn match during the CP contact period and $\gamma_H B_{2H}/2\pi = 40$ kHz for the 90° ^{1}H pulse and the ^{1}H decoupling RF field strength. All CP/MAS NMR experiments were recorded using a repetition delay (D_1) at least five times longer than the ^{1}H spin–lattice relaxation time to ensure full ^{1}H spin–lattice relaxation and thereby quantitative reliability of the ^{29}Si resonances for the ^{29}Si{^{1}H} CP/MAS spectra. For cement mixtures, which generally contain minor quantities of paramagnetic ions (e.g. Fe^{3+}), this is achieved by $D_1 = 8$ s whereas $D_1 = 25$ s is required for the mineral sample of thaumasite. The quantities of thaumasite in the cement mixtures were determined from the intensities for thaumasite observed in CP/MAS NMR spectra of weighed samples using the mineral sample of thaumasite as an external intensity reference and the method described in more detail in Ref. [11]. The ^{29}Si MAS NMR spectra and ^{29}Si chemical shifts are referenced to an external sample of tetramethylsilane (TMS).

2.2. Cement mixtures

Three cement mixtures were prepared from a typical ASTM type II Portland cement and 5, 15, and 30 wt.% RFPD as additives. The RFPD mainly consists of $CaCO_3$ (about 85 wt.%) and has a surface area of approximately 1300 m^2/kg. The Portland cement has a surface area of 390 m^2/kg and a 45 μm residue of 3%. Pastes of the mixtures were prepared using a water/powder ratio of 0.7 and cast in small plastic moulds, 6 mm in diameter and 35 mm in length. The pastes were hydrated at 40 °C for five days followed by a further hydration for 28 days at 20 °C before being demoulded. The paste cylinders were subsequently immersed in 12 ml of a 0.25 M $MgSO_4$ solution where they were stored for periods of time up to nine months at 5 °C.

A second series of cement pastes was prepared from a mixture of 75 wt.% of finely ground ASTM type V Portland cement (surface area of about 600 m^2/kg) and 25 wt.% RFPD (composition as above). Five mixtures including 0, 2, 4, 6, and 10 wt.% SO_3 in the form of gypsum were prepared from this cement–RFPD blend. The mixtures had a water/cement ratio of 0.5 and were cast in 50 ml plastic moulds. After one day the pastes were demoulded and transferred to 100 ml containers. 10 ml of water was added and the containers were sealed and stored at 5 °C for various periods of time up to four years.

Before the NMR studies of the individual samples, a sub-sample of the hardened cement paste was ground and dried at room temperature in air for about 3 h. The powder was subsequently packed into the NMR rotor and the ^{29}Si{^{1}H} CP/MAS NMR experiments were performed immediately after packing of the rotor.

3. Results and discussion

3.1. Quantification of thaumasite by ^{29}Si{^{1}H} CP/MAS NMR

^{29}Si{^{1}H} CP/MAS NMR spectra of mineral samples of thaumasite show a single resonance at $\delta_{\mathrm{iso}} = -179.4 \pm 0.1$ ppm [11] in agreement with the fact that Si is octahedrally coordinated to six oxygen atoms in the unit cell of thaumasite [3]. In ^{29}Si MAS NMR of cement-based materials this forms the basis for an unambiguous detection of thaumasite as illustrated in Fig. 1 for the hydrated Portland cement including 15 wt.% RFPD (i.e., sample RFPD-15) and stored for nine months in a 0.25 M $MgSO_4$ solution at 5 °C. A comparison of the standard ^{29}Si MAS and ^{29}Si{^{1}H} CP/MAS NMR spectra of this sample, obtained using the RF pulse schemes shown in the insets of Fig. 1, clearly illustrates the advantages of ^{29}Si{^{1}H} CP/MAS NMR in the detection of thaumasite. The gain in sensitivity for thaumasite in the ^{29}Si{^{1}H} CP/MAS NMR experiment is caused by the transfer of magnetization from ^{1}H to ^{29}Si during the CP contact time (τ_{CP}), which ideally gives an enhancement in intensity by the factor $G_{\mathrm{CP}} = \gamma_{\mathrm{H}}/\gamma_{\mathrm{Si}} = 5.0$ [12], and the fact that the ^{1}H spin–lattice relaxation time (T_1^{H}) is up to two orders of magnitude shorter than the ^{29}Si spin–lattice relaxation time (T_1^{Si}) for thaumasite [11]. Furthermore, the ^{29}Si{^{1}H} CP/MAS NMR experiment acts as a Si–H filter, since only Si species that are dipolar coupled to ^{1}H are detected by this RF pulse scheme. This is apparent from the spectra in Fig. 1 where resonances from the Q^0 units of SiO_4 tetrahedra in the anhydrous calcium silicates and the Q^1 and Q^2 units in the C–S–H hydration products are only observed in the ^{29}Si MAS spectrum (Fig. 1a). Obviously, the Q^1 and Q^2 units of the C–S–H phase can also be observed by ^{29}Si{^{1}H} CP/MAS NMR, however, this requires that longer CP contact times ($\tau_{\mathrm{CP}} \approx 5$ ms) are used than the value employed here ($\tau_{\mathrm{CP}} = 0.6$ ms) for thaumasite detection.

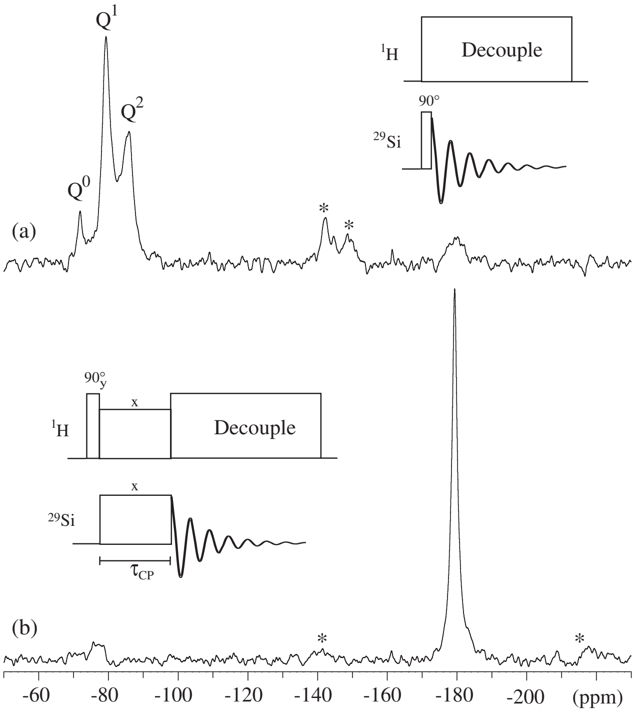

Fig. 1. (a) ^{29}Si MAS and (b) ^{29}Si{^{1}H} CP/MAS NMR spectra of the sample of Portland cement including 15 wt.% RFPD and stored for nine months in a 0.25 M $MgSO_4$ solution. The ^{29}Si MAS spectrum was recorded using the spinning speed $\nu_{\mathrm{R}} = 5.0$ kHz, a 15 s repetition delay, and 5120 scans while the ^{29}Si{^{1}H} CP/MAS NMR spectrum employed $\nu_{\mathrm{R}} = 3.0$ kHz, a 8 s repetition delay, and a CP contact time of $\tau_{\mathrm{CP}} = 0.8$ ms. The spectra are shown on identical vertical scales and asterisks indicate spinning sidebands. The insets illustrate the RF pulse sequences used for the two experiments.

The ^{29}Si{^{1}H} CP efficiency depends strongly on the ^{1}H–^{29}Si dipolar couplings and is also affected by paramagnetic impurities in the sample. Thus, a quantification of thaumasite in different samples from ^{29}Si{^{1}H} CP/MAS NMR spectra requires pre-knowledge of the ^{1}H and ^{29}Si rotating-frame relaxation times ($T_{1\rho}^{\mathrm{H}}$ and $T_{1\rho}^{\mathrm{Si}}$) and the ^{1}H–^{29}Si CP time (T_{SiH}). The build-up of ^{29}Si magnetization ($M_x(t)$) as a function of the contact time ($t = \tau_{\mathrm{CP}}$) in the ^{29}Si{^{1}H} CP NMR experiment is given by

$$M_x(t) = \frac{M^{\mathrm{H}}(0)}{\lambda} \exp(-t/T_{1\rho}^{\mathrm{H}})[1 - \exp(-\lambda t/T_{\mathrm{SiH}})], \qquad (1)$$

where $\lambda = 1 + (T_{\mathrm{SiH}}/T_{1\rho}^{\mathrm{Si}}) - (T_{\mathrm{SiH}}/T_{1\rho}^{\mathrm{H}})$ and $M^{\mathrm{H}}(0)$ is the ^{1}H magnetization after the $90°_y$ ^{1}H pulse. The derivation of Eq. (1) employs the inverse spin–temperature approach [13] and assumes the ^{29}Si spins being diluted relative to the ^{1}H spins, a condition fulfilled for samples with ^{29}Si in natural abundance. The variation in signal intensity as a function of CP contact time is shown in Fig. 2 for thaumasite in two of the studied samples. The build-up of signal intensity for short CP times depends mainly on the ^{1}H–^{29}Si CP time (T_{SiH}), whereas the exponential-like decrease in intensity for longer CP times is governed by the rotating-frame relaxation times $T_{1\rho}^{\mathrm{H}}$ and $T_{1\rho}^{\mathrm{Si}}$. The latter two time constants cannot be independently determined from a fit of Eq. (1) to the variation of $M_x(t)$ as a function of τ_{CP} in the standard CP

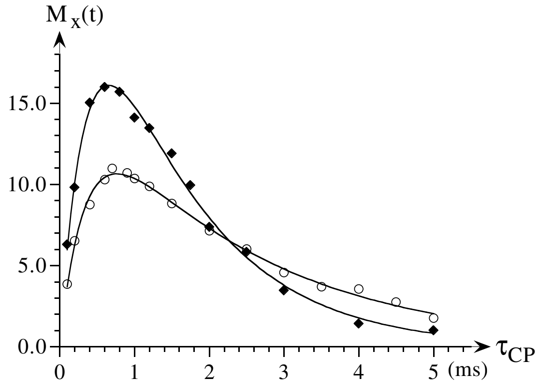

Fig. 2. ^{29}Si intensities ($M_x(t)$) observed in $^{29}Si\{^1H\}$ CP/MAS NMR spectra as a function of the CP contact time (τ_{CP}) for determination of the time constants T_{SiH} and $T_{1\rho}^H$ for thaumasite. Open circles correspond to the type V Portland cement–RFPD blend with 10 wt.% SO_3 added in the form of gypsum and hydrated for four years (i.e., Table 2 last row). Filled diamonds represent data for the type II Portland cement–15 wt.% RFPD blend stored for nine months in a 0.25 M $MgSO_4$ solution (i.e. RFPD-15, Table 1). The curves show the result from a three-parameter least-squares fit of Eq. (2) to the observed intensities, resulting in the T_{SiH} and $T_{1\rho}^H$ time constants listed in Tables 1 and 2 for the two samples.

NMR experiment, but require that separate experiments for monitoring the ^1H and ^{29}Si rotating frame relaxation are performed [11,13]. However, the determination of $T_{1\rho}^H$ and $T_{1\rho}^{Si}$ for thaumasite in several samples of different origin [11] reveals that $T_{1\rho}^{Si}$ is about an order of magnitude longer than $T_{1\rho}^H$, a feature generally observed for $O_{4-x}Si(OH)_x$ units in silicates. This can be utilized to simplify Eq. (1) assuming $T_{1\rho}^{Si} \gg T_{1\rho}^H$ which results in the equation

$$M_x(t) = \frac{M^H(0)}{1 - T_{SiH}/T_{1\rho}^H} \exp(-t/T_{1\rho}^H) \times \left[1 - \exp\left(\left(\frac{1}{T_{1\rho}^H} - \frac{1}{T_{SiH}}\right)t\right)\right]. \tag{2}$$

The time constants T_{SiH} and $T_{1\rho}^H$ can be determined from a three-parameter least-squares fit of Eq. (2) to the signal intensities observed in variable-contact time CP/MAS NMR experiments. This is illustrated in Fig. 2 for thaumasite in two of the studied Portland cement–RFPD samples. Using this approach, T_{SiH} and $T_{1\rho}^H$ have been determined for three of the Portland cement samples containing RFPD as additive (Table 1). These data reveal a significant variation in $T_{1\rho}^H$ when it is taken into account that the compositions of these samples are rather similar.

A determination of T_{SiH} and $T_{1\rho}^H$ is rather time consuming, especially for samples with very low contents of thaumasite. Thus, the quantification of thaumasite in such samples relies on typical values of $T_{SiH}, T_{1\rho}^H$, and $T_{1\rho}^{Si}$ determined from CP/MAS NMR spectra of thaumasite in various samples of Portland cement-based materials. For these materials the time constants exhibit values in the ranges $0.35\ \text{ms} \leqslant T_{SiH} \leqslant 0.45\ \text{ms}$, $0.9\ \text{ms} \leqslant T_{1\rho}^H \leqslant 1.6\ \text{ms}$, and $8.5\ \text{ms} \leqslant T_{1\rho}^{Si} \leqslant 12.0\ \text{ms}$. For samples where T_{SiH} and $T_{1\rho}^H$ are not determined from a variable contact-time CP/MAS experiment, the values $T_{SiH} = 0.40 \pm 0.05$ ms, $T_{1\rho}^H = 1.2 \pm 0.3$ ms, and $T_{1\rho}^{Si} = 10.2 \pm 2.0$ ms are used along with Eq. (1) to calculate the thaumasite content. Employing these values for the Portland cement containing 15 wt.% RFPD (Table 1) and integrated intensities, observed in $^{29}Si\{^1H\}$ CP/MAS NMR spectra for this sample and for the external reference of mineral thaumasite recorded at the same experimental conditions, gives a thaumasite content of 16.5 ± 2.6 wt.%. The error limit is the standard deviation calculated from Eq. (1) using the error limits for the individual parameters. This result indicates that quantities of thaumasite can be determined with a precision of ±15% when the average values for $T_{SiH}, T_{1\rho}^H$, and $T_{1\rho}^{Si}$ are employed. For samples containing thaumasite contents larger than about 5 wt.%, the time constants T_{SiH} and $T_{1\rho}^H$ can rather easily be determined from a variable contact-time $^{29}Si\{^1H\}$ CP/MAS NMR experiment using the approach described above. For the Portland cement containing 15 wt.% RFPD this gives the values for the time constants listed in Table 1. Employing these data to calculate the thaumasite content gives 16.2 ± 1.5 wt.% and thereby an improved accuracy (i.e., a precision of ±10%).

Recently the existence of solid solutions between ettringite and thaumasite has been reported from quanti-

Table 1
Thaumasite contents and time constants for the ^1H rotating-frame relaxation ($T_{1\rho}^H$) and the ^1H–^{29}Si CP time (T_{SiH}) determined from $^{29}Si\{^1H\}$ CP/MAS NMR spectra of the type II Portland cement–RFPD samples stored in a $MgSO_4$ solution

Sample[a]	Storage time[b]	Thaumasite (wt.%)	$T_{1\rho}^H$ (ms)	T_{SiH} (ms)
RFPD-5	Nine months	14.7 ± 2.0	0.93 ± 0.13	0.42 ± 0.06
RFPD-15	Nine months	16.2 ± 1.5	1.22 ± 0.09	0.38 ± 0.03
RFPD-30	Two weeks	0.7 ± 0.3		
RFPD-30	Four weeks	1.3 ± 0.4		
RFPD-30	Ten weeks	1.5 ± 0.4		
RFPD-30	Four months	15.9 ± 1.8	1.57 ± 0.11	0.40 ± 0.04

[a] Results for the mixtures containing 5, 15, and 30 wt.% raw feed precipitator dust (RFPD).
[b] Time of storage in a 0.25 M $MgSO_4$ solution after a preliminary hydration for 33 days (see experimental section).

tative XRD and infrared spectroscopy [14,15]. These studies show an immiscibility gap between ettringite and thaumasite corresponding to up to 50% replacement of Al by Si in ettringite while only about 12% of the Si present in thaumasite can be substituted by Al [15]. The thaumasite contents determined in this work from ^{29}Si{^{1}H} CP/MAS NMR are calculated assuming stoichiometric thaumasite in the samples and thus represent minimum values, because the substitution of a small quantity of Al for Si in thaumasite (i.e., up to 12% of the Si atoms [15]) cannot be excluded for the samples studied here. The possibility of incorporation of Si in ettringite has so far not been studied by ^{29}Si MAS NMR. Although, the ^{29}Si isotropic chemical shift for Si in ettringite will fall in the chemical shift range for thaumasite (i.e., ~−180 ppm), it is expected that δ_{iso} for the Si guest-ions in ettringite will be shifted by a few ppm to higher frequency as a result of the neighbouring $Al(OH)_6^{3-}$ units in the structure. This effect on ^{29}Si isotropic chemical shifts is well documented in ^{29}Si MAS NMR studies of zeolites where each Al in the next-nearest coordination sphere to Si contributes a shift towards higher frequency of about 5 ppm [16].

3.2. Thaumasite in type II Portland cement–RFPD blends stored in MgSO$_4$ solution

The thaumasite contents in the type II Portland cement–RFPD blends stored for various times in a 0.25 M $MgSO_4$ solution are summarized in Table 1. For the samples including 30 wt.% RFPD, thaumasite is already observed after two weeks of storage in the $MgSO_4$ solution and an increasing quantity of thaumasite is detected with increasing storage time. Similar experiments performed for samples containing lower quantities of the RFPD (i.e., RFPD-5 and RFPD-15, Table 1) demonstrate that large quantities of thaumasite are also produced when lower additions of this source of carbonate ion are employed. A similar series of Portland cement and RFPD has been stored at 5 °C in pure water and ^{29}Si{^{1}H} CP/MAS NMR were not able to detect thaumasite in any of these samples, indicating a thaumasite content below 0.5 wt.%, which is estimated to be the lower limit for thaumasite detection by this method. These observations demonstrate the importance of a large supply of sulfate ions for the formation of thaumasite and the fact that the normal content of gypsum in the Portland cement does not result in the formation of thaumasite. The detection of thaumasite in the studied Portland cement–RFPD blends is in good agreement with recent XRD studies of Portland cements with 0–30 wt.% limestone additions cured at 5 °C in solutions with various sources of sulfate ions [17]. In that work thaumasite formation was observed after a few months of exposure to sulfate solutions and the quantity of thaumasite was qualitatively observed to increase with increasing limestone additions. We note that the samples studied in this work are a part of a larger investigation on a model for calculating the stable phases in the pseudoternary $CaSO_4$–$3CaO\cdot Al_2O_3$–$CaCO_3$ system which has been presented elsewhere [18].

3.3. Thaumasite in type V Portland cement–RFPD–gypsum blends

The samples studied in the second series were prepared from an ASTM type V Portland cement–raw feed precipitator dust (Pc–RFPD) blend with additions of gypsum used as the source of sulfate ions. ^{29}Si{^{1}H} CP/MAS NMR spectra of three Pc–RFPD samples containing 4, 6, and 10 wt.% SO_3, and hydrated for one month are shown in Fig. 3. These spectra demonstrate that very small quantities of thaumasite are easily detected using this method, since a low-intensity resonance at −180 ppm is observed in these spectra. A quantitative analysis of the spectra gives the thaumasite contents of 0.6 ± 0.2, 0.7 ± 0.2, and 0.7 ± 0.2 wt.% for the samples containing 4, 6, and 10 wt.% SO_3, respectively. Two similar samples without and with 2 wt.% SO_3 added and hydrated for one month were also analysed and thaumasite (0.2 ± 0.1 wt.%) was only observed for the sample containing 2 wt.% SO_3. These data shows that thaumasite can be formed after a short time of hydration and that additions of 4–10 wt.% SO_3 to the Pc–RFPD blend result in similar quantities of thaumasite formed after hydration for one month. The formation of thaumasite in the Pc–RFPD blend without and with additions of 2 and 10 wt.% SO_3 has been followed over a period of up to four years of hydration. The quantities

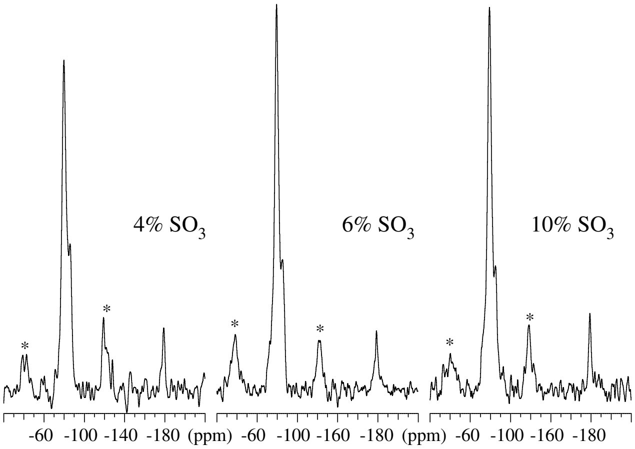

Fig. 3. ^{29}Si{^{1}H} CP/MAS NMR spectra illustrating the detection of very small quantities of thaumasite in the Portland cement–RFPD series containing 4, 6, and 10 wt.% SO_3 and hydrated for one month. Quantification of thaumasite from these spectra gives 0.6 ± 0.2, 0.7 ± 0.2, and 0.7 ± 0.2 wt.% thaumasite for the samples with 4, 6, and 10 wt.% SO_3, respectively. The asterisks indicate spinning sidebands from the Q^1 and Q^2 SiO_4 tetrahedra in the C–S–H phase.

Table 2
Thaumasite contents determined from $^{29}\mathrm{Si}\{^{1}\mathrm{H}\}$ CP/MAS NMR spectra of the type V Portland cement–RFPD samples without and with addition of 2 and 10 wt.% SO_3 in the form of gypsum

Hydration time	Thaumasite (wt.%)		
	0 wt.% SO_3	2 wt.% SO_3	10 wt.% SO_3
One month	0	0.2 ± 0.1	0.7 ± 0.2
Three months	0		1.4 ± 0.3
Six months	0	0.45 ± 0.2	2.2 ± 0.4
One year	0	0.4 ± 0.2	2.0 ± 0.4
Two years	0.2 ± 0.1	0.9 ± 0.4	3.4 ± 0.5
Four years[a]			8.7 ± 1.0

[a] The time constants $T_{\mathrm{SiH}} = 0.34 \pm 0.02$ ms and $T_{1\rho}^{\mathrm{H}} = 1.35 \pm 0.10$ ms were determined from a variable contact-time $^{29}\mathrm{Si}\{^{1}\mathrm{H}\}$ CP/MAS NMR experiment for this sample (c.f. Fig. 2).

of thaumasite determined from $^{29}\mathrm{Si}\{^{1}\mathrm{H}\}$ CP/MAS NMR studies of these samples are summarized in Table 2 and shown as a function of the hydration time in Fig. 4 for the Pc–RFPD blend with 10 wt.% SO_3 added. These data show the continued formation of thaumasite with time of hydration, and that large quantities of thaumasite can be formed after prolonged hydration when an excess of sulfate and carbonate ions are present in the mixture. Comparison of the data for the blends including 2 and 10 wt.% SO_3 demonstrate significant smaller quantities of thaumasite in the samples containing 2 wt.% SO_3, indicating that the concentration of sulfate ions is a limiting factor for this blend. More importantly, after two years of hydration for the Pc–RFPD mixture without SO_3 addition, only a very small quantity of thaumasite (0.2 wt.%) is detected. This indicates that the quantity of SO_3 (2.14 wt.%) in the type V Portland cement, which contain 2.3 wt.% C_3A, is mainly consumed by the formation of ettringite and monosulfate, preventing the formation of thaumasite even though a large quantity of carbonate ions are present in the mixture. The effects of the SO_3 content in the form of gypsum on thaumasite formation has earlier been studied by Gaze [19] for cement-lime-sand mortars crushed and mixed with various quantities of gypsum and stored in water at 5 °C. Gaze found that a minimum amount of gypsum was required for thaumasite formation and that this amount may depend on the quantity of alumina in the Portland cement. For the ordinary Portland cement mixtures studied by Gaze, thaumasite was not observed by XRD for samples containing less than 5 wt.% SO_3 and only traces of thaumasite were detected for samples with 10 wt.% SO_3 after more than two months of storage. The present results from $^{29}\mathrm{Si}\{^{1}\mathrm{H}\}$ CP/MAS NMR show that thaumasite can be produced at low contents of SO_3 (i.e., 2 wt.%), even after one month of hydration, in mixtures containing sulfate resisting Portland cement with very low C_3A contents.

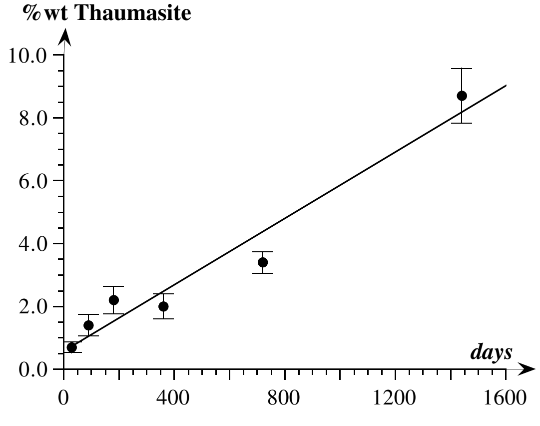

Fig. 4. Thaumasite content as a function of the hydration time for the Portland cement–RFPD samples with 10 wt.% SO_3 added.

4. Conclusion

$^{29}\mathrm{Si}\{^{1}\mathrm{H}\}$ CP/MAS NMR spectroscopy is an efficient and reliable tool for detection and quantification of thaumasite in cement-based materials. For thaumasite contents below about 10 wt.%, quantification with a relative precision of ±15% can be obtained using standard values for the $^{1}\mathrm{H}$–$^{29}\mathrm{Si}$ CP time (T_{SiH}) and the $^{1}\mathrm{H}$ and $^{29}\mathrm{Si}$ rotating-frame relaxation times ($T_{1\rho}^{\mathrm{H}}$ and $T_{1\rho}^{\mathrm{Si}}$). For thaumasite contents above 10 wt.% an improved precision (±10%) can be achieved by determination of T_{SiH} and $T_{1\rho}^{\mathrm{H}}$ from a variable contact-time $^{29}\mathrm{Si}\{^{1}\mathrm{H}\}$ CP/MAS NMR experiment. The method is applicable to a wide variety of cement mixtures containing low concentrations of paramagnetic ions (e.g., Fe^{3+}). The lower detection limit is about 0.5 wt.% thaumasite, although thaumasite contents as low as 0.2 wt.% has been detected in this work.

The quantification of thaumasite in a type II Portland cement with additions of RFPD (RFPD, 85% $CaCO_3$) and stored in a 0.25 $MgSO_4$ solution at 5 °C for up to nine months shows that quantities of about 15 wt.% thaumasite are formed independent of the amount of RFPD added in the range 5–30 wt.%. For a type V Portland cement mixed with a fixed quantity of RFPD and quantities of SO_3 (2–10 wt.%) in the form of gypsum and hydrated for up to four years at 5 °C, the results from $^{29}Si\{^1H\}$ CP/MAS NMR show that the formation of thaumasite depends on the quantity of added SO_3 and that the amount of thaumasite increases with the time of hydration.

Acknowledgements

The use of the facilities at the Instrument Centre for Solid-State NMR Spectroscopy, Department of Chemistry, University of Aarhus, sponsored by the Danish Research Councils (SNF and STVF), Teknologistyrelsen, Carlsbergfondet, and Direktør Ib Henriksens Fond, is acknowledged. J.S. thanks the Danish Natural Science Research Council (J. No. 0001237) for financial support.

References

[1] Taylor HFW. Cement chemistry. 2nd ed. London, UK: Thomas Telford Publishing; 1997.
[2] Moore AE, Taylor HFW. Crystal structure of ettringite. Acta Crystallogr B 1970;26:386–93.
[3] Edge RA, Taylor HFW. Crystal structure of thaumasite, $[Ca_3[Si(OH)_6]\cdot 12H_2O](SO_4)(CO_3)_2$. Acta Crystallogr B 1971;27:594–601.
[4] Crammond NJ. Quantitative X-ray diffraction analysis of ettringite, thaumasite and gypsum in concretes and mortars. Cem Concr Res 1985;15:431–41.
[5] Bensted J. Problems arising in the identification of thaumasite. I1 Cemento 1977;74:81–90.
[6] Bensted J. Uses of Raman spectroscopy in cement chemistry. J Am Ceram Soc 1976;59:140–3.
[7] Brough AR, Atkinson A. Micro-Raman spectroscopy of thaumasite. Cem Concr Res 2001;31:421–4.
[8] Yang R, Buenfeld NR. Microstructural identification of thaumasite in concrete by backscattered electron imaging at low vacuum. Cem Concr Res 2000;30:775–9.
[9] Skibsted J, Hall C, Jakobsen HJ. Nuclear magnetic resonance spectroscopy and magnetic resonance imaging of cements and cement-based materials. In: Bensted J, Barnes P, editors. Structure and performance of cements. 2nd ed. London: Spon Press; 2002. p. 457–76.
[10] Lippmaa E, Mägi M, Tarmak M, Weiker W, Grimmer AR. Structural studies of silicates by solid-state high-resolution silicon-29 NMR. J Am Chem Soc 1980;102:4889–93.
[11] Skibsted J, Hjorth L, Jakobsen HJ. Quantification of thaumasite in cementitious materials by $^{29}Si\{^1H\}$ cross-polarization magic-angle spinning NMR spectroscopy. Adv Cem Res 1995;7:69–83.
[12] Pines A, Gibby MG, Waugh JS. Proton-enhanced nuclear induction spectroscopy. A method for high-resolution NMR of dilute spins in solids. J Chem Phys 1972;56:1776–7.
[13] Mehring M. Principles of high resolution NMR in solids. 2nd ed. Berlin: Springer-Verlag; 1983.
[14] Barnett SJ, Adam CD, Jackson ARW. Solid solutions between ettringite, $Ca_6Al_2(SO_4)_3(OH)_{12}\cdot 26H_2O$, and thaumasite, $Ca_3SiSO_4CO_3(OH)_6\cdot 12H_2O$. J Mater Sci 2000;35:4109–14.
[15] Barnett SJ, Machphee DE, Lachowski EE, Crammond NJ. XRD, EDX and IR analysis of solid solutions between thaumasite and ettringite. Cem Concr Res 2002;32:719–30.
[16] Lippmaa E, Mägi M, Samoson A, Engelhardt G, Grimmer A-R. Structural studies of silicates by solid-state high-resolution ^{29}Si NMR. J Am Chem Soc 1980;102:4889–93.
[17] Hartshorn SA, Sharp JH, Swamy RN. Thaumasite formation in Portland–limestone cement pastes. Cem Concr Res 1999;29:1331–40.
[18] Herfort D, Porsborg, AT, Grundvig S, Jakobsen HJ, Skibsted J. Hydrate phase assemblages of Portland cement pastes stored at 5 and 20 °C. In: Proceedings of the 20th IOM Cement and Concrete Science Conference. University of Sheffield; 2000. p. 120–123.
[19] Gaze ME. The effects of varying gypsum content on thaumasite formation in a cement:lime:sand mortar at 5 °C. Cem Concr Res 1997;27:259–65.