



## Structural characterization of C–S–H and C–A–S–H samples—Part II: Local environment investigated by spectroscopic analyses

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### ABSTRACT

Spectroscopic studies (<sup>1</sup>H, <sup>23</sup>Na and <sup>27</sup>Al MAS NMR and Raman spectroscopy) have been used to characterize three series of C–S–H samples (0.8 < Ca/Si < 1.7): one C–S–H series, one aluminum inserted C–S–H series (named C–A–S–H series), and one sodium and aluminum inserted C–S–H series (named C–N–A–S–H series). Previous Rietveld analyses have been performed on the two first series and have clearly shown that (1) a unique 'tobermorite M defect' structural model allows to describe the C–S–H structure whatever the Ca/Si ratio and (2) the insertion of aluminum into the C–S–H structure led to the degradation of the crystallinity and to a systematic increase of the basal spacing of about 2 Å regardless the Ca/(Si+Al) ratio (at a constant Al/Si ratio of 0.1). Spectroscopic investigations indicate that the main part of the Al atoms is readily incorporated into the interlayer region of the C–S–H structure. Al atoms are mainly inserted as four-fold coordinated aluminates in the dreierketten silicate chain (either in bridging or paired tetrahedra) at low Ca/Si ratio. Four-fold aluminates are progressively replaced by six-fold coordinated aluminates located into the interlayer region of the C–S–H structure and bonded to silicate chains. Investigation of the hydrogen bonding in C–S–H indicates that the main part of the hydrogen bonds is intra-main layer, and thus explains the low stacking cohesion of the C–S–H structure leading to its nanometric crystal size and the OD character of the tobermorite like structures.

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### 1. Introduction

The insertion of Al atom in the C–S–H (calcium silicate hydrate) phase, the main component of Portland cement hydrated paste responsible for cohesion properties and durability, has been extensively studied [1–7]. Due to the lack of long-range ordering, NMR spectroscopy has been employed to characterize C–A–S–H phase (i.e. the Al inserted C–S–H phase) [8]. Indeed solid state <sup>29</sup>Si NMR studies have been performed to investigate the tobermorite-like structure of C–S–H (with a Ca/Si ratio varying between 0.6 and 2.0 for synthetic samples and a Ca/Si ratio close to 1.7 for Portland cement pastes [9–14]) which includes layers of seven-fold coordinated Ca<sup>2+</sup> ions sandwiched in-between dreierketten chains of silicate tetrahedra (three-unit silicate tetrahedra) [12–20]. Results confirm the tobermorite-like structure of C–S–H with the observation of resonance lines coming from silicate

end-groups (Si[Q<sup>1</sup>]:  $\delta \approx -79.5$  ppm) and from silicate tetrahedra taking part in chains as pure Q<sup>2</sup> units (Si[Q<sub>B</sub><sup>2</sup>]:  $\delta \approx -85.9$  ppm for the paired tetrahedra, and Si[Q<sub>B</sub><sup>2</sup>]:  $\delta \approx -82.6$  ppm for the bridging tetrahedra). At low Ca/Si ratio, a Si[Q<sup>3</sup>]:  $\delta \approx -92.5$  ppm has been observed and attributed to linking across the interlayer space of two silicate chains of two adjacent layers, which represents a defect in comparison with the tobermorite structure. An increase in the Ca/Si ratio results in the disappearance of Q<sup>3</sup>, decreasing proportion of Q<sup>2</sup> and increasing proportion of Q<sup>1</sup> up to the complete elimination of the bridging silicon site, leading to a silicate structure only composed of dimers. <sup>27</sup>Al NMR spectroscopy has also been widely used to investigate the Al insertion into C–S–H phase [8,18–24]. Related <sup>27</sup>Al NMR spectra may exhibit diverse resonances from Al in IV-, V- and VI-fold oxygen coordination. Three Al[IV] signals are assigned to three types of aluminum incorporation in the tetrahedra of the dreierketten silicate chain: an Al[Q<sup>3</sup>] bridging site ( $\delta \approx 61$  ppm) across the interlayer [22] or between two dreierketten chains adjacent to the same main calcium oxide plan [24], an Al[Q<sub>B</sub><sup>2</sup>] bridging site charge-balanced by interlayer Ca<sup>2+</sup> ( $\delta \approx 67$  ppm) and a third signal for  $\delta \approx 72$  ppm. The latter resonance was first assigned to an Al[Q<sub>B</sub><sup>2</sup>] bridging site charge-balanced by an interlayer or a surface Al[V]

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and/or Al[VI] [22], and was then attributed to an Al[Q<sub>p</sub><sup>2</sup>] paired site [24]. Significant evidences were obtained (1) to locate the Al[VI] site (resonance at  $\delta \approx 39.9$  ppm) in the interlayer region of the C–S–H structure, potentially as Al<sup>3+</sup> ions substituting for interlayer Ca<sup>2+</sup> ions, and (2) to indicate that aluminum does not enter the Ca<sup>2+</sup> main layer sites. Three Al[VI] resonances have been encountered and described in hydrated Portland cements:  $\delta \approx 13$  ppm for ettringite,  $\delta \approx 11$  ppm for AFm phases and  $\delta \approx 5$  ppm related to C–A–S–H formation. The latter resonance, previously assigned to Al[VI] insertion in the interlayer space of C–S–H [22], has been recently assigned to an amorphous aluminate hydrate associated with the C–A–S–H precipitation [23].

In the first part of the present study [25], Rietveld refinements performed on C–S–H and C–A–S–H series (0.8 < Ca/Si < 1.7) have shown the systematic worsening of the crystallinity and a systematic layer spacing increase of about 2 Å when aluminum is inserted in C–S–H whatever the Ca/Si ratio between 0.8 and 1.7 (as already mentioned in the literature [22,24]). The aluminum insertion in the silicate tetrahedra (Al[IV] signals of the <sup>27</sup>Al NMR spectra) or in the interlayer calcium site (Al[V] and/or Al[VI] signals of the <sup>27</sup>Al NMR spectra) as reported in the literature did not allow to explain such a large increase in the interlayer space. This prompts us to investigate here more precisely the aluminum incorporation into the C–S–H structure (i.e. the highly disordered interlayer region of C–A–S–H) by rationalizing the data obtained from a combination of techniques (<sup>1</sup>H, <sup>23</sup>Na, <sup>27</sup>Al NMR and Raman spectroscopy) over the different substitution domains.

## 2. Experimental

### 2.1. CSH and CASH syntheses

Syntheses of C–S–H and Na-free C–A–S–H samples are described in the first part of the study [25]. The samples studied have been designed by C–S–H<sub>n</sub> and C–A–S–H<sub>n</sub>, with  $n=0.8, 1.0, 1.1, 1.3, 1.5$  and  $1.7$  for, respectively, the Al-free and Al-containing series.

A third series of samples, Na containing C–A–S–H with  $0.8 < \text{Ca/Si} < 1.7$ , have been synthesized in order to examine the correlations between the <sup>23</sup>Na NMR signals and the <sup>27</sup>Al NMR signals. These Na-containing samples have been labeled C–N–A–S–H<sub>n</sub> with  $n=0.8, 1.0, 1.1, 1.5$  and  $1.7$ . Samples from the C–N–A–S–H series were synthesized from silica (Degussa, Aerosil 380), calcium oxide (Aldrich, 99.9% pure) freshly decarbonated 3 h at 900 °C and sodium aluminate NaAlO<sub>2</sub> (Sigma-Aldrich,  $\leq 0.05\%$  total Fe impurities) following the protocol described in [23]. Demineralized and decarbonated water were added to reach a water/solid ratio of 50 and the Al/Si and Na/Si molar ratios were adjusted to 0.1. All the syntheses were stored at 20 °C under N<sub>2</sub> atmosphere for three weeks under stirring in closed polypropylene bottles. They were then filtered under nitrogen and rinsed with acetone. The precipitates were subsequently dried in a desiccator, under slight vacuum, over silica gel, at room temperature. Experimental conditions are summarized in Table 1. The chemical analyses of the filtered solutions in equilibrium with the solid phases show that the amount of sodium incorporated in C–N–A–S–H samples decreases with increasing alumina+silica content.

### 2.2. Analytical techniques

#### 2.2.1. <sup>1</sup>H, <sup>23</sup>Na and <sup>27</sup>Al MAS NMR spectroscopies

High resolution <sup>1</sup>H, <sup>23</sup>Na, and <sup>27</sup>Al MAS NMR spectra were collected on a Bruker 300 instrument operating at 7.04 T, the

**Table 1**  
Starting material amounts for the different syntheses.

	Nominal composition: Ca/Si ratio				
	0.8	1.0	1.1	1.5	1.7
C–N–A–S–H					
CaO (mmol)	39.64	44.85	47.10	54.37	57.25
SiO <sub>2</sub> (mmol)	45.04	40.78	38.93	32.95	30.61
NaAlO <sub>2</sub> (mmol)	4.55	4.15	3.97	3.40	3.17
Water (mL)	265	265	265	265	265
Experimental Ca/(Al+Si) ratio <sup>a</sup>	0.76	0.91	0.99	1.26	1.44
Experimental Ca/Si ratio <sup>a</sup>	0.84	1.00	1.09	1.39	1.58
Experimental Na/Al <sup>a</sup>	0.56	0.30	0.24	0.08	0.08

<sup>a</sup> Calculated from ICP-MS analyses of the filtered solutions after the three weeks of synthesis in polypropylene bottle.

Larmor frequencies being, respectively, equal to 300, 79.39 and 78.20 MHz. 4 mm-diameter zirconia rotors were spun at 10 kHz during the MAS conditions, therefore the central transition ( $+\frac{1}{2}, -\frac{1}{2}$ ) was recorded only.

Single pulse experiment was applied for the three nuclei, and the parameters were optimized for each nucleus. However, the quadrupolar nature of the <sup>23</sup>Na (3/2) and <sup>27</sup>Al (5/2) nuclei required that the flip angle should satisfy the condition  $(I+\frac{1}{2}) \cdot \omega_{\text{RF}} \cdot t_p \leq \pi/6$  where  $\omega_{\text{RF}}$  (rad s<sup>-1</sup>) is the Larmor frequency of the corresponding quadrupolar nuclei and  $t_p$  (s) the pulse time. Small pulse angle of about 10° corresponding to 0.8–1.2 ms pulses were used in the MAS sequence. This was associated to a recycling time of 2 s. Calibration was adjusted with the resonance line of adamantane at 1.7 ppm, NaCl at 0 ppm, and AlCl<sub>3</sub> at 0 ppm for <sup>1</sup>H, <sup>23</sup>Na, and <sup>27</sup>Al, respectively. A collection of 10, 500, and 2000 transients to get a proper signal to noise response was necessary for <sup>1</sup>H, <sup>23</sup>Na, and <sup>27</sup>Al nuclei, respectively. Single pulse experiment is quantitative and therefore the relative nuclei site population was accessible. However, for noninteger quadrupolar nuclei, the central transition is not perturbed by the first order quadrupolar interaction, while the second order is known to broaden the resonance line as well as to shift its position from the isotropic chemical shift. The fast MAS spectrum of the central ( $+\frac{1}{2}, -\frac{1}{2}$ ) is then shifted from the center of gravity by the second order quadrupolar interaction

$$\delta_{\text{QS}(+1/2,-1/2)}^{(2)} = -\frac{3C_Q^2}{40\omega_0^2} \cdot \left[ \frac{I(I+1) - 3/4}{I^2(2I-1)^2} \right] \cdot \left( 1 + \frac{\eta^2}{3} \right)$$

where  $C_Q$  is the quadrupolar coupling ( $C_Q = e^2 \cdot q \cdot Q/h$ , where  $e \cdot q$  is the electric field gradient and  $e \cdot Q$  is the quadrupolar moment of values of  $0.1 \times 10^{28}$  Q/m<sup>2</sup> for <sup>23</sup>Na nuclei and  $0.15 \times 10^{28}$  Q/m<sup>2</sup> for <sup>27</sup>Al nuclei), and  $\eta$  the asymmetry parameter. The isotropic chemical shift position and the quadrupolar frequency  $\nu_Q$  (responsible for  $\delta_{\text{QS}(+1/2,-1/2)}^{(2)}$ ) may be obtained by measurements either at different magnetic fields [23] or of the central and of the sideband patterns of the satellite transitions [26]. The shift of the central band is then given by

$$\delta_{\text{QS}(+1/2,-1)}^{(2)} = -\frac{\nu_Q^2}{30\nu_0^2} [I(I+1) - 3/4] \times 10^6$$

which can be further calculated for <sup>23</sup>Na and <sup>27</sup>Al by

$$\delta_{\text{QS}(+1/2,-1/2)}^{(2)} = -\frac{\nu_Q^2}{10\nu_0^2} \times 10^6$$

and

$$\delta_{\text{QS}(+1/2,-1/2)}^{(2)} = -\frac{8\nu_Q^2}{30\nu_0^2} \times 10^6,$$

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