Solid-state ^{27}Al and ^{29}Si NMR investigations on Si-substituted hydrogarnets

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Abstract

Partially deuterated $\text{Ca}_3\text{Al}_2(\text{SiO}_4)_{3-x}(\text{OH})_{4x}$ hydrates prepared by a reaction in the presence of D_2O of synthetic tricalcium aluminate with different amounts of amorphous silica were characterized by ^{29}Si and ^{27}Al magic-angle spinning nuclear magnetic resonance (NMR) spectroscopy. The ^{29}Si NMR spectroscopy was used for quantifying the non-reacted silica and the resulting hydrated products. The incorporation of Si into $\text{Ca}_3\text{Al}_2(\text{SiO}_4)_{3-x}(\text{OH})_{4x}$ was followed by ^{27}Al NMR spectroscopy: Si:OH ratios were determined quantitatively from octahedral Al signals ascribed to $\text{Al}(\text{OH})_6$ and $\text{Al}(\text{OSi})(\text{OH})_5$ environments. The NMR data obtained were consistent with the concentrations of the Al and Si species deduced from transmission electron microscopy energy-dispersive spectrometry and Rietveld analysis of both X-ray and neutron diffraction data.

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1. Introduction

The development of new monolithic materials based on mixtures of coarse and medium aggregates (a few millimeters in size) with calcium aluminates (grain sizes lower than 120 μm) and amorphous silica (microspheres <150 nm) is becoming more and more important in a wide scope of applications for furnace lining in metallurgy, petroleum chemistry, clinker production, glass foundries and ceramics [1]. On the other hand, amorphous silica is also used as an additive to ordinary Portland cements [2] for modifying the rheology. This use is very critical since a careful control of

the rheology allows more densely packed and stronger concretes to be obtained. In dealing with this subject it is of paramount importance to know the reactivity of silica with the other components and, although most of the silica does not react chemically, it is necessary to understand how the fraction that actually does behaves. It is known that some silicon species can react with calcium and alumina ionic species in solution to precipitate hydrogarnet-related phases of katoite ($\text{Ca}_3\text{Al}_2(\text{SiO}_4)_{3-x}(\text{OH})_{4x}$, where $3 \leq x \leq 2.67$) [3,4].

Hydrogarnet $\text{Ca}_3\text{Al}_2(\text{OH})_{12}$, the only thermodynamically stable calcium aluminate hydrate formed in calcium aluminate cements, is a quaternary compound that crystallizes in the space group $\text{Ia}3\text{d}$ (230) and displays the cubic unit cell [5–8] $a = 12.55695$ (3) Å, $V = 1986$ Å³ and $z = 8$. The structure of hydrogarnet consists of a three-dimensional framework built up by $[\text{Al}(\text{OH})_6]$ octahedra and $[\text{Ca}(\text{OH})_8]$ dodecahedra. In these compounds, the substitution of 4 $[\text{OH}]^-$ by $[(\text{SiO}_4)]^{4-}$ in grossular garnets was first reported by Cohen-Addad and Ducros [9] using neutron

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diffraction, infrared and nuclear magnetic resonance (NMR) spectroscopy of protons (Fig. 1). The Si incorporation produces intermediate compositions between $\text{Ca}_3\text{Al}_2(\text{OH})_{12}$ and $\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ [9].

Most cementitious phases are poorly crystallized and therefore X-ray powder diffraction cannot provide satisfactory structural information. On the other hand, ^{27}Al and ^{29}Si NMR spectroscopies are useful techniques for analyzing the local structure of both crystalline and amorphous materials. They provide an accurate insight of the first shell neighborhood, namely their atom coordination.

In this work structural sites occupied by Al and Si atoms in hydrogarnets ($\text{Ca}_3\text{Al}_2(\text{SiO}_4)_{3-x}(\text{OH})_{4x}$, where $3 \leq x \leq 2.67$), formed by reaction of tricalcium aluminate with amorphous microspheres of silica, were characterized by ^{27}Al and ^{29}Si magic angle spinning (MAS) NMR spectroscopy. The incorporation of Si into the hydrogarnet's network was investigated from the quantitative analysis of the two signals. The analytical values deduced by NMR were compared with those deduced by neutron diffraction,

X-ray diffraction and transmission electron microscopy (TEM) techniques. Finally, the precursor compounds used were also analyzed with ^{27}Al and ^{29}Si MAS NMR spectroscopy.

2. Experimental

2.1. Preparation and characterization of materials

The chemicals used for the solid-state synthesis of calcium aluminate were aluminum hydroxide hydrate (Aldrich, Milwaukee, WI, USA) and calcium carbonate (CaCO_3 , Merck, Darmstadt, Germany). The tricalcium aluminum oxide $\text{Ca}_3\text{Al}_2\text{O}_6$ was prepared from a stoichiometric mixture of $\text{Al}(\text{OH})_3 \cdot 0.949\text{H}_2\text{O}$ and CaCO_3 . The starting powders were attrition milled with partially stabilized zirconia balls in isopropanol, dried, isostatically pressed and heated in platinum crucibles at 1300°C for 12 h. The samples were prepared by heating them twice with an intermediate grinding in order to ensure chemical homogeneity. The X-ray diffraction pattern matched the cubic $\text{Ca}_3\text{Al}_2\text{O}_6$ phase with no other peaks of impurities. The synthetic polycrystalline powder of $\text{Ca}_3\text{Al}_2\text{O}_6$ was mixed with the required stoichiometric amounts of amorphous silica (Elkem microsilica® 983, Elken Materials, Inc., Pittsburgh, PA, >98% reactive SiO_2 , 150 nm amorphous microspheres) to obtain nominal compositions of $\text{Ca}_3\text{Al}_2(\text{SiO}_4)_{3-x}(\text{OH})_{4x}$, with $x = 0, 0.6, 1.3$ and 2.6 . The time and temperature of synthesis are gathered in Table 1. The finely grinded and homogenized powder mixtures were treated with D_2O at a water:solid ratio by weight of 2 and introduced in a recipient which was kept tightly closed at 40° , 65° and 90°C for several days. Deuterated pastes were sieved to get the 120- μm fraction powder and treated once more with D_2O in a closed vessel for 24 h at the same temperature. This process was repeated several times (7 days at 40° and 65°C and 31 days at 90°C). All resulting powders analyzed by X-ray diffraction displayed the katoite structure [10].

2.2. Diffraction analysis

X-ray diffraction patterns were recorded with a graphite monochromated Cu $K\alpha$ radiation in a Kristalloflex D5000 (Siemens, Germany) diffractometer (Bragg–Brentano geometry) working at 40 kV and 30 mA. Data collection was taken on samples rotating at 15 r.p.m in the interval 0 – 90° (in 2θ). The samples were not rotated in the range 90 – 130° in order to avoid the samples spilling. In both ranges the X-ray patterns were acquired with a step size of 0.03° and a time step of 20 s.

Powder neutron diffraction experiments were carried out using the high-resolution powder diffractometer for thermal neutrons instrument [11] of the Swiss Spallation Neutron Source [12] in the Paul Scherrer Institut (Villigen, Switzerland). Neutron diffraction patterns were recorded in high-intensity mode with $\lambda = 1.8857 \text{ \AA}$ in the (2θ)

Fig. 1. Crystallographic structure of Si-substituted hydrogarnet showing the structural sites of (a) Al and (b) Si.

Table 1
Results of the X-ray and neutron diffraction Rietveld analysis for every target composition

Target composition	Specimen number					
	SH0	SH1	SH2	SH3	SH4	SH5
	$\text{Ca}_3\text{Al}_2(\text{OH})_{12}$	$\text{Ca}_3\text{Al}_2\text{Si}_{0.4}(\text{OH})_{5.2}$	$\text{Ca}_3\text{Al}_2\text{Si}_{2.4}(\text{OH})_{2.4}$	$\text{Ca}_3\text{Al}_2\text{Si}_{1.7}(\text{OH})_{2.4}$	$\text{Ca}_3\text{Al}_2\text{Si}_{2.4}(\text{OH})_{2.4}$	$\text{Ca}_3\text{Al}_2\text{Si}_{2.4}(\text{OH})_{2.4}$
T (°C)/ t (h)	65/168	40/168	40/168	65/168	65/168	90/744
a (Å)	12.5748 ± 0.0004	12.5632 ± 0.0003	12.5474 ± 0.0006	12.5280 ± 0.0006	12.5286 ± 0.0007	12.4947 ± 0.0015
Si occupancy	–	0.04 ± 0.01	0.10 ± 0.01	0.18 ± 0.01	0.18 ± 0.01	0.33 ± 0.01
H	5.88	0.1	–	–	–	–
D	6.12 ± 0.01	11.8 ± 0.3	–	–	–	–
H + D	12	11.9 ± 0.3	11.61 ± 0.04	11.24 ± 0.04	11.30 ± 0.04	10.7 ± 0.5
R_{wp}	2.99	10.40	8.43	8.15	8.64	9.79
R_{B}	9.07	5.84	3.69	2.25	2.36	1.78
R_{F}	6.43	4.78	2.60	1.50	2.94	1.22

The thermal treatment and some values obtained are listed: cell parameter, occupancies of Si, D (when neutron data were available), H and standard statistics indicators of the fitted specimen.

interval 2.45–163° with a step size of 0.05°. In these experiments 5 g portions of sample were inserted into a cylindrical stainless steel tube with an internal diameter of 10 mm and a height of 60 mm. Diffraction patterns were accumulated during ~1 h to obtain 10^6 monitor counts.

2.3. TEM analysis

Microstructural analyses and visual phase identification of the samples were performed by TEM (Hitachi–H7100, Japan) at 125 kV with an energy dispersive spectrometry (EDS) analyzer (Rentec–M-series, Germany) with an acquisition time of 600 s. Powdered samples were dispersed in propan-2-ol and mounted on carbon-coated copper grids.

2.4. NMR measurements

High-resolution MAS NMR experiments were performed at room temperature in a Bruker ADVANCE-400 spectrometer operating at 104.26 MHz (^{27}Al) and 79.49 MHz (^{29}Si). ^{29}Si MAS NMR spectra were recorded after $\pi/2$ pulse irradiation (4 μs) using a 500 kHz filter. ^{27}Al MAS NMR spectra were recorded after $\pi/8$ pulse irradiation (1.5 μs) using 100 kHz and 2 MHz filters. The powdered samples were spun at 12 kHz for ^{27}Al and 5 kHz for ^{29}Si . The number of scans was 400 for silicon and 50 for aluminum. In both cases the time between accumulations was chosen to minimize saturation effects. Quantitative analysis of the ^{29}Si and ^{27}Al MAS NMR spectra was carried out with the Winfit program (Bruker). This program allows the position, line width and intensity of the components to be determined with a nonlinear iterative least-squares method. However, quadrupolar C_Q and η constants had to be determined by a trial and error procedure.

3. Results and discussion

3.1. Neutron diffraction

Structural refinement of five stable hydrates of the katoite series $\text{Ca}_3\text{Al}_2(\text{SiO}_4)_{3-x}(\text{OH})_{4x}$ was undertaken by the

Rietveld method following the strategy and recommendations of McCusker et al. [13]. The zero displacement was corrected by using an NIST Si internal standard. There was a linear dependence between the cell lattice parameter of katoite and the amount of silicon substituted in the crystal structure. Data published by various authors and gathered in the Inorganic Crystal Structure Database [10] were used to obtain this linear relationship. This correlation was introduced as a constraint during the Rietveld refinements. A second constraint for the hydrogen population was also imposed, since it depends on the amount of silicon present in the formula [3].

Both X-ray and neutron data recorded at room temperature were available for some samples. In this case, the amounts of hydrogen and deuterium were refined. The graphics output of these analyses can be seen in Fig. 2. The most relevant parameters deduced from the structural refinements are given in Table 1. The atom positions, thermal factors and site occupations were reasonable in all cases. The reliability R_{B} (Bragg) factors are also included in Table 1.

The first thing noticed was the small amount of silicon incorporated into the katoite structure $\text{Ca}_3\text{Al}_2(\text{SiO}_4)_{3-x}(\text{OH})_{4x}$: the x values obtained ($3 \leq x \leq 2.67$) were much lower than those expected from nominal compositions. Rietveld analysis allowed also the measurement of ionic distances. They agreed with data published in the literature and with the values tabulated by Shannon [14]: 1.895 Å for Al–O, 2.48 Å for Ca–O and 0.94 Å for O–H (Table 2). The variation in tetrahedral T–O distances is shown in Fig. 3a as a function of the Si content in the katoite structure. For comparison, the results reported by other authors for katoite phases are also given in Fig. 3b. The same trend was observed in both: the T–O distances diminished with the amount of Si incorporated in the structure of the katoite (Table 2). Bearing in mind that most of sites that could be occupied by Si were empty, it was not odd that the T–O distances obtained (in the vicinity of 1.95 Å) were quite far from the ideal ones reported by Shannon [14] (1.66 Å). Indeed, the repulsion of atoms around the empty site was responsible for the tetrahedra

Fig. 2. X-ray Rietveld analysis of a $\text{Ca}_3\text{Al}_2\text{O}_6 + 0.24\text{SiO}_2$ composition hydrated for 90 days at 90 °C. It corresponds to the katoite $4\text{Ca}_3\text{Al}_2(\text{SiO}_4)_{0.19}(\text{OH})_{11.24}$.

Table 2
Experimental inter-atomic distances obtained from Rietveld analysis expressed in ångström

Formula	Specimen number					
	SH0	SH1	SH2	SH3	SH4	SH5
	$\text{Ca}_3\text{Al}_2(\text{OH})_{12}$	$\text{Ca}_3\text{Al}_2\text{Si}_{0.04}(\text{OH})_{11.8}$	$\text{Ca}_3\text{Al}_2\text{Si}_{0.10}(\text{OH})_{11.6}$	$\text{Ca}_3\text{Al}_2\text{Si}_{0.18}(\text{OH})_{11.3}$	$\text{Ca}_3\text{Al}_2\text{Si}_{0.18}(\text{OH})_{11.3}$	$\text{Ca}_3\text{Al}_2\text{Si}_{0.33}(\text{OH})_{10.7}$
[VIII]Ca–O (s)	2.456	2.463	2.450	2.449	2.450	2.447
[VIII]Ca–O (l)	2.535	2.521	2.521	2.526	2.517	2.524
[VI]Al–O	1.905	1.924	1.915	1.909	1.911	1.901
[IV](□, Si–O)	–	1.939	1.942	1.940	1.938	1.925
H–O	0.924	0.919	0.907	0.914	0.914	0.903
Bov	1.07	0.90	0.82	0.92	1.00	0.95

Two distances, short and long, are determined for Ca–O. The overall Debye–Waller ($\text{\AA}^2$) factor is also included in the last row.

expansion detected in the structural refinements of the katoite with small amounts of Si.

3.2. TEM

Fig. 4 shows a typical TEM image of hydrated samples. The presence of a significant quantity of unreacted spherical amorphous silica particles was detected in Si-substituted samples. The composition of the spherical amorphous particles and the crystalline cubic grains was analysed by TEM EDS. The stoichiometry obtained corresponded to the averages of ten analyses. Specimen SH0 (pure hydrogarnet) gave the formula $\text{Ca}_{3.0 \pm 0.2}\text{Al}_{2.1 \pm 0.1}(\text{OH})_{12}$, while specimen SH1 gave the formula $\text{Ca}_{3.0 \pm 0.2}\text{Al}_{2.3 \pm 0.2}(\text{SiO}_4)_{0.04 \pm 0.02}(\text{OH})_{11.84}$ and specimen SH5 gave the formula $\text{Ca}_{3.0 \pm 0.1}\text{Al}_{2.0 \pm 0.1}(\text{SiO}_4)_{0.5 \pm 0.2}(\text{OH})_{10}$. These values showed an overestimation of the Si content as compared to those found by Rietveld

analysis (Table 2). The apparent discrepancies are understandable since the TEM technique introduces errors due to the size of the microanalyses area and the presence of small silica particles (<150 nm) around crystalline phases. Since the silicon atomic occupation of the katoite inferred from X-ray diffraction and neutron diffraction Rietveld analyses and TEM EDS was much lower than the target one, it was clear that an amorphous Ca–Si–Al–OH phase had formed. Therefore it was judged necessary to carry out more in-depth NMR analysis.

3.3. NMR

The hydration of the tricalcium aluminate $\text{Ca}_3\text{Al}_2\text{O}_6$ yielded $\text{Ca}_3\text{Al}_2(\text{OH})_{12}$. During this reaction the coordination of Al changed from tetrahedral (AlO_4) to octahedral ($\text{Al}(\text{OH})_6$). It was possible to substitute four OH^- groups

Fig. 3. (a) Comparison between Si-O distances reported by different authors for different katoites and hibschites and those obtained in this work. (b) Si-O distances found in the katoites analysed. Progressive crystal cell shrinkage was observed as silicon entered into the lattice.

Fig. 4. Typical TEM micrographs of a $\text{Ca}_3\text{Al}_2\text{O}_6/\text{SiO}_2$ composition hydrated at 90 °C for 1 week showing cubic $\text{Ca}_3\text{Al}_2\text{O}_6(\text{SiO}_4)_{0.5\pm0.2}(\text{OH})_{10}$ katoite crystals and unreacted silica spheres.

by one Si^{4+} ion in the hydrogarnet structure to form the continuous solid solution $\text{Ca}_3\text{Al}_2(\text{SiO}_4)_{3-x}(\text{OH})_{4x}$. The structural changes associated with the Si incorporation into the hydrogarnet's structure were analyzed.

3.3.1. Precursor phases

Mondal and Jeffrey [15] determined that the crystal structure for $\text{Ca}_3\text{Al}_2\text{O}_6$ was cubic: space group Pa3 (205) with $Z = 24$ and $a = 15.263$ Å. Rings of six AlO_4 tetrahedra (Al_6O_{18}) formed the structure with Ca^{2+} ions holding the rings together. In this compound, the AlO_4 tetrahedra were much less distorted than the CaO_6 octahedra. The structural analysis of $\text{Ca}_3\text{Al}_2\text{O}_6$ indicated the presence of two different crystallographic sites for aluminium cations.

The ^{27}Al ($I = 5/2$) MAS NMR spectra of the starting $\text{Ca}_3\text{Al}_2\text{O}_6$ (Fig. 5a) displayed a broad signal centered at 37 p.p.m. that corresponded to tetrahedral aluminium (denoted Al^{IV}) [16]. A careful study of the central transition revealed the presence of two components. Taking into account the whole spectrum, two components with similar quadrupole coupling constants (C_Q) and asymmetry parameters (η) were found ($C_Q = 8$ MHz and $\eta = 0$ and $C_Q = 8.7$ MHz and $\eta = 0.3$) (see Table 3). The chemical shift values corrected from quadrupolar effects were 88.0 and 86.0 p.p.m. One of these values, 85 p.p.m. ($C_Q = 9.7$ MHz and $\eta = 0.3$), was similar to that reported by Müller et al. [17]. The distortion of the Al tetrahedra was characterized by means of two parameters (Δd and $\Delta\theta$) deduced from experimental crystallographic data according to the equations [23].

$$\Delta d = \sum_i |\ln(d_i/d_0)| \quad (1)$$

$$\Delta\theta = \sum_i |\tan(\theta_i - \theta_0)| \quad (2)$$

where d_0 and θ_0 are average distances and angles and d_i and θ_i are the individual values. The analysis of these parameters given in Table 4 shows that Δd and $\Delta\theta$ increased with the dispersions produced on the Al-O distances and Al-O-Al angles with respect to the mean values [23]. These variations were responsible for the differences observed in the quadrupole constants of the two signals.

3.3.2. Hydrated phases

The structural transformations produced during the hydration of $\text{Ca}_3\text{Al}_2\text{O}_6$ with and without amorphous silica were examined by ^{29}Si and ^{27}Al MAS NMR spectroscopy. During hydration, the Al coordination changed from tetrahedral (AlO_4) to octahedral ($\text{Al}(\text{OH})_6$). As indicated previously it is possible to substitute four OH^- groups by one Si atom in hydrogarnet series.

3.4. ^{27}Al MAS NMR spectroscopy

The hydrated $\text{Ca}_3\text{Al}_2(\text{SiO}_4)_{3-x}(\text{OH})_{4x}$ products obtained by reaction with different amounts of microspheres of silica are shown in Fig. 5. In these spectra peaks corresponding to the tetrahedral Al of $\text{Ca}_3\text{Al}_2\text{O}_6$ have completely disappeared, indicating that hydration of the starting phase was complete. According to structural data reported for $\text{Ca}_3\text{Al}_2(\text{OH})_{12}$, the ^{27}Al MAS NMR spectrum displays one symmetric peak at 12.35 p.p.m. that corresponds to

Fig. 5. ²⁷Al MAS NMR components in spectra of (a) pure Ca₃Al₂O₆ and (b–f) Ca₃Al₂(SiO₄)_{3–x}(OH)_{4x} series. The continuous line corresponds to the actual spectrum, while dotted lines correspond to the NMR components of the simulated spectra. The vertical lines represent isotropic chemical shift values corrected for second-order quadrupolar quadruple interactions.

Table 3
Values obtained after fitting the ²⁷Al MAS NMR spectra

Specimen	Assignment	δ _{iso} ± 0.5 (p.p.m.)	C _Q ± 0.1 (MHz)	Proportions ± 2 (%)
Ca ₃ Al ₂ O ₆	Al ^{IV} (1)	88.0	8.0	57
	Al ^{IV} (2)	86.0	8.7	43
SH0	Al ^{VI} (1)	12.4	0.6	100
SH1	Al ^{VI} (1)	12.2	0.6	92
	Al ^{VI} (2)	5.8		8
SH3	Al ^{VI} (1)	12.3	0.6	65
	Al ^{VI} (2)	4.2		35
SH4	Al ^{VI} (1)	12.3	0.6	57
	Al ^{VI} (2)	4.1		43
SH5	Al ^{VI} (1)	12.2	0.6	44
	Al ^{VI} (2)	4.1		56

In the case of Ca₃Al₂O₆ an asymmetry parameter for Al^{IV}(2) was refined: η = 0.3 ± 0.1. In addition, the relative proportion of every neighborhood is listed.

Table 4
Distortions of aluminum coordination polyhedra

Crystal phase	Site	d (Å)	θ ₀ (°)	Δd (Å)	Δθ ₀ (°)
Ca ₃ Al ₂ O ₆ [15]	Al ^{VI} (1)	1.751	109.4	0.0369	0.55
	Al ^{VI} (2)	1.754	109.5	0.0148	0.66
Ca ₃ Al ₂ (OH) ₁₂	Al ^{VI}	1.908	85.102 94.898	0	0.171

Δd and Δθ were calculated from Eqs. (1) and (2). The values in the last row were deduced from the structural data of this work.

octahedral aluminum surrounded by six OH groups (denoted Al^{VI}(1) in Fig. 5). This signal was scarcely affected by quadrupolar interactions (C_Q = 0.63 MHz and η = 0) (Table 3). This spectrum is similar to that reported in previous works [18–21].

The ²⁷Al MAS NMR spectra of the Ca₃Al₂-(SiO₄)_{3–x}(OH)_{4x} series displayed a major peak centered at 12.3 p.p.m. and a shoulder at around 4.2 p.p.m. (Fig. 5 and Table 3). Both signals were associated with octahedral

Al surrounded by six OH (the $\text{Al}^{\text{VI}}(1)$ signal) and Al surrounded by five OH and one Si (the $\text{Al}^{\text{VI}}(2)$ signal) in the hydrogarnet structure [17]. The appearance of the $\text{Al}^{\text{VI}}(2)$ band supported the formation of Al–O–Si bonds in the katoites studied. The substitution of four OH^- by a $[\text{SiO}_4]^{4-}$ induced a perturbation in the four nearest Al neighbours of the katoite (Fig. 1). The ^{27}Al MAS NMR spectra were deconvoluted using Gaussian/Lorentzian functions. Taking into account that each Si shared four corners with four Al

octahedra (see the structure of Si hydrogarnet in Fig. 1b), the Si content of the sample could be deduced from the ^{27}Al MAS NMR spectra with the expression

$$y = 3 - x = [I\text{Al}^{\text{VI}}(2)]/2 \quad (3)$$

where $I\text{Al}^{\text{VI}}(2)$ represents the relative intensity of the Al component ascribed to Al surrounded by five OH and one Si. For this calculation the integrated intensity of the Al signal had to be normalized to the amount of Al

Fig. 6. ^{29}Si NMR spectra deconvoluted into their components for the $\text{Ca}_3\text{Al}_2(\text{SiO}_4)_{3-x}(\text{OH})_{4x}$ series. (a) Amorphous silica spheres, (b) katoites with nominal $x = 2.6$, (c) $x = 1.3$ and (d) $x = 0.6$.

per structural formula. The amount of Si incorporated into different samples is given in Table 1. In general it was observed that the amount of Si incorporated (0–0.33 per formula unit) was much lower than deduced from nominal compositions. The substitution extent of silica in the katoite was approximately one-tenth of the quantity added according to both NMR and diffraction Rietveld analyses.

3.5. ^{29}Si MAS NMR spectroscopy

The ^{29}Si ($I = 1/2$) MAS NMR spectra of the amorphous silica precursor and $\text{Ca}_3\text{Al}_2(\text{SiO}_4)_{3-x}(\text{OH})_{4x}$ hydrates formed are given in Fig. 6. The spectra in all of the samples analyzed were formed by five peaks at ~ -110 , -99 and -89 p.p.m. and two peaks at -79 p.p.m. (Table 5).

In general the ^{29}Si chemical shifts became more negative with the silicate condensation. Because of this the ^{29}Si spectrum of the amorphous silica displayed a single peak at -110 p.p.m. that was associated with tetrahedral Si in $\text{Q}^4[\text{Si}(\text{OSi})_4]$ environments (Fig. 6a). The intensity of the -112 p.p.m. peak was important in the hydrated compounds, indicating that a considerable part of the silica had not reacted [2]. The peak at approximately -99 p.p.m. corresponded to $\text{Q}^3[\text{Si}(\text{OSi})_3\text{OH}]$ environments at the surface of the activated microspheres of the silica [2,22]. The amount of unreacted silica was estimated from the relative intensity of the -110 and -99 p.p.m. peaks, which were associated with Si atoms in Q^4 environments. Most of the unreacted silica (80%) remained as nanospheres homogeneously mixed with the katoite and the amorphous phase formed during the reaction (see Fig. 4).

The partial dissolution of the silica particles produced depolymerized species that could interact with Ca and Al ions. In this process Q^n species with $n = 0, 1, 2, 3$ and 4 could be formed (a $\text{Si}(\text{OSi})_n(\text{OM})_{4-n}$ environment). Therefore, the two lines detected at around -79.9 ± 0.5 p.p.m.

were assigned to Q^0 species chemically bound to Ca ions $\text{Q}^0[\text{Si}(\text{OAl})_{4-x}(\text{OCa})_x]$. The detection of these species indicated that a part of the dissolved silica had been incorporated into the katoite amorphous precursors (Fig. 6b–f).

The formation of $[\text{SiO}_4]^{4-}$ groups in hydrogarnets was ascribed by the presence of the ^{29}Si NMR peak at -89.5 p.p.m. These signals corresponded to isolated $[\text{SiO}_4]$ groups in $\text{Q}^0(4\text{Al})$ environments. In this compound the Si atoms would share oxygens with four neighboring $\text{Al}(\text{OH})_6$ octahedra. This was consistent with the intensity values deduced from the quantitative analysis of both the ^{29}Si MAS NMR and ^{27}Al MAS NMR analyses. The NMR analyses were in agreement with the Rietveld refinements. The amount of Si substituted in the crystal structure estimated by both techniques is plotted (NMR versus Rietveld) in Fig. 7. Their agreement is remarkably good.

Fig. 7. Correlation of the $[\text{SiO}_4]$ substitution levels deduced by MAS NMR and diffraction Rietveld techniques.

Table 5

Degree of condensation of the silicate tetrahedra and percentage of the different silicon sites obtained from the simulation of the ^{29}Si MAS spectra of the studied samples

Specimen	Phase	Assignment	$\Delta \pm 0.5$ (p.p.m.)	Proportions ± 2 (%)
SH1	Silica	$\text{Q}^4(\text{Si}(\text{OSi})_4)$	-107.5	63
	Silica	$\text{Q}^3(\text{Si}(\text{OSi})_3(\text{OH}))$	-98.1	13
	Amorphous	$\text{Q}^0(\text{Si}(\text{OAl})_{4-x}\text{Ca}_x)$	-79.8	14
	Katoite	$\text{Q}^0(4\text{Al})$	-89.6	10
SH3	Silica	$\text{Q}^4(\text{Si}(\text{OSi})_4)$	-110.0	56
	Silica	$\text{Q}^3(\text{Si}(\text{OSi})_3(\text{OH}))$	-98.8	17
	Amorphous	$\text{Q}^0(\text{Si}(\text{OAl})_{4-x}\text{Ca}_x)$	-79.5	17
	Katoite	$\text{Q}^0(4\text{Al})$	-89.7	10
SH4	Silica	$\text{Q}^4(\text{Si}(\text{OSi})_4)$	-110.5	63
	Silica	$\text{Q}^3(\text{Si}(\text{OSi})_3(\text{OH}))$	-99.5	13
	Amorphous	$\text{Q}^0(\text{Si}(\text{OAl})_{4-x}\text{Ca}_x)$	-79.8	14
	Katoite	$\text{Q}^0(4\text{Al})$	-89.5	10
Unhydrated silica	Silica	$\text{Q}^4(\text{Si}(\text{OSi})_4)$	-110	100

4. Conclusions

The appropriate combination of NMR and Rietveld analyses of the X-ray and neutron diffraction patterns allowed a better understanding of the formation of $\text{Ca}_3\text{Al}_2(\text{SiO}_4)_{3-x}(\text{OH})_{4x}$ hydrates ($0 \leq x \leq 0.33$) during the hydration of $\text{Ca}_3\text{Al}_2\text{O}_6$ in the presence of nanospheres of amorphous silica. Moreover, it was possible to identify intermediate species formed during dissolution of the silica particles. The incorporation of Si into the katoite structure was then followed by NMR and Rietveld techniques. A careful analysis of the katoite by NMR indicated that the incorporation of a small amount of Si ($x < 0.5$ per formula) produced the differentiation of the two Al signals associated with Al(6OH) and Al(5OH,1Si) environments. The quantification of the relative intensities of the two peaks allowed the evaluation of the amount of Si incorporated into the katoite. The amount of silica in the katoite was approximately one-tenth of the nominal silica added, in agreement with diffraction Rietveld analysis.

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