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The role of Al in cross-linking of alkali-activated slag cements

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Abstract

The structural development of a calcium (sodium) aluminosilicate hydrate (C-(N-)A-S-H) gel system, obtained through the reaction of sodium metasilicate and ground granulated blast furnace slag, is assessed by high resolution ²⁹Si and ²⁷Al MAS NMR spectroscopy during the first 2 years after mixing. The cements formed primarily consist of C-(N-)A-S-H gels, with hydrotalcite and disordered alkali aluminosilicate gels also identified in the solid product assemblages. Deconvolution of the ²⁷Al MAS

24 NMR spectra enables the identification of three distinct tetrahedral Al sites, consistent with the ²⁹Si
25 MAS NMR data, where Q³(1Al), Q⁴(3Al) and Q⁴(4Al) silicate sites are identified. These results suggest
26 significant levels of cross-linking in the C-(N-)A-S-H gel and the presence of an additional highly
27 polymerized aluminosilicate product. The mean chain length, extent of cross-linking and Al/Si ratio of
28 the C-(N-)A-S-H gel decrease slightly over time. The de-cross-linking effect is explained by the key role
29 of Al in mixed cross-linked/non-cross-linked C-(N-)A-S-H gels, because the cross-linked components
30 have much lower Al-binding capacities than the non-cross-linked components. These results show that
31 the aluminosilicate chain lengths and chemical compositions of the fundamental structural
32 components in C-(N-)A-S-H gels vary in a way that is not immediately evident from the overall bulk
33 chemistry.

34

35 **Keywords:** Aluminosilicate gel, calcium silicate hydrate (C-S-H), blast furnace slag, ²⁹Si and ²⁷Al MAS
36 NMR, nanostructural evolution

37

38 1. Introduction

39 Many modern cements contain Portland cement (PC) blended with Al-containing supplementary
40 cementitious materials (SCMs).¹ The solid binders in these cements contain calcium aluminosilicate
41 hydrate (C-A-S-H) gels with moderate Ca content ($\text{Ca}/(\text{Al}+\text{Si})\approx 1$) rather than the more Ca-rich
42 ($1.5\leq\text{Ca}/\text{Si}\leq 2$) calcium silicate hydrate (C-S-H) gels that form as the primary reaction product in neat
43 PC materials. To reduce complexities related to secondary phases in these materials, studies of C-A-S-
44 H chemistry have often focused on laboratory-synthesized pastes with compositions in the CaO-SiO₂-
45 Al₂O₃-H₂O(-Na₂O/K₂O) system,²⁻⁵ and on alkali-activated slag (AAS) cements.⁶⁻⁸

46 AAS cements are now finding industrial application in the production of concretes with high
47 mechanical performance, low life cycle CO₂ emissions relative to PC-based materials, and good
48 durability.^{9; 10} Understanding the durability of such concretes remains a key scientific challenge,

49 because durability is closely related to the chemistry and the pore network geometry of the solid
50 binder.¹¹ Therefore, elucidation of the binder chemistry, and in particular the details of the C-A-S-H
51 gel which is the key space-filling and strength-giving component, is essential.

52 It has been shown that the processes of incorporation of Al and alkalis in C-S-H gels are directly
53 related,^{12; 13} meaning that calcium (alkali) aluminosilicate hydrate (C-(N-)A-S-H) gels are formed in
54 systems that are rich in both Al and alkalis (denoted 'N' to reflect the activators used in AAS, which
55 are typically Na-based). This is also consistent with the increase in alkali uptake in systems with lower
56 Ca/Si ratios through a valence compensation mechanism,¹² in which the charge imbalance created by
57 Al/Si substitution or silanol deprotonation is balanced by positively-charged species in the interlayer.

58 The variable molecular structure of C-(N-)A-S-H gel, as well as the nanoparticulate nature of the gel
59 formed through agglomeration of structural units around several nanometers in size,¹⁴ results in a
60 structure with limited long-range ordering. Elucidation of the structure of this phase in AAS cements
61 and blended PC/Al-containing SCM materials challenging because of this high level of structural
62 disorder, and also because the C-(N-)A-S-H gel almost always coexists with unreacted remnant
63 precursor particles and secondary reaction products. Thus, important questions remain about its
64 molecular chemistry, including the following possibilities:

- 65 i) the presence of cross-linked chains;¹⁵⁻¹⁸
- 66 ii) Al substitution into paired tetrahedra;^{3; 5; 19}
- 67 iii) the role and importance of five-coordinated Al (denoted Al[5]).^{2; 4; 20}

68 Various studies applying ²⁹Si magic angle spinning nuclear magnetic resonance (MAS NMR) and ²⁷Al
69 MAS NMR spectroscopy to silicate-activated slag cements have been published,^{7; 8; 15} but where
70 deconvolution of the spectra has been undertaken, the contribution of unreacted slag is not always
71 distinguished. Quadrupolar lineshapes are also not always used in deconvolutions of ²⁷Al MAS NMR

72 spectra, which greatly affects the calculated contributions of the different identifiable site
73 environments.

74 Therefore, this study presents detailed ^{29}Si and ^{27}Al MAS NMR analysis of a sodium silicate-activated
75 slag cement as a function of the time of curing, to clarify the complex relationship that exists between
76 the chemical composition and nanostructure of C-(N-)A-S-H gels, and the solid phase assemblage in
77 these materials. The spectra are deconvoluted with consideration of remnant unreacted slag particles
78 and quadrupolar coupling effects, enabling quantification of the chemistry of the reaction products,
79 with secondary phases identified by X-ray diffraction (XRD). Application of a model that represents
80 the C-(N-)A-S-H gel as a mixture of non-cross-linked and cross-linked tobermorite-like structures¹⁶
81 provides further information regarding the structure and chemical composition of this phase.

82

83 **2. Experimental**

84

85 **2.1. Materials and sample preparation**

86 Granulated blast furnace slag supplied by Zeobond Pty Ltd. (Australia) was used in this study, with a
87 chemical composition as listed in Table 1, specific gravity of 2800 kg/m^3 , Blaine fineness of $410 \text{ m}^2/\text{kg}$,
88 and $d_{50} = 15 \text{ }\mu\text{m}$ according to laser granulometry (Malvern Mastersizer).

89 The alkali activator was prepared by dissolution of solid NaOH pellets (Sigma-Aldrich, Australia) into D
90 grade (PQ, Australia) sodium silicate, to reach a solution modulus ($\text{SiO}_2/\text{Na}_2\text{O}$ molar ratio) of 1.0. The
91 overall molar $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ ratio was fixed at 0.50, including Na supplied by the activator and the slag,
92 corresponding to an overall activator dose of $8 \text{ g Na}_2\text{SiO}_3/100 \text{ g slag}$. Water was added to the activator
93 to reach a water/binder (w/b) ratio of 0.40, which was then allowed to cool to room temperature prior
94 to preparation of the specimens. Paste specimens were cured in sealed bags at 23°C until testing.
95 Samples were crushed by hand before analysis.

96

97 **2.2. Tests conducted**

98 XRD was conducted using a Bruker D8 Advance instrument with Cu K α radiation and a nickel filter. The
99 tests were conducted with a step size of 0.020°, for a 2 θ range of 5° to 70°.

100 Solid-state ²⁹Si MAS NMR spectra were collected at 119.1 MHz on a Varian VNMRS-600 (14.1 T)
101 spectrometer using a probe for 4 mm o.d. zirconia (PSZ) rotors and a spinning speed (ν_R) of 10.0 kHz.
102 The ²⁹Si MAS experiments employed a pulse width of 4 μ s, a relaxation delay of 20 s, and 4096 scans.
103 Solid-state ²⁷Al MAS NMR spectra were acquired at 156.3 MHz on the same instrument for the
104 unreacted slag and samples cured for 1-180 days, with a pulse width of 0.5 μ s, a relaxation delay of 2
105 s, and at least 1000 scans. All spectra were collected with a tip angle of 51°. Additional ²⁷Al MAS NMR
106 spectra were acquired at 104.2 MHz on a Varian VNMRS 400 (9.4 T) spectrometer for the unreacted
107 slag and the sample cured for 2 years with $\nu_R = 14$ kHz, a pulse duration of 1 μ s, recycle delay of 0.2 s
108 and 7000 repetitions. ²⁹Si chemical shifts are referenced to external tetramethylsilane (TMS), and ²⁷Al
109 chemical shifts are referenced to external 1.0 M aqueous Al(NO₃)₃ via internal referencing using the
110 hydrotalcite peak at $\delta_{iso} = 9.68$ ppm (the isotropic chemical shift), using the parameters $C_Q = 1.2$ MHz
111 and $\eta_Q = 0.8$ as determined for a pure hydrotalcite sample (S.A. Walling and S.A. Bernal, unpublished
112 data) and the calculation method reported in ²¹.

113 Deconvolutions of the ²⁹Si MAS NMR spectra were performed using the minimum number of
114 component peaks needed to describe the spectra. The spectra were manually fitted with Gaussian
115 functions, with the full width at half height (FWHH) of each component peak constrained to be <10
116 ppm, and peaks assigned to connectivity states based on information available in the literature for
117 cements,^{13; 22} zeolites,²³ and silicate-activated slag cements.²⁴ Peak positions and widths for each
118 identified species were held constant throughout the deconvolution process. The component peaks

119 assigned to the remnant slag were rescaled vertically by a single factor in each spectrum, to provide
120 the appropriate lineshape in the corresponding regions of the spectra.

121 ²⁷Al MAS NMR spectra were deconvoluted manually using Dmfit²⁵ and the (Czjzek) Gaussian Isotropic
122 Model^{26; 27} to model quadrupolar peak shapes. The secondary reaction products identified by XRD
123 were quantified in the spectra using component peaks consistent with the literature.^{20; 28} Quadrupolar
124 coupling parameters (C_Q) from the literature were used to define peak shapes, as outlined in section
125 3.3. Full details regarding spectral quantification are provided in Appendix A. Isotropic chemical shifts
126 (δ_{iso}) were calculated for the peaks in the deconvoluted spectra using the method described in ²⁰, using
127 the observed chemical shift (δ_{obs}) values determined here.

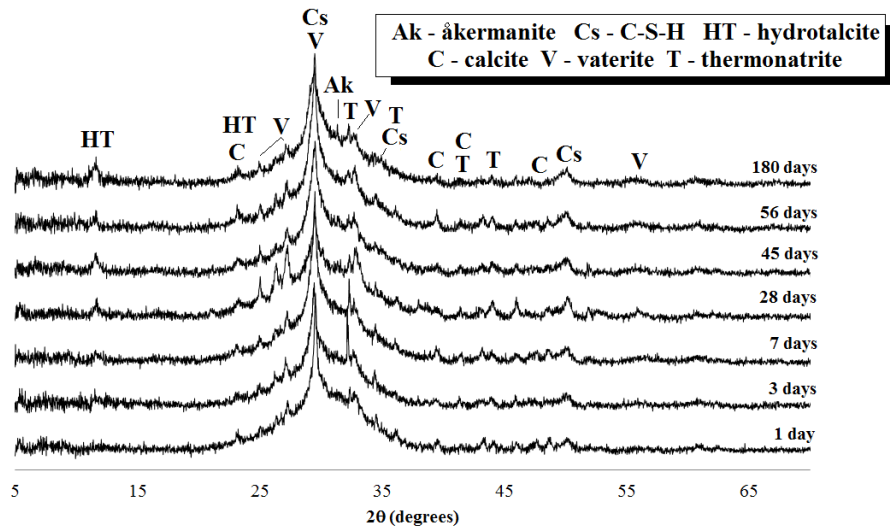
128

129 **3. Results and discussion**

130

131 **3.1. X-ray diffraction**

132 The XRD results are presented in Figure 1. There is a small quantity of åkermanite ($\text{Ca}_2\text{MgSi}_2\text{O}_7$,
133 PDF#00-035-0592) in the remnant slag.²⁴ Peaks corresponding to a poorly crystalline tobermorite-like
134 C-S-H type gel are observed (similar to $\text{Ca}_5(\text{Si}_6\text{O}_{16})(\text{OH})_2$, PDF#01-089-6458), consistent with the
135 literature for sodium silicate-activated slag cements.^{24; 29; 30} Hydrotalcite ($\text{Mg}_6\text{Al}_2(\text{CO}_3)(\text{OH})_{16}\cdot 4\text{H}_2\text{O}$,
136 PDF#00-041-1428) is also identified as a reaction product, which is consistent with other studies^{6; 24;}
137 ³⁰⁻³³ of AAS with significant magnesium content. The increase in intensity of the main hydrotalcite peak
138 ($11.4^\circ 2\theta$) with increasing time of curing, and similarly the peak of the C-S-H type gel at $29.5^\circ 2\theta$, are
139 consistent with the activation reaction continuing with age.



140

141 **Figure 1.** Cu K α diffractograms of the Na₂SiO₃-activated slag cement as a function of curing time.

142

143 Minor traces of calcite (PDF#01-083-0577) and vaterite (PDF#01-074-1867), along with thermonatrite

144 (Na₂CO₃·H₂O, PDF#01-072-0578), are associated with slight atmospheric carbonation of the

145 specimens during sample preparation and analysis.

146

147 3.2. ²⁹Si MAS NMR spectroscopy

148 The ²⁹Si MAS NMR spectrum of the unreacted slag (Figure 2) is in good agreement with results for a

149 melilite-type glass,³⁴ consistent with the identification of åkermanite by XRD in the slag used in this

150 study. The activation of the slag precursor results in the formation of at least three intense bands at -

151 80 ppm, -83 ppm and -86 ppm in the ²⁹Si MAS NMR spectra (Figure 2), which are assigned to Q¹, Q²(1Al)

152 and Q² sites respectively in the C-(N-)A-S-H gel.^{7; 17; 22; 24; 35}

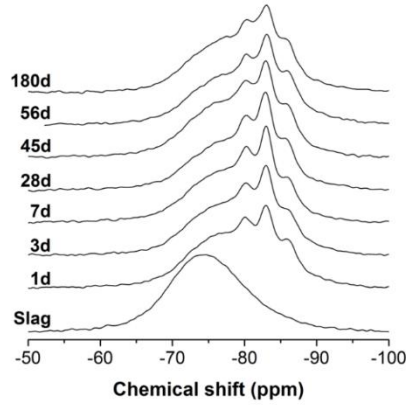


Figure 2. ^{29}Si MAS NMR spectra of the Na_2SiO_3 -activated slag cement as a function of curing time.

A reduction in the intensity of the band corresponding to the remnant slag is observed, which is attributed to the progress of the activation reaction. A Q^0 site at -74 ppm and an additional Q^1 site at -78 ppm (Figure 3 and Appendix B), distinct from the site at -80 ppm, were assigned because the lineshapes of the experimental spectra in the less negative chemical shift region (> -80 ppm) could not all be matched using a single peak attributed to the remnant slag, or to any two out of the three aforementioned components, under the deconvolution constraints applied here.

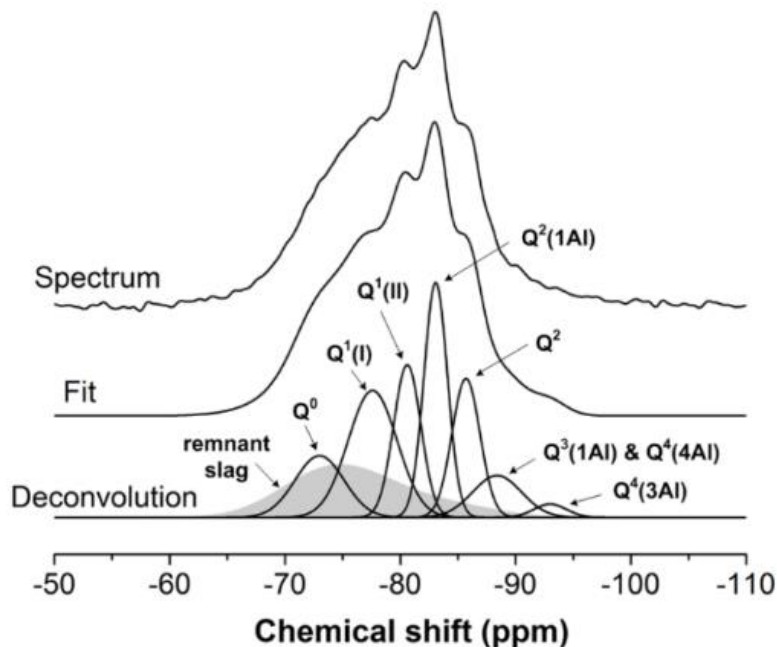
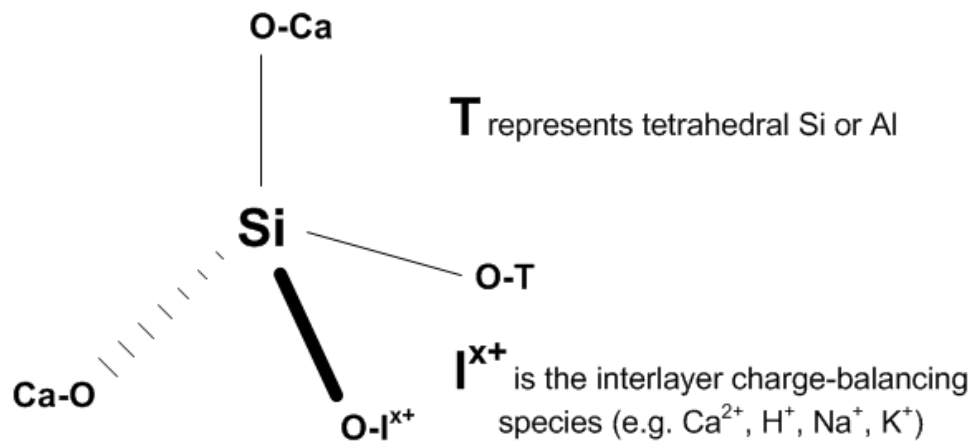


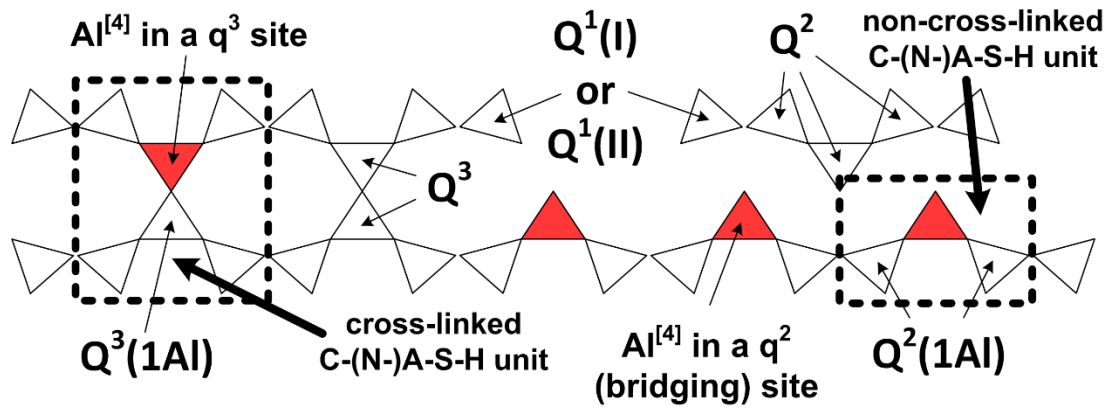
Figure 3. Deconvoluted ^{29}Si MAS NMR spectrum of the Na_2SiO_3 -activated slag cement cured for 180 days. The dark grey band represents the contribution of the remnant slag, which is directly scaled from the spectrum collected for the unreacted slag. Deconvolutions of the spectra obtained at the other ages studied are given in Appendix B.

168 The identification of two non-equivalent Q¹ environments in the binder is consistent with molecular
 169 dynamics studies of non-isolated C-S-H gels, which identified significant differences between the
 170 shielding behavior (and hence chemical shifts) of Q¹ sites charge-balanced by Ca²⁺ or H⁺ (Figure 4).³⁶
 171 Charge-balancing by Na⁺ is also likely in the systems studied here. There are many possible
 172 combinations of potential charge-balancing species for Q¹ sites; these are represented in the
 173 deconvolutions by two Gaussian peaks as this is the smallest number of peaks which can adequately
 174 represent this region of the spectra, while acknowledging that there are in fact many more chemically
 175 distinct sites than this within the material. For the purposes of the analysis, these peaks are labelled
 176 Q¹(I) and Q¹(II), where it is likely that Q¹(I) at -78 ppm corresponds generally to sites connected to
 177 charge-balancing atoms (e.g. H⁺, Na⁺) with less strong positive charges than those associated with
 178 Q¹(II) at -80 ppm (e.g. Ca²⁺). It is also noted that the differences in calculated chemical shift values for
 179 Q² units as a function of charge-balancing species are much less pronounced,³⁶ supporting the
 180 assignment of a single site for structurally-similar Q² species in the deconvolutions. The site
 181 environments marked in Figure 3 are shown in Figure 5.



182 **Figure 4.** Illustration of the variety of charge-balancing species which can bind to a Q¹ site in C-(N-)A-
 183 S-H gel, leading to multiple peaks in the spectra. The Ca species are located in the Ca-O sheets.
 184

185



186
 187 **Figure 5.** Schematic representation of cross-linked and non-cross-linked chain structures which
 188 represent the generalized structure of C-(N)-A-S-H type gels. The red and white tetrahedra are
 189 aluminate and silicate species respectively.

190

191 Significant non-zero intensity at approximately -91 ppm becomes apparent at 56 and 180 days of
 192 curing (Figure 3 and Appendix B). This signal is assigned in part to $Q^4(3Al)$ and $Q^4(4Al)$ in a disordered
 193 aluminosilicate product, tentatively proposed here to resemble an alkali aluminosilicate (hydrate) (N-
 194 A-S(-H)) gel, and in part to $Q^3(1Al)$ units in C-(N)-A-S-H gel. In the deconvolutions here, a combined
 195 band for $Q^4(4Al)/Q^3(1Al)$ and a peak for $Q^4(3Al)$ are positioned at -89 ppm and -93 ppm respectively,
 196 consistent with a recent structural model and interpretation of ^{29}Si MAS NMR results,¹⁶ without
 197 precluding the presence of a small concentration of Q^3 units that could also be present at
 198 approximately -93 ppm in AAS cements.^{5, 15} These assignments are also chosen because this is the
 199 minimum number of peaks that can satisfactorily fit the lineshape of the spectra in this chemical shift
 200 range.

201 Recently,¹⁶ a generalized model for Al-substituted, alkali charge-balanced cross-linked and non-cross-
 202 linked tobermorite-like structures, the 'Cross-linked Substituted Tobermorite Model' (CSTM), was
 203 developed and applied to describe the C-(N)-A-S-H gels present in AAS cements. It was found that a
 204 mixture of cross-linked and non-cross-linked tobermorite-like C-(N)-A-S-H and established secondary
 205 product phases could not fully explain the chemistry of the sodium-silicate activated slag binder alone,
 206 due to the inherent structural constraints of C-(N)-A-S-H gels, suggesting the presence of an additional

207 Al-containing activation product. If this product contains aluminosilicate species contributing to the
208 intensity of the -89 ppm and -93 ppm bands in ^{29}Si MAS NMR spectra, these are most likely $\text{Q}^4(4\text{Al})$
209 and $\text{Q}^4(3\text{Al})$ units respectively and the additional product is probably a N-A-S(-H) gel with $\text{Si}/\text{Al} \leq 1.2$.³⁷
210 Therefore, the assignment of the -93 ppm peak to $\text{Q}^4(3\text{Al})$ in a N-A-S(-H) gel, rather than Q^3 in C-(N-)A-
211 S-H, is necessary to satisfy the structural constraints of mixed non-cross-linked/cross-linked
212 tobermorite-like C-(N-)A-S-H gels.¹⁶

213 The small band at -89 ppm (Figure 3) increases slightly in intensity with curing time. This peak is
214 attributed to cross-linked $\text{Q}^3(1\text{Al})$ silicate sites in the C-(N-)A-S-H gel, as well as $\text{Q}^4(4\text{Al})$ in the N-A-S(-
215 H) gel, which is again consistent with the structural model and interpretation of ^{29}Si MAS NMR results
216 recently proposed by Myers et al.,¹⁶ and with previous studies on sodium silicate-activated and sodium
217 carbonate-activated slag cements.^{17; 24; 32; 38} It is necessary here to attribute part of this band to $\text{Q}^4(4\text{Al})$,
218 because the inclusion of $\text{Q}^4(3\text{Al})$ sites into the ^{29}Si MAS NMR spectral deconvolution results requires
219 the presence of additional Q^4 type units; there is no aluminosilicate gel which consists solely of $\text{Q}^4(3\text{Al})$
220 sites.³⁷ It was previously shown³⁷ that Al-rich ($\text{Si}/\text{Al} \leq 1.2$) geopolymers contain almost exclusively
221 $\text{Q}^4(3\text{Al})$ and $\text{Q}^4(4\text{Al})$ units. This strongly supports the inclusion of $\text{Q}^4(3\text{Al})$ and $\text{Q}^4(4\text{Al})$ into the ^{29}Si MAS
222 NMR spectral deconvolutions here, and indicates that AAS cements may contain disordered
223 nanoparticulate, possibly zeolite-like, products similar to the N-A-S(-H) gels formed through activation
224 of low-calcium aluminosilicate precursors.^{39; 40} This assignment is also consistent with the observation
225 of zeolites in some AAS cements after extended curing periods.⁴¹⁻⁴³ The assigned $\text{Q}^4(3\text{Al})$ and $\text{Q}^4(4\text{Al})$
226 peaks may alternatively be attributed to $\text{Q}^4(m\text{Al})$ -containing aluminosilicate gels formed through
227 degradation of C-(N-)A-S-H during superficial carbonation of the specimen,²⁴ however the XRD results
228 (Figure 1) do not show the systematic increase in carbonation with curing time needed for full
229 consistency with this assignment ($\text{Q}^4(m\text{Al})$ sites are only apparent at 56 and 180 days here).

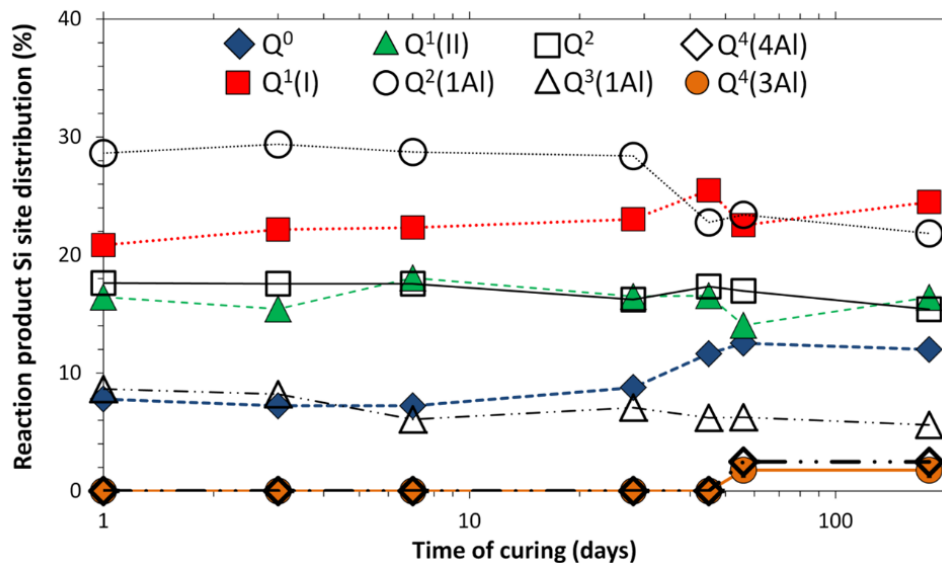
230 Quantification of ^{29}Si sites, determined through deconvolution of the ^{29}Si MAS NMR spectra as a
231 function of curing duration, is reported in Table 2, with full deconvoluted spectra presented as

232 Supporting Information in Appendix B. As much as 54% of the slag is seen to have reacted within the
233 first day of curing, and 77% after 56 days, assuming congruent dissolution of the slag and complete
234 uptake of the silica supplied by the activator into the solid binder (Electronic Supporting Information,
235 Appendix A). The reaction extent of the slag identified by this method is greater than was determined
236 by SEM image analysis for slag particles (of unspecified fineness) reacted with a $\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O}$ activator
237 (~ 3 g Na_2O equivalent/100 g slag) at $w/b = 0.40$ and 23°C ,¹⁸ which gave hydration degrees of
238 approximately 40% at 1 day and 55% at 56 days. Similar or lower extents of reaction have been
239 observed for AAS cements activated at 20°C using sodium silicate and NaOH solutions (~ 3 g Na_2O
240 equivalent/100 g slag),⁴⁴ and in water-activated blended slag/PC materials,⁴⁵ suggesting that the slag
241 precursor used here is more reactive under alkaline activation conditions compared to the slags used
242 in those studies.

243 A single band was fitted for Q^2 sites despite the known ~ 2 ppm difference between Si present in paired
244 (Q^2_{p}) environments relative to bridging (Q^2_{b}) sites within C-S-H type gels,⁵ because assigning peaks for
245 both Q^2_{b} and Q^2_{p} sites would lead to an unconstrained deconvolution procedure.

246 Significant amounts of $\text{Q}^2(1\text{Al})$ are present, indicating high levels of Al substitution in the C-(N-)A-S-H
247 gel. The presence of $\text{Q}^3(1\text{Al})$ units also shows that the C-(N-)A-S-H gel is significantly cross-linked.
248 Constant non-zero quantities of $\text{Q}^4(3\text{Al})$ and $\text{Q}^4(4\text{Al})$ sites are resolved at 56 and 180 days of curing.
249 Quantification of the $\text{Q}^4(4\text{Al})$ site was performed assuming that the additional N-A-S(-H) gel only
250 contains $\text{Q}^4(3\text{Al})$ and $\text{Q}^4(4\text{Al})$ units at an Si/Al ratio of 1.2, and the remainder of the intensity of the
251 peak at -89 ppm was assigned to $\text{Q}^3(1\text{Al})$. This Si/Al ratio was selected as it is at the upper end of the
252 range in which an aluminosilicate gel would be comprised almost entirely of $\text{Q}^4(3\text{Al})$ and $\text{Q}^4(4\text{Al})$
253 units,^{37,46} a higher Si/Al ratio would also require the presence of $\text{Q}^4(2\text{Al})$ sites, and these are not
254 evident in the spectra here. Full details regarding the assignment of the bands at -93 ppm and -89 ppm
255 are provided in Electronic Supporting Information, Appendix C.

256 The evolving structure of the C-(N-)A-S-H gel is represented in Figure 6, by normalizing the
 257 contributions of reaction products to sum to 100%.



258
 259 **Figure 6.** Deconvolution results of the ²⁹Si MAS NMR spectra, normalized to the total intensity of the
 260 reaction products.
 261

262 The normalized ²⁹Si MAS NMR spectral deconvolutions (Figure 6) show that the relative concentrations
 263 of the Q¹(II) and Q² sites do not vary greatly from 1 to 180 days of curing. An increasing trend in the
 264 relative concentrations of Q⁰ and Q¹(I) sites, and a decreasing trend in the relative concentrations of
 265 Q²(1Al) and Q³(1Al) sites, are observed over the entire range of curing ages studied. The increasing
 266 prevalence of Q¹(I) sites, and the corresponding reduction in the concentrations of Q²(1Al) and Q³(1Al)
 267 units, are associated with the gradual transformation of the C-(N-)A-S-H gel to structures with lower
 268 mean chain length (MCL; see section 3.4) and increasing secondary product formation (Figure 1 and
 269 section 3.3) as the time of curing increases. This reduction in MCL can also potentially be reconciled
 270 with the relative increase in percentage of the bands at -74 ppm (tentatively assigned to Q⁰ here) if
 271 these peaks represent surface-bound Q⁰ units, as increasing the relative surface area of C-(N-)A-S-H
 272 gel can be consistent with a reduction in MCL. The decreasing trend in the concentration of Q³(1Al)
 273 sites (in cross-linked C-(N-)A-S-H gel) is also consistent with the observed decreasing relative
 274 percentage of Q²(1Al) sites, because a reduction in Q³(1Al) necessitates a lower concentration of

275 Q²(1Al) (Figure 5). Therefore, these results indicate that the degree of cross-linking of the C-(N-)A-S-H
276 gel decreases over time, which is to some extent a counterintuitive result, and which will be explored
277 in more detail in section 3.4 below.

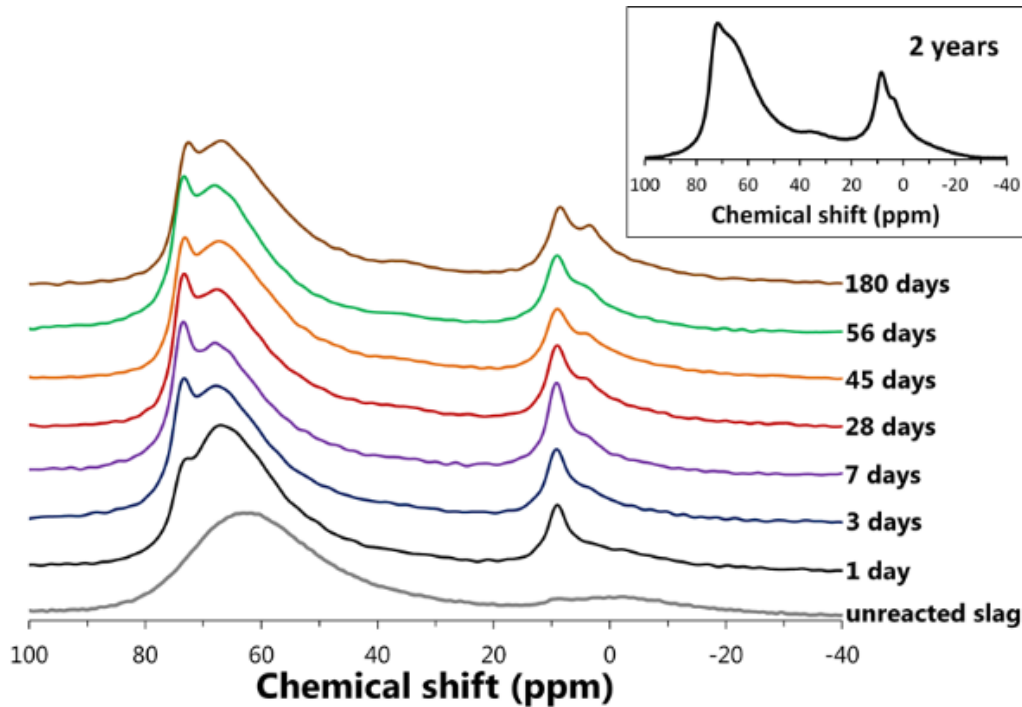
278 The Q⁰ site at -74 ppm is assigned to partially hydrated silicate monomers or Q⁰ components of the
279 remnant slag that have not reacted congruently without precluding the possibility that Q¹(1Al) species
280 contribute to a small fraction of this peak. The presence of Q¹(1Al) in the ²⁹Si MAS NMR spectra would
281 imply Al substitution in paired tetrahedral sites in the C-(N-)A-S-H gel, given that tetrahedral site
282 vacancies only occur in the bridging position (as described by 3n-1 chain length models for C-(N-)A-S-
283 H⁴⁷). Al substitution into paired sites is not expected because atomistic simulations of Al-substituted
284 pentameric chains in environments representative of 14 Å tobermorite,⁴⁸ in sheets representing 14 Å
285 tobermorite,¹⁹ and in isolated chains,⁴⁹ have shown significant energetic preferences for Al
286 substitution in bridging sites instead. Deconvolutions of the ²⁹Si MAS NMR spectra have also been
287 performed without including Qⁿ components related to Al substitution into paired sites, because
288 Q¹(1Al) units are not often observed in published ²⁹Si MAS NMR spectra of calcium silicate hydrate-
289 based gels,^{2; 7; 17; 22; 50} and also because inclusion of these additional Qⁿ components (Q¹(1Al), Q²(2Al)
290 and Q³(2Al) species) would lead to an underconstrained deconvolution procedure. This band at -74
291 ppm has been observed previously in sodium silicate-activated slag cements,¹⁸ where (similar to the
292 conclusion reached here) it was assigned to Q⁰ units, but no strongly established assignment for this
293 peak to a specific site environment within the AAS cement phase assemblage currently exists.

294

295 **3.3. ²⁷Al MAS NMR spectroscopy**

296 Three distinct Al environments (Al[4], Al[5] and Al[6]) are observed in the ²⁷Al MAS NMR spectra
297 (Figure 7), at $\delta_{obs} = 52-80$ ppm (i.e. the observed chemical shift), 30-40 ppm and 0-20 ppm,
298 respectively.²³ The profiles of the experimental spectra remain similar as the duration of curing
299 increases, but some variation in all three environments is observed between 1-180 days, including:

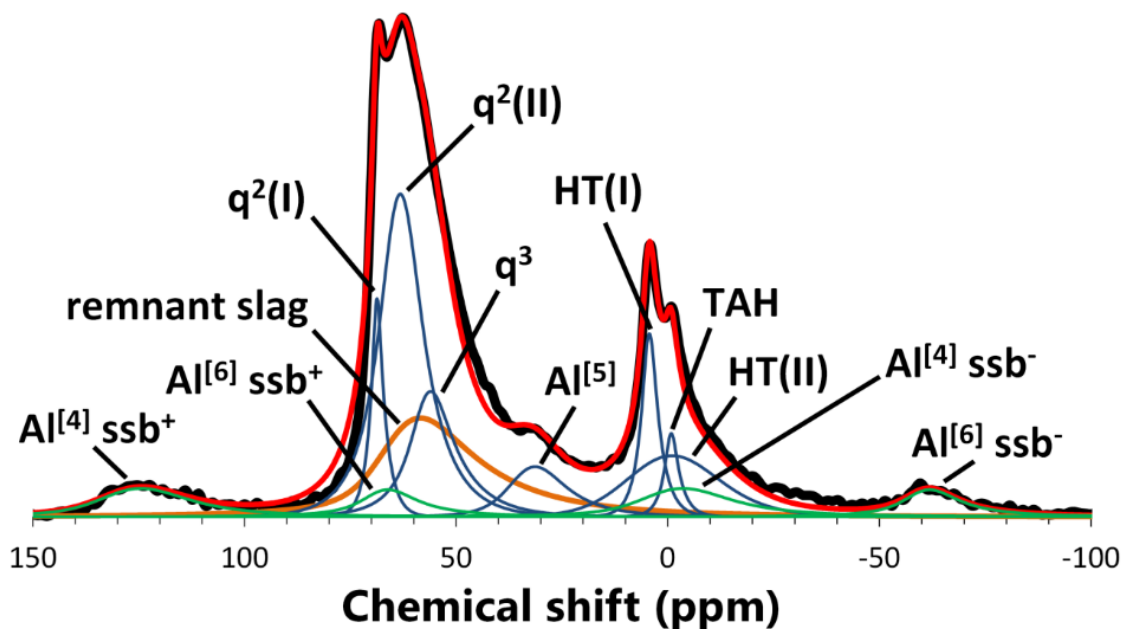
- 300 i) formation of two distinct Al[4] sites at $\delta_{obs} = 74$ ppm and 68 ppm, which is consistent with
 301 the dissolution of the slag and the formation of aluminosilicate reaction products;
 302 ii) an increase in the concentration of Al[5] sites, and a sharpening of the peaks
 303 corresponding to Al[5] with increasing curing time; and
 304 iii) the increased sharpness and intensity of the Al[6] peak at $\delta_{obs} = 4$ ppm.



305 **Figure 7.** ^{27}Al MAS NMR spectra of the Na_2SiO_3 -activated slag paste up to 180 days of curing (14.1 T,
 306 $\nu_R=10$ kHz) and the spectrum for the sample cured for 2 years (9.4 T, $\nu_R=14$ kHz).
 307
 308

309 The four-coordinated Al environments are assigned to the remnant slag particles in the AAS cement,
 310 according to the spectrum of the unreacted slag, and also to C-(N-)A-S-H gel. Three distinct Al sites in
 311 the C-(N-)A-S-H gel are identified at $\delta_{obs} = 74$ ppm, 68 ppm and 62 ppm ($\delta_{iso} = 75$ ppm, 68 ppm and 62
 312 ppm respectively), in agreement with the literature.^{2; 3; 5} The peaks present in the Al[6] region are
 313 assigned to hydrotoalcite at $\delta_{obs} = 9.3$ ppm and 5.9 ppm ($\delta_{iso} = 9.68$ ppm and 9.1 ppm respectively),^{28; 51}
 314 which is consistent with the observation of this phase in the XRD results (Figure 1), as well as the third
 315 aluminate hydrate (TAH) at $\delta_{obs} = 3.9$ ppm ($\delta_{iso} = 4.6$ ppm). Contributions from TAH are evident because
 316 the sharp lineshape of the $\delta_{obs} \approx 4$ ppm peak cannot be described as hydrotoalcite alone.

317 The quadrupolar coupling parameters used to describe the component peak shapes for the reaction
 318 products in the ^{27}Al MAS NMR deconvoluted spectra and the quantified site fractions for these phases
 319 are reported in Table 3 and illustrated in Figure 8 for the sample cured for 180 days. Full spectral
 320 deconvolutions and fits for each sample are supplied in the Supporting Information. Accurate
 321 descriptions of the quadrupolar coupling effects 27 in these phases are typically absent in the alkali-
 322 activated cement chemistry literature (where Gaussian/Lorentzian peak shapes are often assumed,
 323 even for quadrupolar nuclei), despite the importance of the quadrupolar coupling parameter in
 324 determining the component peak shapes and hence intensities, although quadrupolar effects have
 325 been accounted for in analysis of ^{27}Al MAS NMR spectra for hydrated PC-based materials $^{27, 52}$ and
 326 laboratory synthesised C-A-S-H. 5 It is therefore noteworthy that the ^{27}Al MAS NMR spectral
 327 deconvolutions presented here provide a greatly enhanced description of the experimental spectra.
 328 The proposed peak assignments (where the q^n notation for Al sites is equivalent to the Q^n notation for
 329 Si sites 53) are also consistent with the phases identified through XRD (Figure 1).



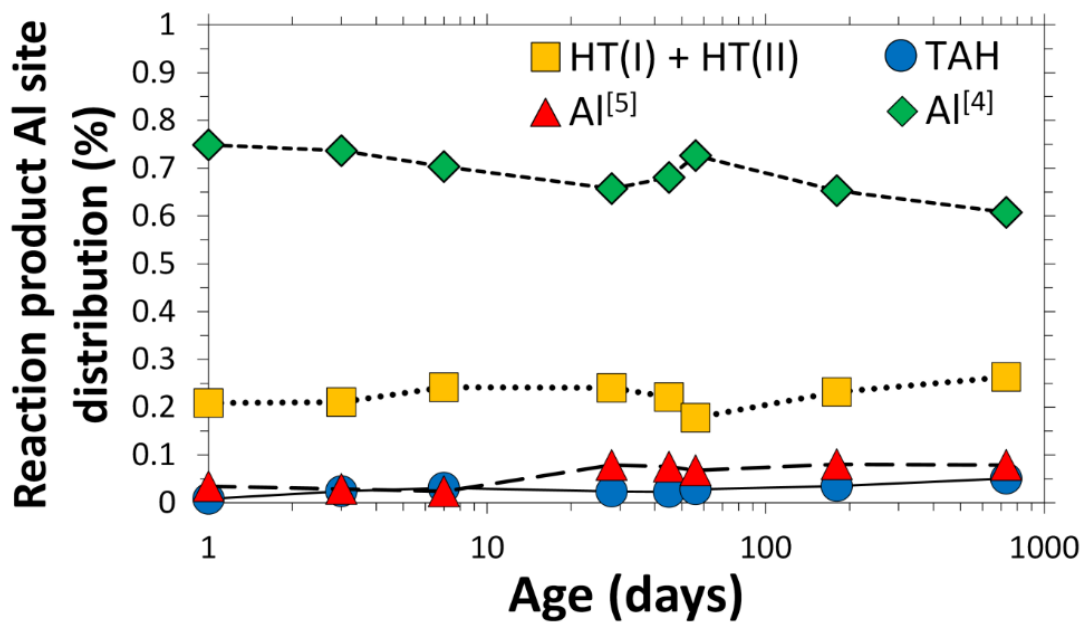
330
 331 **Figure 8.** Deconvoluted ^{27}Al MAS NMR spectrum of the Na_2SiO_3 -activated slag paste cured for 180
 332 days (14.1 T, $\nu_R=10$ kHz). The contribution of the remnant slag is directly scaled according to the
 333 extent of reaction defined from the ^{29}Si MAS NMR spectra. The green sub-peaks are spinning
 334 sidebands, and the red line is the sum of the deconvoluted components of the spectrum.
 335 Deconvolutions of the spectra obtained at other ages are provided in Appendix B.

337 The ^{27}Al MAS NMR deconvolution results (Table 3) show that hydrotalcite is the dominant Al[6]-
338 containing phase at all ages, which is consistent with the prominent reflections for this phase in the
339 XRD results (Figure 1). Contributions from hydrotalcite are represented by two asymmetric peaks here
340 (marked as HT(I) and HT(II) in Figure 8 and Table 3), to match the known spectrum of this phase.^{28; 51}
341 Here, the HT(II) site ($\delta_{iso} = 9.1$ ppm) is assigned specifically to octahedral Al in hydrotalcite that are
342 coordinated to CO_3^{2-} as the interlayer charge-compensating anion,²⁸ whereas the HT(I) site ($\delta_{iso} = 9.68$
343 ppm) is assigned to contain contributions from octahedral Al bonded to OH^- in addition to CO_3^{2-} .
344 Despite careful handling and preparation to minimise carbonation of the paste specimen, the XRD
345 results (Figure 1) do show that the samples were slightly carbonated, and recent results by Bernal et
346 al.³³, which suggest that carbonation of hydrotalcite occurs preferentially to the other reaction
347 products in AAS cements, indicates that the hydrotalcite phases formed here may contain carbonate
348 species. The deconvolution results show that the intensity of the HT(II) band is generally greater
349 relative to the HT(I) peak at advanced ages of curing, which is also consistent with the assignment
350 made here because it is reasonable to expect that the specimens are slightly more carbonated at later
351 times of curing. However, the isotropic chemical shift of the reference HT(I) peak and the HT(II) band
352 are 2-3 ppm lower than the reported values of $\delta_{iso} = 11.8$ ppm²⁸ and $\delta_{iso} = 11$ ppm,⁵¹ meaning that this
353 assignment cannot be made unequivocally.

354 The q^2 aluminate species at $\delta_{obs} = 74$ and 68 ppm are assigned to two different local environments,
355 $q^2(\text{I})$ and $q^2(\text{II})$ respectively, with lower electron density in the $q^2(\text{I})$ site. The $q^2(\text{I})$ peaks are significantly
356 narrower (Figure 8), suggesting more ordered environments in these sites. Earlier studies have
357 assigned this site to Al substituted into paired tetrahedra in C-A-S-H;⁵ however, this site has been left
358 to the more general $q^2(\text{I})$ assignment here, analogously to the $Q^1(\text{I})$ and $Q^1(\text{II})$ silicate sites discussed
359 above. The peak widths of the specific site types are also likely to be affected by the disorder of the
360 aluminosilicate chains in C-(N-)A-S-H gel.⁵⁴ The $q^2(\text{II})$ site is assigned to Al[4] in bridging sites of the
361 aluminosilicate chains in C-(N-)A-S-H gel (Figure 5).^{5; 55}

362 The deconvolutions show significant intensity at chemical shifts corresponding to q^3 (and possibly q^4)
 363 coordinated Al ($\delta_{iso} = 62$ ppm), suggesting high levels of cross-linking in the C-(N)-A-S-H gel. This is
 364 consistent with the literature for silicate-activated slag cements.^{32; 38} It is expected that this site
 365 contains overlapping contributions from q^3 units with different charge-balancing environments,
 366 similar to the situation discussed above for the $q^2(I)$, $q^2(II)$, $Q^1(I)$ and $Q^1(II)$ sites, and potentially also
 367 from q^4 sites. These are expected given the assignment of $Q^4(3Al)$ and $Q^4(4Al)$ silicate units in the ^{29}Si
 368 MAS NMR spectral deconvolutions. However, quantification of q^4 sites in the deconvoluted ^{27}Al MAS
 369 NMR spectra has not been performed here because the deconvolution becomes underconstrained
 370 with the inclusion of an additional q^4 peak.

371 The evolving nature of the Al environments in the AAS cement can be illustrated by normalizing the
 372 reaction product intensities to 100% and removing the contributions attributed to the remnant slag
 373 component (Figure 9), comparable to Figure 6 describing Si environments. The relative intensities
 374 assigned to the q^3 (and possibly q^4) and q^2 sites, and the HT(I) and HT(II) sites, have also been combined
 375 in Figure 9 because these site environments are not yet well defined in AAS cements.



376
 377 **Figure 9.** Deconvolution results for the ^{27}Al MAS NMR spectra normalized to the total intensity of the
 378 reaction products as a function of the time of curing. Samples aged for 1-180 days were measured at
 379 14.1 T, $\nu_R=10$ kHz, and the sample cured for 2 years was measured at 9.4 T, $\nu_R=14$ kHz.
 380

381 In general, the normalized ^{27}Al MAS NMR spectral deconvolution results (Figure 9) show that as curing
382 time increases, the relative percentage of Al[4] environments in the solid binder decreases and the
383 combined relative intensity of the HT peaks remain approximately constant. The intensity of the TAH
384 and Al[5] peaks increase as a function of curing time. Here, Al[5] is tentatively assigned to interlayer
385 species in the C-(N-)A-S-H gel that charge-balance the aluminosilicate chains present in this phase.^{2; 20;}
386 ⁵⁶ The increased amount of this component at 28 days and later in the ^{27}Al MAS NMR spectra is
387 consistent with experimental ^{27}Al MAS NMR spectra of AAS cements,^{6; 8} laboratory-synthesised C-(N-
388)A-S-H gels,^{2; 3} and PC-based materials.^{20; 56; 57}

389 No clear contributions from AFm or hydrogarnet are observed in the ^{27}Al MAS NMR spectra, which is
390 consistent with the absence of prominent reflections corresponding to these phases in the XRD results
391 (Figure 1). These results indicate that the solid phase assemblage varies only slightly between 1 day
392 and 2 years of curing (noting again that the effect of the extent of reaction has been removed from
393 these data), with the exception of the appearance of a small amount of N-A-S(-H) gel at 56 days and
394 later, as discussed in section 3.2.

395

396 **3.4. Characterisation of the C-(N-)A-S-H gel**

397 The deconvoluted ^{29}Si MAS NMR spectra (Table 2) are analyzed using the CSTM structural description
398 of cross-linking in tobermorite-type gels,¹⁶ to characterize the chemistry and structure of the C-(N-)A-
399 S-H gel formed here (Table 4).

400

401 Fixed values of interlayer calcium content ($\omega=\varphi=0.25$) were used in the model to match the average
 402 binder composition (Ca/Si and Ca/(Al+Si)) of this AAS cement measured by environmental scanning
 403 electron microscopy with energy-dispersive X-ray spectroscopy (ESEM-EDS) as a function of curing
 404 time.¹⁶ The structure of the C-(N-)A-S-H gel is mostly cross-linked between 1-180 days, despite the low
 405 apparent intensity of the Q³(1Al) component in the deconvoluted ²⁹Si MAS NMR spectra (Table 2). The
 406 Al/Si ratio of the C-(N-)A-S-H gel decreases slightly as curing time increases, reflecting the reduction in
 407 the relative Q²(1Al), Q³(1Al) and Al[4] site percentages (Figures 6 and 9). The decreasing fraction of
 408 the cross-linked component of the gel at later ages is a consequence of the relative reduction in
 409 Q³(1Al) sites and the formation of the additional disordered (Q⁴ and possibly q⁴ containing) activation
 410 product at extended ages. A similar decreasing trend in MCL is found with increasing curing time,
 411 indicating that the cross-linked phase fraction – so also the intensities of the Q³(1Al) sites and the
 412 formation of the additional Q⁴-containing product – are the key parameters influencing the extent of
 413 polymerization of the partially cross-linked C-(N-)A-S-H gels characterized here. The Ca/Si ratio of the
 414 binder was not found to increase from 7 to 56 days by ESEM-EDS,¹⁶ in support of this analysis. The
 415 percentage of Al in the cross-linked component of the gel is between 40-60 % at all curing times, which
 416 suggests that Al substitutes into both cross-linked and non-cross-linked components of C-(N-)A-S-H
 417 gels without a clear preference for either structural type.

418 The percentages of Al in the cross-linked gel components are calculated according to eq.(1):

$$419 \quad \% Al_{[C]} = 100 \frac{(Al/Si)_{[C]} [Q^1 + Q^2(1Al) + Q^2 + Q^3(1Al) + Q^3]_{[C]}}{\sum_k ((Al/Si)_k [Q^1 + Q^2(1Al) + Q^2 + Q^3(1Al) + Q^3]_k)} \quad (1)$$

420 where the subscripts [C] and [NC] represent the cross-linked and non-cross-linked components of the
 421 C-(N-)A-S-H gel respectively, $k \in \{[C],[NC]\}$, the Qⁿ site fractions are taken from the ²⁹Si MAS NMR
 422 spectral deconvolution results (Table 2), and (Al/Si)_[C] and (Al/Si)_[NC] are defined by eqs.(2-3):

423
$$(Al/Si)_{[C]} = \frac{Q^3(1Al)}{Q^1 + Q^2 + Q^2(1Al) + Q^3 + Q^3(1Al)} \quad (2)$$

424
$$(Al/Si)_{[NC]} = \frac{(\frac{1}{2})Q^2(1Al)}{Q^1 + Q^2 + Q^2(1Al)} \quad (3)$$

425 Maximum partitioning of Q^1 units into the cross-linked component of the gel ($\eta \rightarrow \eta_{max}$) was specified
 426 because the MCL and Al/Si ratio of this phase are similar (MCL \approx 10 and Al/Si \approx 0.11) at all values of η
 427 that satisfy the structural constraints of the gel,¹⁶ for the C-(N-)A-S-H gel formed here. Partitioning of
 428 Q^1 sites can be defined differently (e.g. specifying the minimum value of η that satisfies the structural
 429 constraints of the gel), but as long as the method used is consistent, the structural trends obtained
 430 from the CSTM are the same. Hence the trends related to the structure of the C-(N-)A-S-H gel, rather
 431 than the absolute values, are the key targets for analysis. The choice of η does not affect the calculated
 432 overall Al/Si ratio of the C-(N-)A-S-H gel or the concentration of Al in the cross-linked component of
 433 the gel.

434 A strong link between the Al content and MCL of the C-(N-)A-S-H gel is found by distinguishing the
 435 cross-linked and non-cross-linked components of the gel (Table 4). This is a consequence of the low
 436 capacity of cross-linked C-(N-)A-S-H structures to incorporate Al, as illustrated by Figure 5: only one in
 437 each six tetrahedral sites in cross-linked C-(N-)A-S-H units can accommodate Al, compared to one in
 438 three tetrahedral sites in non-cross-linked C-(N-)A-S-H units. The data in Table 4 indicate that if the
 439 average Al/Si ratio of the C-(N-)A-S-H gel is significantly greater than 0.11 (the Al/Si ratio of Al-
 440 saturated, MCL = 10 cross-linked tobermorite), then the non-cross-linked chain structures are
 441 significantly more polymerized and Al-rich than the C-(N-)A-S-H gel as a whole, because these
 442 structures must incorporate all of the remaining Al. Therefore, small variations in the overall Al/Si ratio
 443 of the C-(N-)A-S-H gel can lead to major structural and chemical changes in the non-cross-linked
 444 component of C-(N-)A-S-H gels, meaning that significant variations in the structure and chemistry of
 445 the C-(N-)A-S-H gel can be expected in AAS cements of superficially similar composition.

446

447 **3.5. Perspectives**

448 This new understanding of C-(N-)A-S-H gel further highlights the importance of a fundamental
449 scientific approach to the design and formulation of modern cement materials. The relationship
450 between structure and Al content in C-(N-)A-S-H may be important in determining the mechanical and
451 thermodynamic properties of blended PC/Al-containing SCM materials and alkali-activated cements.
452 The results presented here strongly indicate that single-phase structural representations of C-(N-)A-S-
453 H gel are insufficient to accurately characterize the chemical composition and structure of this phase;
454 multi-phase models for C-(N-)A-S-H gels^{15; 58} should be used to describe these materials.

455 However, because the CSTM does not embody a description of the Q⁴-containing disordered
456 aluminosilicate phase, separate quantification is needed. Here, this phase is discussed as resembling
457 an intimately-mixed zeolite-like phase similar to the N-A-S(-H) gels formed through the alkali-
458 activation of low-calcium aluminosilicate precursors,³⁹ which was quantified from the ²⁹Si MAS NMR
459 spectral deconvolutions, enabling use of the CSTM to fully characterise the structure and chemistry of
460 the C-(N-)A-S-H gel formed here. It may also possibly be described as a degradation product of
461 carbonated C-(N-)A-S-H gel, although the application of multinuclear NMR techniques to better
462 distinguish the Qⁿ(mAl) environments in the solid binder seems to be essential in further refining the
463 understanding in this area. The identification of this disordered aluminosilicate phase also indicates a
464 need to understand the structural relationship(s) of this phase in the solid binder, as it is known that
465 the phase stability of calcium-deficient sodium-aluminosilicate gels and C-(N-)A-S-H gels differ
466 significantly.⁵⁹

467

468 **4. Conclusions**

469 Spectroscopic and diffractometric analysis of the nanostructural development of a sodium silicate-
470 activated slag cement up to 180 days of curing shows the presence of a dominant C-(N-)A-S-H gel, with
471 hydrotalcite and TAH secondary products. Five-coordinated Al, tentatively assigned to interlayer
472 charge-balancing species in the C-(N-)A-S-H gel, was also observed at all ages.

473 Application of the 'Cross-linked Substituted Tobermorite Model', describing mixed cross-linked/non-
474 cross-linked tobermorite-like structures, showed decreasing trends in the MCL, extent of cross-linking
475 and Al/Si ratio of the C-(N-)A-S-H gel over time. The C-(N-)A-S-H gel was highly cross-linked despite the
476 low relative intensity of Q³(1Al) sites, and an additional highly-polymerized aluminosilicate phase,
477 containing Q⁴(3Al) and Q⁴(4Al) sites and proposed here to potentially resemble the nanocrystalline
478 products found in calcium-deficient sodium-aluminosilicate hydrate ('geopolymer') gels, was required
479 for consistency with the spectra collected at later ages. This has important implications for
480 understanding the durability of AAS cement-based materials, as the phase stabilities of geopolymer
481 gels and C-(N-)A-S-H gels are known to differ significantly. The chemical and structural nature of the
482 C-(N-)A-S-H gel varied significantly across a relatively narrow range of chemical compositions. A
483 complex relationship exists between the Al content and the extent of polymerization of the C-(N-)A-
484 S-H gels, due to the lower relative capacity of cross-linked C-(N-)A-S-H to structurally incorporate Al.
485 Increasing the Al content of cross-linked C-(N-)A-S-H gels may not necessarily induce increased
486 polymerization.

487 These results, and the methods for analysis of ²⁹Si and ²⁷Al MAS NMR spectra developed here, will
488 have significant implications for the ways in which AAS cements and blended PC/Al-containing SCM
489 materials are described, understood and modeled.

490

491 **5. Supporting information**

492 Additional material is provided as Electronic Supporting Information: the quantification procedure for
493 the ²⁷Al MAS NMR spectra is provided in Appendix A; deconvoluted ²⁹Si MAS NMR spectra (Figure S1)
494 and deconvoluted ²⁷Al MAS NMR spectra (Figures S2 and S3) are presented in Appendix B; and detailed
495 discussion regarding the deconvolutions of bands at -93 ppm and -89 ppm in the ²⁹Si MAS NMR spectra
496 is provided in Appendix C.

497

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504

505

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