

Characterization of Calcium Aluminate Hydrates and Related Hydrates of Cement Pastes by ^{27}Al MQ-MAS NMR

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^{27}Al multi quantum (MQ) MAS NMR spectroscopy was used for the first time to characterize calcium aluminate hydrates, which are of importance in the chemistry of high alumina and Portland cements. Substitution sites of silicon by aluminum in the calcium silicate hydrates (C-S-H) which are the main component of Portland cement paste were studied too. Synthetic samples of $\text{Ca}_3\text{Al}(\text{OH})_{12}$, $[\text{CaAl}(\text{OH})_4][\text{OH}(\text{H}_2\text{O})_{1.5}]$, $[\text{Ca}_2\text{Al}(\text{OH})_6](\text{OH})\cdot 3\text{H}_2\text{O}$, $[\text{Ca}_2\text{Al}(\text{OH})_6]_2(\text{CO}_3)\cdot 5\text{H}_2\text{O}$, $[\text{Mg}_2\text{Al}(\text{OH})_6](\text{CO}_3)_{0.5}\cdot 3\text{H}_2\text{O}$, $\text{Al}(\text{OH})_3$, and C-S-H substituted by aluminum were prepared. In most of the samples, the two dimension 3Q-MAS NMR spectra allow one, more easily than the MAS-only NMR spectra, to obtain the chemical shift, δ_{iso} , and the quadrupolar parameters ν_{Q} and η , which label each site and bring information on its symmetry and environment. The distributions of the aluminum environments were observed for each site. In $[\text{Ca}_2\text{Al}(\text{OH})_6](\text{OH})\cdot 3\text{H}_2\text{O}$, ^{27}Al MAS spectrum demonstrates the presence of two octahedral aluminum sites. In the C-S-H substituted with Al, tetrahedral aluminum is observed, in bridging and nonbridging sites of the silicate chains, mostly in the bridging sites for the sample investigated.

Introduction

Cement paste constitutes a very complex mineralogical system. X-ray diffraction was the first technique used to characterize this system. However, in poorly crystallized or amorphous materials other methods are to be used, among which solid-state NMR can yet provide structural information, even in the absence of long-range structural order.

^{29}Si magic angle nuclear magnetic resonance (^{29}Si MAS NMR) has proven to be a valuable technique to understand the calcium silicate hydrates (C-S-H) structure¹ (the cement shorthand nomenclature where C = CaO , S = SiO_2 , A = Al_2O_3 , F = Fe_2O_3 , and $\bar{\text{C}}$ = CO_2 is employed throughout this paper). As ^{29}Si has a spin of $1/2$, magic angle spinning (MAS) averages out the anisotropy of chemical shift and allows one to obtain well-resolved spectra. The position of each line in the spectrum, here its isotropic chemical shift δ_{iso} , is, in a first approximation, characteristic of a crystallographic site.² Thus in C-S-H, even when the material is poorly crystallized, ^{29}Si MAS NMR allows one to detect the different types of SiO_4 silicon tetrahedra in the structure. This is a favorable case: the resolution between

unequivalent crystallographic sites may become much less easily achievable for other nuclei, like ^{27}Al .

^{27}Al MAS NMR has often been used to characterize materials where Al occurs in several environments, which are labeled by very different isotropic chemical shifts, as for instance tetrahedral and octahedral aluminum atoms. In cement pastes this technique allowed one to follow the hydration of anhydrous aluminates:³ in the anhydrous phases (C_3A , CA , C_{12}A_7 , CA_2) (with the exception of the ferrite phase C_4AF)⁴ aluminum occurs only in tetrahedral sites, whereas in the aluminate hydrates, which precipitate after the dissolution of the anhydrous phases, aluminum occurs only in octahedral sites,³ unless it substitutes for silicon in tetrahedral sites.⁵ Adversely in all these hydrated system, it is often impossible to separate several ^{27}Al octahedral sites, relying only on their isotropic chemical shifts, whose spread (all within about 10 ppm)⁶ is smaller than the broadening of the lines. That broadening comes from the quadrupolar

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interaction which exists for those nuclei with spin $I > 1/2$, such as ^{27}Al , whose spin is $I = 5/2$.

A new method, MQ-MAS NMR,⁷ has been recently introduced which allows one to get rid of this quadrupolar broadening. In this paper ^{27}Al 3Q-MAS NMR is, for the first time, used to identify the different aluminum sites (chemical surrounding, site symmetry) which occur in the aluminate hydrates found in a cement paste and to obtain the NMR parameters which characterize these different sites. The increase of resolution brought by 3Q-MAS NMR makes that determination more easy and accurate and also allows one to disentangle different aluminum sites indiscernible by MAS-only NMR, for instance within the octahedral ones.

^{27}Al 3Q-MAS NMR is also used to study the substitution of silicon by aluminum in C-S-H, with low Ca/Si molar ratio, in sodic medium. This phase is often found in hardened alkali-activated blast-furnace slag pastes. As told above, it is known that aluminum may substitute for silicon in tetrahedral sites.⁵ By quantum or molecular simulations, some authors have indeed mentioned the possible substitution of aluminum in two different silicon sites in the structure.⁸ Until now, the resolution of ^{27}Al MAS NMR was too low to distinguish the two sites.⁵ It will be seen below that using MQ-MAS NMR clearly establishes the existence of such two substituted sites. The present study demonstrates the efficiency of the 3Q-MAS method for the characterization of the cement paste hydrates.

NMR Methods for Quadrupolar Nuclei

MAS-Only NMR. A nucleus with half integer spin $I > 1/2$ has $2I$ observable $\Delta m = 1$ transitions which can be separated into two groups: the central one ($1/2 \leftrightarrow -1/2$) and the other ones, often called the satellite transitions. The satellite transitions are very strongly broadened by the quadrupole interaction. Under sample spinning these transitions split into numerous sidebands. To first order, the central transition, being symmetrical, is not affected by the quadrupole interaction.⁹ It suffers only a second-order quadrupolar broadening which is only partially averaged out by MAS. Besides line broadening, the second-order quadrupolar affects the shift ($\delta_{1/2}$) of the central transition (defined as its first moment; in other words, its barycenter) which is shifted away from the isotropic chemical shift position.¹⁰ For a spin $5/2$ like ^{27}Al , the shift of the central band is given by

$$\delta_{1/2} = \delta_{\text{iso}} - \frac{8}{30} \frac{\nu_Q^2}{\nu_0^2} 10^6 \quad (1)$$

where ν_0 is its Larmor frequency and ν_Q its quadrupole frequency. The whole sideband pattern of each ($m \leftrightarrow m - 1$)

satellite transition is also subjected to a shift δ_m which has the same expression as $\delta_{1/2}$, with only different numerical weighting factors for the quadrupolar contribution. The quadrupolar interaction of a quadrupolar nucleus with the electric field gradient originating from its electronic environment (bonds, charges, ...) is described by two characteristic constants which are the quadrupole coupling constant (C_Q) and the asymmetry parameter (η). The quadrupolar coupling constant can be expressed as

$$C_Q = \frac{eV_{zz}Q}{h} \quad (2)$$

where V_{zz} is the electric field gradient and Q the quadrupole moment of the nucleus. C_Q and η are related to the quadrupolar frequency ν_Q by

$$\nu_Q = \frac{3C_Q}{2I(2I-1)} \sqrt{1 + \frac{\eta^2}{3}} \quad (3)$$

In MAS-only NMR, δ_{iso} and ν_Q can be obtained by measuring, at different magnetic fields, the shift $\delta_{1/2}$ of the central transition. This method is not often used because it requires several spectrometers. Using only one magnetic field, the determination of δ_{iso} and ν_Q is however possible by measurements of the shifts $\delta_{1/2}$ and δ_m of the central and of the sideband patterns of the satellite transitions. When this is precluded by the broadening of the lines, one may use the simulation of the line shape of the central band as well as of the shape (relative amplitude of the sidebands) of the full sideband comb of the satellite transitions. However, this adjustment depends on three parameters (δ_{iso} , C_Q , and η), making the exercise quite difficult. These methods were successfully applied to pure crystallographic phases with only a few aluminum sites.¹⁰ In any case, without well-resolved lines, δ_{iso} and ν_Q cannot be obtained. Unfortunately, this is often the case in the cement pastes, where there are several sites with almost equal chemical shifts and distributions of quadrupolar interactions and/or strong quadrupolar interactions.

DAS, DOR, and MQ-MAS NMR. Several years ago, dynamic angle spinning (DAS) and double-rotation (DOR) methods were devised in order to increase the resolution of the NMR spectra of half-integer quadrupole nuclei.¹² This is achieved by mutual annihilation of the broadening occurring in different complementary orientations of the axis of rotation of the sample. However, both types of experiments require especially designed NMR probes and suffer limitations due to technically achievable spinning rates (DOR) or to the loss of signal by spin diffusion which occurs during the orientational jumps (DAS) when the dipolar interaction is strong, as for instance in the aluminate hydrates.

Recently, a new method has been devised,⁷ which allows one to obtain high-resolution spectra with an usual MAS probe. In that method called MQ-MAS, the reorientations of the spinning axis of the sample are replaced by a coherence transfer within the multilevel system of the quadrupolar nuclei. This can be

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viewed as a coherence transfer echo or as a correlation of the evolution of a multiple-quantum (MQ) coherence ($m \leftrightarrow -m$; $m > 1/2$) with that of the central one ($-1/2 \leftrightarrow 1/2$). In the resulting two-dimensional (2D) spectrum, the projection of each 2D line shape on the two dimensions allows one to determine the parameters of the site.¹³ After a shear transformation¹⁴ on the 2D spectrum, the projection in the first dimension, called "the isotropic dimension", provides a spectrum without any broadening due to the second-order quadrupole effect. For spin $5/2$ ^{27}Al , in that dimension of the 3Q-MAS NMR spectrum, the line exhibits an "isotropic shift" (δ_1) expressed as

$$\delta_1 = -\frac{17}{31}\delta_{\text{iso}} - \frac{8}{93}10^6\frac{\nu_Q^2}{\nu_0^2} \quad (4)$$

This expression is similar to that of $\delta_{1/2}$ (eq 1), with only different numerical weighting factors for the chemical shielding and the quadrupolar contributions. If the coherence transfer is total, taking for each site, at its position δ_1 , a slice of the 2D 3Q-MAS spectrum gives in the second dimension sometimes called the "MAS dimension" a line shape which is identical to the corresponding line in the MAS-only spectrum. The shift (first moment) of this "MAS" projection of the 3Q-MAS spectrum has exactly the same expression $\delta_{1/2}$ as in the usual MAS spectrum. Thus, for ^{27}Al in a resolved given site, the measurement in a MQ-MAS spectrum of the shifts δ_1 and $\delta_{1/2}$ of the two projections (isotropic and MAS) of the signal (central transition) allows one to separate and determine easily the chemical shift δ_{iso} and the quadrupolar frequency ν_Q . Then the simulation of the 2D MQ-MAS line shapes allows one to get separately C_Q and η .

Experimental Section

NMR Measurements. Solid-state ^{27}Al NMR spectra were acquired on a Bruker DMX-300 (7.1 T) spectrometer operating at 78.617 MHz for ^{27}Al . A commercial MAS probe (4 mm) was used, and the spinning speed was 12.5 kHz for all the spectra with accuracies of ± 5 Hz. For MAS experiments, the single pulse duration was 15°. The 3Q MAS spectra were acquired using a combination of three techniques: Z-filtering method;¹⁵ rotor synchronization;¹⁶ hypercomplex phase cycling,^{13b} which allows one to obtain pure absorption spectra with great sensitivity. With a radio frequency (rf) field strength of 110 kHz (150 kHz for the C-S-H spectrum), the first and second pulses length were respectively 4 μs (2.5 μs for the C-S-H) and 1.3 μs (0.8 μs for the C-S-H). The third pulse was adjusted to be a selective 90° pulse on the central transition by using a rf field strength of 20 kHz and a pulse length of 4 μs . The delay (τ) between the second and the third pulse was set equal to two rotor periods (200 μs). The MAS-only as the 3Q-MAS spectra were accumulated with a recycle time of 1 s using a high-power ^1H decoupling of 60 kHz. The data processing, including the shear transformation, has been performed using a home-built program.

Unless otherwise specified, the chemical shift and quadrupolar parameters are obtained, as explained above, in the following way: the shift δ_1 is calculated for each line from the projection of the 3Q-MAS spectrum in the isotropic dimension. Then for each line,

Table 1. Shifts and Quadrupolar Interaction Parameters for ^{27}Al in Calcium Aluminate Hydrates and C-S-H Substituted by Aluminum^a

compd	δ_1	$\delta_{1/2}$	δ_{iso}	ν_Q	C_Q	η
C_3AH_6	-6.95	11.82	12.36	0.111	0.74	0
C_2AH_8	-6.1	8.7	10.3	0.19	1.2	0.6
$\text{C}_4\text{ACH}_{11}$	-5.9	5.1	8.7	0.29	1.7	0.8
$\text{M}_4\text{ACH}_{12}$	-6.2	8.2	10.1	0.20	1.2	0.8
C_4AH_{13} Al(I)	[-4.5; -5.5]	[7; 8]	[7.5; 9.5]	[0.13; 0.21]		
C_4AH_{13} Al(II)	[-7; -6]	[7; 8]	[9.5; 11]	[0.21; 0.29]		
AH_3	-12.9	-7.8	11.9	0.67	4.3 ^b	0.48 ^b
	-5.2	5.5	8.0	0.24		
C-S-H Al(I)	-45.5	66.3	76.3	0.48		
C-S-H Al(II)	-36.3	59.5	63.7	0.31		

^a Chemical shifts are in ppm; C_Q and ν_Q in MHz. All the sites are octahedral, with the exception of the sites of C-S-H which are tetrahedral. ^b Using MAS projection singularities of the 3Q-MAS spectrum of the site.²⁸

at its δ_1 offset, a slice is taken in the MAS dimension; $\delta_{1/2}$ is the shift of that MAS line shape. From these δ_1 and $\delta_{1/2}$ values, using eqs 1 and 4, one gets δ_{iso} and ν_Q . Then η and C_Q are obtained by a fit of the shape of the MAS spinning sideband pattern, using the WINFIT Bruker software package developed by D. Massiot.¹⁷ The values of those NMR parameters δ_1 , $\delta_{1/2}$, δ_{iso} , ν_Q , η , and C_Q are given for each compound in the Table 1. The precision is about ± 1 on the last number of each value given in the table. ^{27}Al isotropic chemical shifts (δ) are reported in ppm relative to an external sample of 1.0 M $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$.

^{29}Si MAS NMR has been used to add further information to discuss the ^{27}Al 3Q-MAS results on the C-S-H samples. ^{29}Si MAS NMR spectra were recorded, at the ^{29}Si frequency of 59.617 MHz, with a spinning rate of approximately 4 kHz in double-bearing 7-mm ZrO_2 rotors. Spectra were accumulated using single-pulse excitation and high-power ^1H decoupling with a 60 kHz rf field. The recycle time was 59 s and the number of scans 800. $[\text{Si}(\text{CH}_3)_3]_3\text{Si}_8\text{O}_{20}$ was used as a secondary external reference standard, the major peak being at -11.6 ppm relative to tetramethylsilane (TMS, $\text{Si}(\text{CH}_3)_4$).

Materials. In the present paper, we have studied most of the different aluminate hydrates C_3AH_6 , C_2AH_8 , C_4AH_{13} , the carboaluminate or hydrocalumite $\text{C}_4\text{ACH}_{11}$, the hydrotalcite $\text{M}_4\text{ACH}_{12}$, the aluminum hydroxide AH_3 , and the calcium silicate hydrates C-S-H, where aluminum substitutes for some silicon atoms. All these hydrates commonly form by direct hydration of clinker cements, as well as by carbonation of these materials upon contact with the atmosphere. They occur under the following conditions.

C_3AH_6 is the stable form at the high basic pH found in a cement paste.¹⁸

In ordinary Portland cement, C_2AH_8 may precipitate before C_3AH_6 . This phase is thermodynamically unstable.

The presence of gypsum in cement, added to slow the hydration of the clinker, is responsible for precipitation of ettringite and monosulfaluminate. As the characterization of aluminum in these two phases was already made by Skibsted et al.,⁶ it has not been performed again in the present study. But, on the contrary, in an excess of $\text{Ca}(\text{OH})_2$ and a lack of sulfate, C_4AH_{13} may appear. In contact with the atmosphere, carbonation of the aluminate hydrates can occur. One of the principal resulting carboaluminates is $\text{C}_4\text{ACH}_{11}$.

Upon leaching of cement paste by water, the precipitation of magnesium hydrates as hydrotalcite, very stable at a pH of about 8, has been observed.^{19,20} This is the reason the aluminum site of $\text{C}_4\text{ACH}_{11}$ was compared with the aluminum structural position of hydrotalcite $\text{M}_4\text{ACH}_{11}$ obtained by substitution of Ca^{2+} in $\text{C}_4\text{ACH}_{11}$ by Mg^{2+} .

In rich aluminate pastes, AH_3 can precipitate.

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The precipitation of C-S-H, in which silicon is substituted by aluminum, is currently observed in hardened alkali-activated blast-furnace slag pastes.⁵

Sample Preparation. To obtain the pure C_3AH_6 phase, 0.6 g of tricalcium aluminate (C_3A) was mixed with 250 g of water at 80 °C during 24 h, filtered, and dried with acetone and ether.

C_2AH_8 has been prepared by mixing 0.869 g of calcium aluminate (CA) in 250 cm³ of water during 1 h. Then 0.196 g of calcium oxide decarbonated at 1000 °C was added and stirred during 3 days at 25 °C. The suspension was then filtered and dried in the same way as previously.

C_4AH_{13} has been synthesized by mixing CA in a saturated lime solution. It is only possible by this way to obtain a mix of α - and β - C_4AH_{13} .

$C_4\bar{A}CH_{11}$ has been prepared by mixing C_3A and calcite in stoichiometric conditions during 1 week at 25 °C.

Hydrotalcite was prepared by mixing 10 g of $MgCl_2 \cdot 6H_2O$ with 5.93 g of $AlCl_3 \cdot 6H_2O$ in 100 mL of water; a solution of 1.2 M NaOH is added until reaching pH > 12. A 0.867 g amount of Na_2CO_3 is then added, and the suspension is stirred at 80 °C during 1 week. The mix is heated at 130 °C during 24 h. After cooling, the sample is water washed and then dried with acetone and ether.

Extrapure AH_3 (Prolabo Co.) was used in this paper.

C-S-H substituted by aluminum was prepared from calcium hydroxide freshly decarbonated at 1000 °C during 24 h, with silica (aerosil 200 from Degussa) and gypsum added in a 1 M NaOH solution in such a way as $Ca/(Si + Al) = 0.66$ and $Al/Si = 0.5$. The mix is stirred during 3 weeks at 25 °C, filtered, and dried with acetone and then ether. From X-ray diffraction, we know that the sample contains an excess of some $Al(OH)_3$, as an impurity.

Experimental Results and Discussion

The studied aluminate compounds belong to three structural types. C_3AH_6 is a cubic hydrated phase. C_4AH_{13} , $C_4\bar{A}CH_{11}$, C_2AH_8 , and M_4ACH_{12} are hydrated layered compounds, the structure of which derives from the calcium or magnesium hydroxides, Al^{3+} substituting some Ca^{2+} (or Mg^{2+}) with water and anions in an interlayer for compensating the excess of positive charge due to the Ca^{2+} (or Mg^{2+}) substitution by Al^{3+} . The third one is the substituted C-S-H, with a layered structure.

C_3AH_6 . C_3AH_6 has a hydrogarnet cubic structure.²¹ The ^{27}Al 3Q-MAS and MAS-only spectra are given in Figure 1. There is only one line. The values of δ_{iso} and ν_Q agree with that obtained by Skibsted et al. using several MAS spectra recorded at different fields.⁶ From the chemical shift value δ_{iso} , one knows that the corresponding site has an octahedral symmetry. The asymmetry parameter, η , is found approximately equal to zero. The aluminum site in C_3AH_6 has then a quasi-perfect axial symmetry.

The characteristic lines of pure distribution in ν_Q or in δ_{iso} are drawn on the 3Q-MAS spectrum. The chemical shift distribution is small as expected. The chemical shift of aluminum is poorly sensitive to changes of its local environment. This is well-known for octahedral aluminum which in all the cement hydrates has an isotropic chemical shift about of 10–13 ppm.^{3–6} As the Al–O bond is quite ionic, the Al electronic environment is less affected by chemical changes in its second coordination sphere than for instance that of silicon which has somewhat stronger covalent Si–O bonds. Adversely, the electric field around Al and therein the quadrupole interaction remains quite sensitive to changes of the charge environment even in the second coordination sphere. In the C_3AH_6 , the second coordination sphere of Al is constituted of 6 protons.²¹ A ν_Q distribution clearly appears in the 3Q-MAS spectrum: it

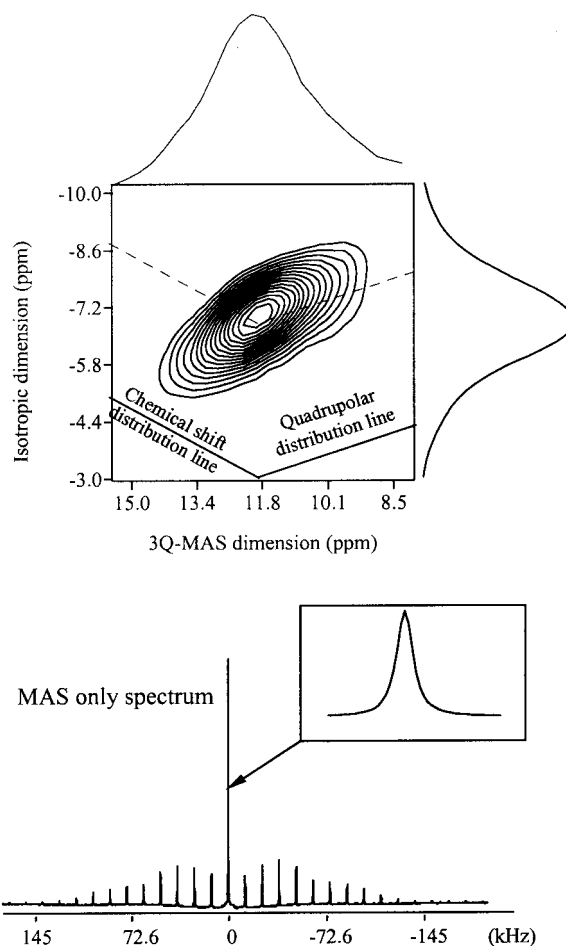


Figure 1. ^{27}Al MAS-only and 3Q-MAS NMR spectra of the C_3AH_6 with 1H decoupling. The contour lines are drawn every 5%, from 20% to 100% of the maximum point in the spectrum.

may reflect a distribution in the Al–O bonds (angles, length, charge allocation) induced by the presence of the protons in the structure.

C_2AH_8 . The structure of C_2AH_8 is not well-known. It has the general structure of the AFm compounds,^{22,23} which may be viewed as that of portlandite $Ca(OH)_2$, where some calcium atoms are substituted by aluminum, the positive charge excess being compensated by incorporation of OH^- or other anions (CO_3^{2-} , ...), together with water molecules, in the interlayer space between the cationic Ca–Al layers. For C_2AH_8 , there are two hypotheses:¹⁸ all Al^{3+} may substitute Ca^{2+} in the cation layer, in an ordered or a disordered way, with a general formula $[CaAl(OH)_4]^+[OH(H_2O)_{1.5}]^-$, or alternatively, aluminum may substitute in two different sites, one Al^{3+} in substitution of a Ca^{2+} in the cation layer and another one in the interlayer as an $[Al(OH)_4(H_2O)_2]^-$ ion, with a general formula $[Ca_2Al(OH)_6]^+[Al(OH)_4(H_2O)_3]^-$.

The ^{27}Al 3Q-MAS spectrum of C_2AH_8 as well as the MAS spectrum (Figure 2) are characteristic of a unique octahedral site. This shows that the first model is the best one: all aluminum atoms substitute in the cation layer. There is a slight distribution of the quadrupole parameters. Like in C_3AH_6 , this distribution may be due to a disordered positioning of the Al–OH protons as well as of water molecules and the counterions in the interlayer space. The aluminum site is found asymmetric

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(22) Ahmed, S. J.; Taylor, H. F. W. *Nature* **1967**, 215, 622.

(23) Taylor, H. F. W. *Cement Chemistry*; Academic Press Ltd.: London, 1990; p 167–185.

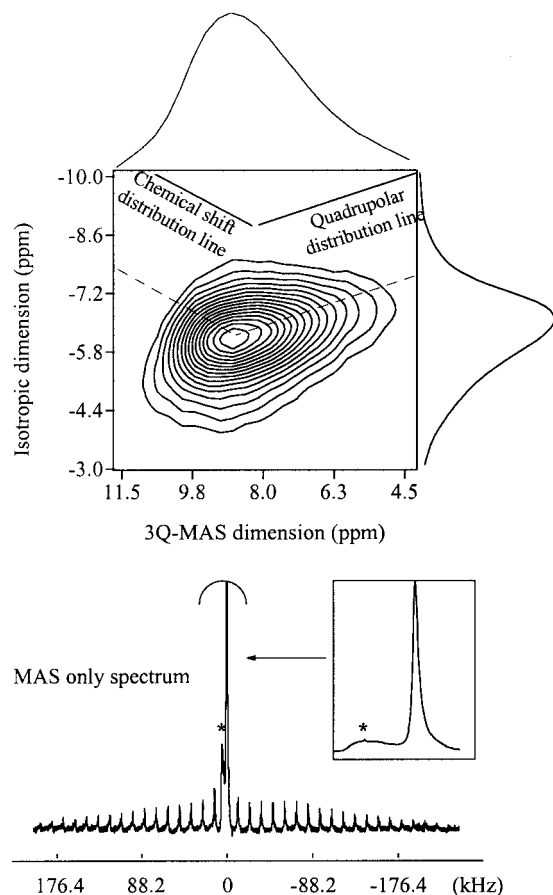


Figure 2. ^{27}Al MAS-only and 3Q-MAS NMR spectra of the C_2AH_8 with ^1H decoupling. The contour lines are drawn every 5%, from 20% to 100% of the maximum point in the spectrum. (An asterisk indicates the residual anhydrous aluminate impurity.)

($\eta = 0.6$), its quadrupole constant ($C_Q = 1.2$ MHz) being higher than that found in the C_3AH_6 structure ($C_Q = 0.74$ MHz). This increase of η and C_Q may be due to higher distortion of the first aluminum sphere and/or for instance to a higher content of positive charges such as protons in the second sphere of coordination.

$\text{C}_4\text{A}\bar{\text{C}}\text{H}_{11}$. Ahmed and Taylor²² have partially resolved the structure of carbonated C_4AH_{13} . It is an AFm phase in which the compensation is made by OH^- groups and/or carbonated CO_3^{2-} ions. Recently, the $\text{C}_4\text{A}\bar{\text{C}}\text{H}_{11}$ structure was completely resolved by Renaudin et al.²⁴ Hydrocalumite usually designates such naturally occurring carbonated calcium aluminate hydrate AFm phases.²³ The ^{27}Al 3Q-MAS and MAS-only spectra are given in Figure 3. Here too the ^{27}Al 3Q-MAS spectrum, as well as the MAS-only spectrum, is characteristic of a single octahedral site, in agreement with the data from X-ray diffraction.²⁴ The asymmetry parameter ($\eta = 0.8$) and the quadrupole coupling constant $C_Q = 1.7$ MHz are higher than in C_2AH_8 . This may be related to the substitution of the CO_3^{2-} groups and may be from the H_2O molecules in the second sphere of aluminum coordination, in the interlayer space.²⁴ No chemical shift distribution is detected. The small quadrupole distribution which appears in the 3Q-MAS spectrum can be easily explained, as in C_2AH_8 , by a statistical distribution of the OH^- and CO_3^{2-} groups on the same crystallographic sites as observed by Renaudin et al.²⁴

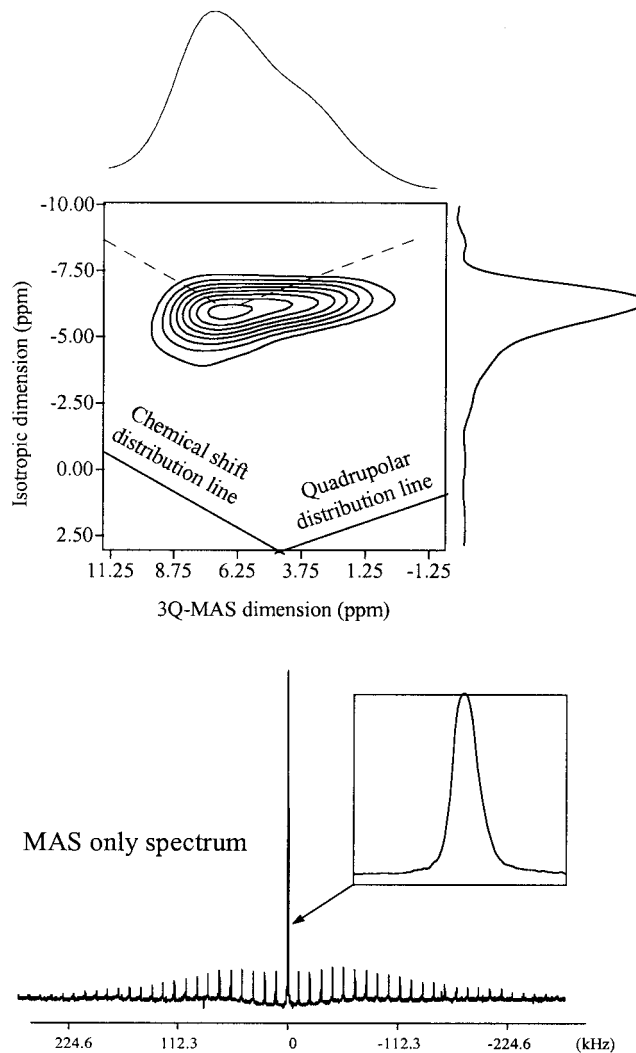


Figure 3. ^{27}Al MAS-only and 3Q-MAS NMR spectra of $\text{C}_4\text{A}\bar{\text{C}}\text{H}_{11}$ with ^1H decoupling, in which the contour lines are drawn every 5%, from 20% to 100% of the maximum point in the spectrum.

$\text{M}_4\text{A}\bar{\text{C}}\text{H}_{12}$. The calcium magnesium AFm hydrates,²³ called hydrocalcites, are polytypes of hydrocalumite. Their structure is derived from that of brucite $\text{Mg}(\text{OH})_2$ by substitution of magnesium for aluminum,²⁵ the charge deficit being compensated by incorporation in the structure of OH^- or CO_3^{2-} ions. The ^{27}Al 3Q-MAS and MAS-only spectra are given in Figure 4. As in hydrocalumite, there is a single octahedral site with a small quadrupole distribution. The asymmetry parameter $\eta = 0.8$ is the same as in hydrocalumite. The quadrupole constant $C_Q = 1.2$ MHz is lower than in hydrocalumite.

C_4AH_{13} . As already mentioned, the C_4AH_{13} sample used by Ahmed and Taylor²² for their study contained some structural carbonate ions. Furthermore, the structure of that sample was only partially determined. The structure of C_4AH_{13} is assumed to be a polytype of that hydrocalumite sample. Thus, the positions of the H_2O molecules in the interlayer space are not well determined.

The interpretation of a simple ^{27}Al MAS spectrum (Figure 5) is not straightforward. The line can be understood as a single octahedral line with a high quadrupole broadening or as two

(24) Renaudin, G.; François, M.; Evrard, O. *10th International Congress on the Cement Chemistry*, Göteborg, 1997.

(25) (a) Allman, A.; Jepsen, H. P. *Neues Jb. Miner.* **1969**, Mh., 544. (b) Mascolo, G.; Marino, O. *Miner. Magn.* **1980**, 43, 619. (c) Koritnig, S.; Susse, P.; Tschermaks. *Mineral. Petrogr. Mitt.* **1975**, 22, 79. (d) Jiang, S. *Acta Mineral. Sinica* **1984**, 296.

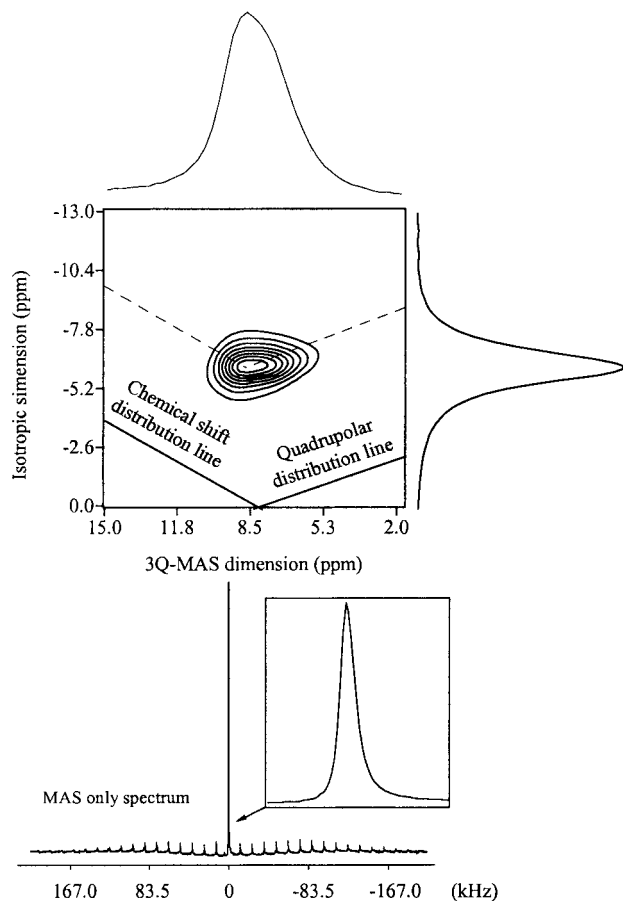


Figure 4. ^{27}Al MAS-only and 3Q-MAS NMR spectra of the $\text{M}_4\bar{\text{A}}\text{CH}_{12}$ with ^1H decoupling. The contour lines are drawn every 5%, from 20% to 100% of the maximum point in the spectrum.

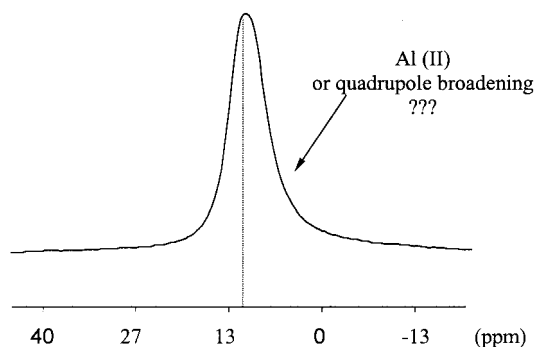


Figure 5. ^{27}Al MAS NMR spectrum of C_4AH_{13} .

lines. In contrast, the two- and three-dimensional representations (Figure 6) of the ^{27}Al 3Q-MAS spectrum clearly reveal the presence of two lines (Figure 6). However the overlapping between these two lines Al(I) and Al(II) leaves the determination of their NMR parameters difficult. Only estimations can be given, which are listed in Table 1. These two sites might be due to the concomitant presence in the sample of the α and β modifications of C_4AH_{13} , corresponding to differences in the layer stacking as mentioned by Ahmed and Taylor.²² Although NMR parameters are quite imprecise, the 3Q-MAS spectra indicate a distribution of the quadrupolar interactions. Together with the distribution of the chemical shift, it precludes the resolution in two lines by MAS NMR only, as observed in that work (Figure 5), in agreement with the previous MAS-only NMR study on C_3AH_{13} by Skibsted et al.,⁶ who concluded on

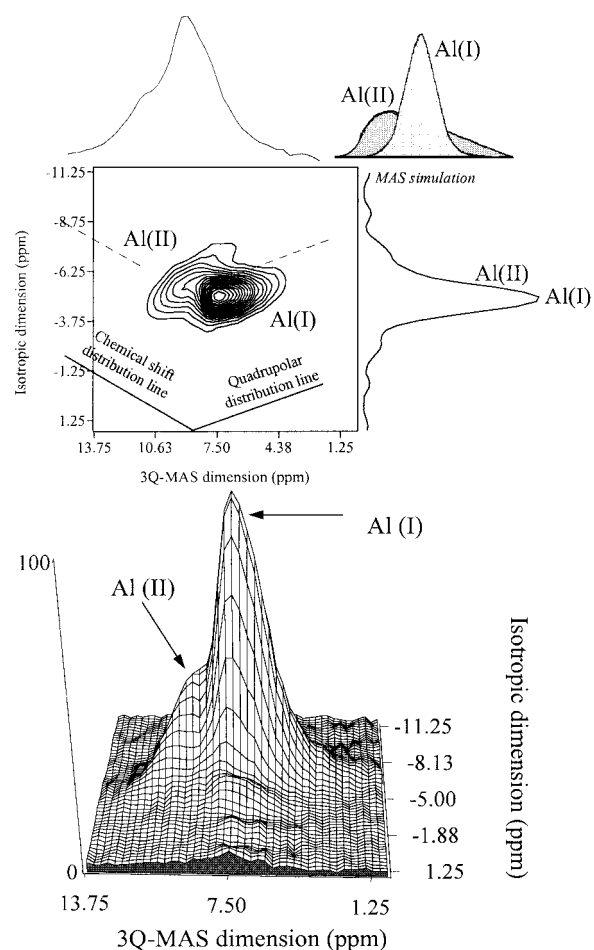


Figure 6. 2D and 3D representations of the ^{27}Al 3Q-MAS NMR spectrum of C_4AH_{13} with ^1H decoupling.

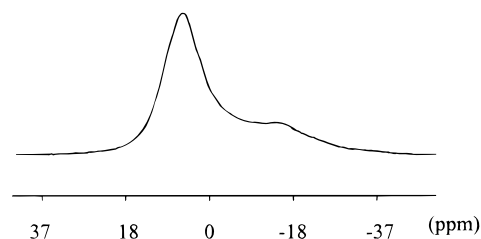


Figure 7. ^{27}Al MAS NMR spectrum of AH_3 with ^1H decoupling.

the presence of a single site. Only MQ-MAS allows, as shown here, to distinguish the two sites. It may also be that the sample prepared for the present study was more crystalline than that used by Skibsted et al.⁶

AH₃. In this hydrate, aluminum is known to occur in two nonequivalent crystallographic positions.²⁶ As observed by Woessner²⁷ and Skibsted et al.,⁶ the central band ($1/2 \leftrightarrow -1/2$) of the MAS spectrum (Figure 7) reveals the presence of two ^{27}Al lines in the shift range of octahedral sites. However, the resolution is not high enough to allow the determination of the site parameters. On the other hand, the 3Q-MAS spectrum (Figure 8) is perfectly resolved. It splits in two lines Al(I) and Al(II). Because of its high quadrupole frequency ($\nu_Q = 0.67$ MHz), the shape of the Al(I) MAS projection of the 3Q spectrum presents clearly, without almost any broadening, all the features of a second-order quadrupolar spectrum. Using the positions of the singularities of this spectrum ($\delta_d = -3.3$ ppm, $\delta_h =$

(26) Saalfeld, H.; Wedde, M. *Z. Kristallogr* **1974**, *139*, 129.

(27) Woessner, D. E. *Am. Mineral.* **1989**, *74*, 203.

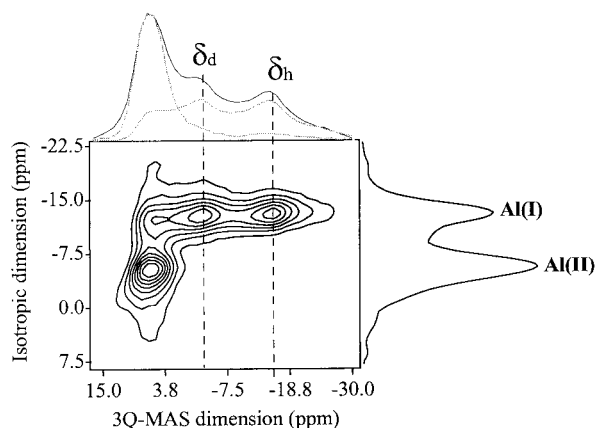


Figure 8. ^{27}Al 3Q MAS NMR spectrum of AH_3 with ^1H decoupling. The contour lines are drawn every 5%, from 20% to 100% of the maximum point in the spectrum. (The divergences are observed at $\delta_d = -3.3$ ppm and $\delta_h = -15.8$ ppm.)

Table 2. Shifts and Quadrupolar Frequency of the Two ^{27}Al Sites (I and II) in AH_3 , As Found by Different Studies^a

	Al(I)		Al(II)	
	δ_{iso}	ν_Q	δ_{iso}	ν_Q
MAS ²⁷	9	0.66	11	0.33
MAS ⁶	11.5	0.69	10.4	0.32
3Q-MAS ^b	11.9	0.67	8.0	0.24

^a All these parameters are deduced from 3Q-MAS spectra, unless otherwise specified. Shifts are in ppm, C_Q and ν_Q in MHz. Note that all the sites are octahedral ^b Present study.

–15.8 ppm), it is possible to calculate the asymmetry parameter and the coupling constant of the Al(I) site ($\eta = 0.48$ and $C_Q = 0.43$ MHz).²⁸ These results are to be compared those of previous works (see Table 2). There is a good agreement for the Al(I) parameters between our results and those of Skibsted et al.⁶ This is not surprising, because, owing to its high value, the quadrupolar frequency $\nu_Q[\text{Al(I)}]$ can be obtained with a good precision from the shape of the central ($1/2 \leftrightarrow -1/2$) band in a simple MAS spectrum. The complete determination of the other parameters from a MAS spectrum requires the evaluation of the population ratio of each site (1:1 employed by Skibsted et al.⁶ and 58:42 by Woessner²⁷), which is not needed in the present study where the two lines are well resolved in the 2D 3Q-MAS spectrum. In the same way, the calculation of the shift $\delta_{1/2}$ of each MAS contribution can be performed much more easily and accurately from the 3Q-MAS spectrum than from the MAS-only spectrum. These reasons account for the differences in the Al(II) site parameters from different works.

Calcium Silicate Hydrates (C-S-H). Another illustration of the greater efficiency of the 3Q-MAS method over the usual MAS-only NMR is brought by the study of calcium silicate hydrates (C-S-H) substituted by aluminum. By analogy with clays,²⁷ aluminum may be expected to substitute in the tetrahedral silicon sites of the silicate chains. These expectations are to be handled carefully, as C-S-H are not exactly clays. In the ^{27}Al MAS NMR spectrum of an aluminum-substituted C-S-H sample (Figure 9) two well-separated broad lines are observed, from which it is clear that aluminum is present in the sample in octahedral as well as in tetrahedral sites. However, the spectrum is not enough resolved to distinguish different octahedral or different tetrahedral sites.

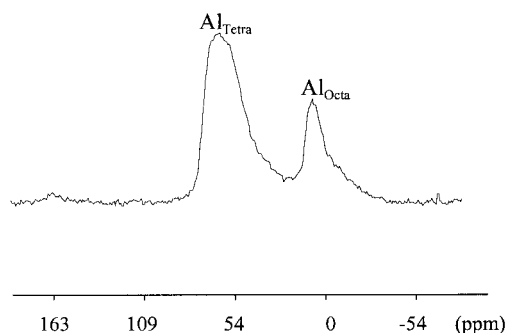


Figure 9. ^{27}Al MAS NMR spectrum of the sample with C-S-H substituted by aluminum.

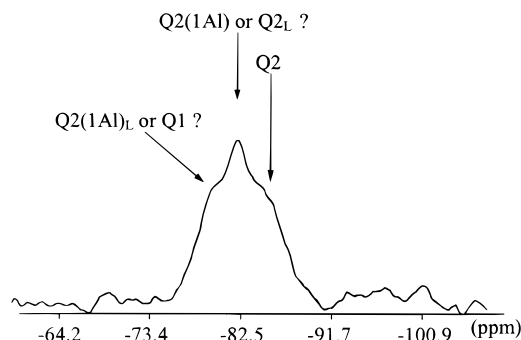


Figure 10. ^{29}Si MAS NMR spectrum of the sample with C-S-H substituted by aluminum.

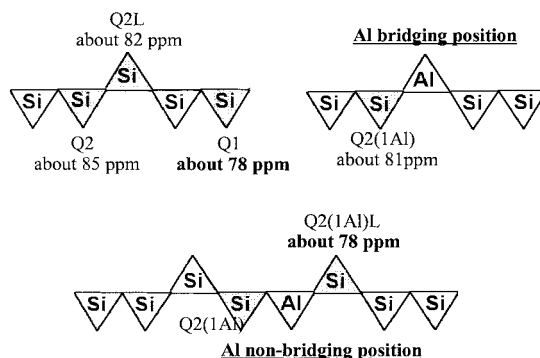


Figure 11. Silicon tetrahedra in the aluminum-substituted C-S-H. The chemical shifts of each type of tetrahedron are given according to ref 29.

The same is true for the ^{29}Si MAS NMR spectrum (Figure 10). The comparison with a nonsubstituted C-S-H with a Ca/Si ratio about 0.66 clearly demonstrates changes in the silicate chains. It is known that substitution of a silicon by an aluminum lowers the chemical shift of the silicon neighbors by 3–5 ppm.²⁹ Some different types of configurations for the Si substitution by Al are reported in Figure 11 with the corresponding chemical shifts. In the aluminum-substituted C-S-H, Q1(1Al) silicon, which are expected at 75 ppm, have never been detected⁵ and are neither observed in the present work. Substitution therefore occurs in Q2 sites. But, the attribution of the Q2 silicon lines is not easy. As the Q2(1Al) are expected in the same shift range as the Q2_L, and the Q2(1Al)_L in the same range as the Q1, it is difficult to conclude from the ^{29}Si MAS in which Q2 silicon site is the aluminum incorporated in the C-S-H.

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(29) (a) Mägi, M.; Lipmaa, E.; Samoson, A.; Engelhardt, G.; Grimmer, A. *R. J. Phys. Chem.* **1984**, 88, 1518. (b) Engelhardt, G.; Michel, D. *High-Resolution Solid-State NMR of Silicates and Zeolites*; John Wiley and Sons: Chichester, U.K., 1987.

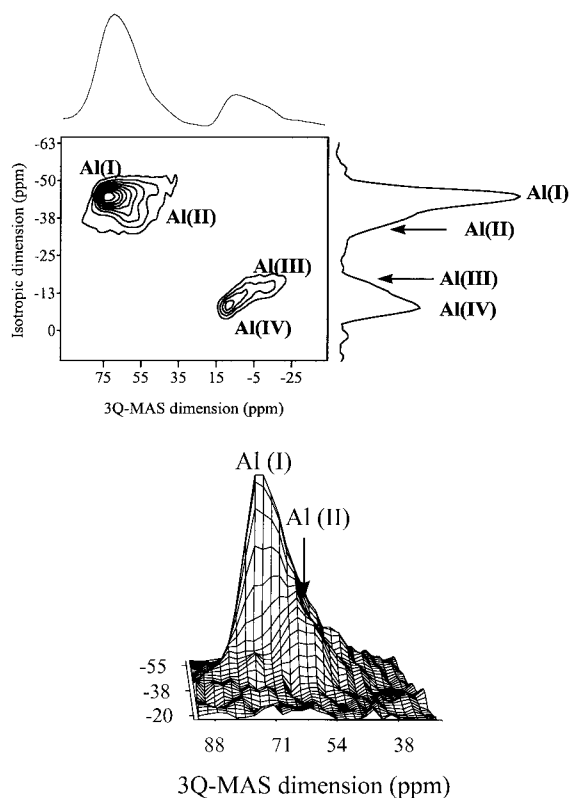


Figure 12. 2D and 3D representations of the ^{27}Al 3Q-MAS NMR spectrum of the sample with C-S-H substituted by aluminum.

The situation is much better with ^{27}Al 3Q-MAS NMR. The 2D and 3D (Figure 12) representations of the substituted C-S-H allow one to identify clearly four sites, two octahedral and two tetrahedral ones. The two octahedral sites Al(III) and Al(IV) might be aluminum in substitution in the C-S-H. However they must be, at least partially, be attributed to AH_3 (Figure 8), which we know by X-ray diffraction to be present in the sample as impurity. The Al(IV) which correspond to the AH_3 site with the lower quadrupole constant exhibits a quadrupolar interaction distribution. This would mean that AH_3 is less crystallized in this C-S-H sample. From that sample, the occurrence of octahedral aluminum in the C-S-H cannot be proved or rejected. Further experiments are in progress.

In the MAS-only spectrum, the line shape of ^{27}Al in tetrahedral sites (Figure 9) could be analyzed as a single line with second-order quadrupolar broadening and/or a distribution of the quadrupolar coupling constant. The projection in the isotropic dimension of the ^{27}Al 3Q-MAS spectrum tetrahedral band (Figure 12) shows that there are in fact two lines, which

however are not well resolved, so that their overlapping makes difficult the determination of the quadrupolar constants of each site. An estimation of δ_1 can however be made. Then a fit with two Lorentzians of the tetrahedral band in the MAS-only spectrum allows one to estimate the position of the shifts $\delta_{1/2}$ of each site. The resulting δ_{iso} and ν_Q for Al(I) and Al(II) are given in Table 1. The two sites have significantly different isotropic chemical shift δ_{iso} . Because of the overlapping of the sites, the quadrupolar frequencies ν_Q are obtained with a low precision (± 0.1 MHz) and are equal within this error. No conclusions can be drawn from those quadrupolar frequencies. Alternately, since for ^{29}Si the silicon bridging tetrahedra lines ($\text{Q}_{2\text{L}}$) appear at lower field than the silicon in nonbridging position (Q_2), it may be expected by analogy, from the measured chemical shifts of ^{27}Al , that the Al(I) site corresponds to the Al-bridging tetrahedra and Al(II) to the Al nonbridging tetrahedra. Aluminum substitution in tetrahedral sites of C-S-H may thus occur in bridging as well as in nonbridging sites.

As the 3Q-MAS projection (Figure 12) and the MAS-only spectrum (Figure 9) are approximately similar, the 3Q-MAS intensities of the two sites can be compared without recalibration by the coherence transfer efficiency. From the line intensities in MQ-MAS spectra, Al(I) clearly appears to be more abundant than Al(II). This indicates that, in the present C-S-H sample, the incorporation of Al would occur preferentially in the bridging sites.

Conclusion

3Q-MAS NMR spectroscopy is a powerful method to increase the resolution of ^{27}Al NMR spectra of cement hydrates. It has allowed us to disentangle with a higher precision the different Al sites. For instance, in C_4AH_{13} , two sites were observed, whereas in previous works the ^{27}Al MAS spectrum was analyzed as a single site with a high distribution. In the C-S-H substituted by aluminum in a alkaline (Na) solution, the ^{27}Al 3Q-MAS spectrum reveals the presence of two sites. Bridging and nonbridging positions in the silicon tetrahedra chains can be substituted by aluminum, with a preference for the bridging site in the C-S-H investigated in this work.

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