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Effect on fresh C-S-H gels of the simultaneous addition of alkali and aluminium

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ABSTRACT

Reducing Portland cement content in cementitious binders offers a means to address the adverse environmental impacts of Portland cement manufacture. This paper investigates the impacts on hydration product chemistry of partially replacing Portland cement with alkali-activated aluminosilicates. Here, short-term effects of soluble alkali and aluminium, likely to be available in an alkali-activated system, on the structure of synthetic C-S-H gels are assessed. .C-S-H gels (synthesized at pH values of over 13) were mixed with different concentrations of aluminium nitrate and sodium hydroxide. The gels were characterized by FTIR, TEM/EDX and XRD 72 h later. The results showed that both alkali and aluminium increased the degree of silicate polymerisation in the C-S-H gels and precipitated a crystalline calcium aluminosilicate phase.

1. Introduction

In recognition of the adverse environmental impacts of Portland cement manufacture, increasing research effort is being directed towards alternative binder systems, including those with reduced Portland cement content. Increasing the proportion of supplementary cementitious materials (SCMs) such as fly ash is limited by the ability of the diluted Portland cement fraction to 'activate' the SCM. However, one promising direction is to consider alkali activation of cement–fly ash mixes with very high ash contents [1,2].

The chemistry of alkali-activated aluminosilicates has featured increasingly in the materials literature in the last 10 years and it has been established that the principle hydration product (binder) is a three-dimensional alkaline aluminosilicate gel (N-A-S-H) [3]. This is in contrast to the two-dimensional C-S-H gel [4] characteristic of Portland cement hydration products. Alonso and Palomo [5,6] and van Deventer et al. [7] observed that the precipitation of both gels is possible in alkali-activated blends made with metakaolin and $Ca(OH)_2$ but thermodynamically incompatible phases are commonly found to co-exist in cementitious systems due to diffusion limitations in maturing pastes. This paper seeks to establish the compatibility relationships between the different gel types by enhancing the interaction (encouraging equilibrium) between reactive constituents. In this case, synthetic C-S-Hs are brought into intimate contact with alkaline solutions containing aluminate species. In a previous similar study [8], the effect of high concentrations of alkaline oxides to C-S-H gel structures was found to increase the degree of silicate polymerisation (increasing Q^2) in the gel, even in the very early stages of reaction.

Aluminate species are also expected to enhance polymerisation due to their tendency to form bridging tetrahedra between silicate units [9–11]. Faucon et al. [12], proposed that 4-co-ordinated aluminium replaces the silicon in both the bridging and paired tetrahedra in the drierkette chains of C-S-H gel but Taylor had previously reported that aluminium only replaces silicon in bridging tetrahedra [4]. This was subsequently confirmed by Andersen et al. [13,14] and Sun et al. [11].

The influence of alkali concentration also appears to be important. Previous studies on alkali-activated slags and other systems, indicate that bridging of tetrahedra extend to three-dimensional structures rather than just two, the implication being that the increased linkages between tetrahedra is promoted by the higher alkali concentrations and the consequent increased levels of hydrolysis of the aluminosilicate. For example, Fernandez Jimenez et al., observed the presence of Q^3 silicate species in gels arising from alkali activation of slag, which appeared to be favoured by the presence of aluminium in bridging position [15–17].

The above [11–16] studies addressed the effect of the aluminate in mature C-S-H gels. Alkali activation of Portland cement–aluminosilicate blends is likely to initiate changes to hydration products at much earlier ages and so the present study seeks to investigate the effect of aluminate in the early reaction stages (within 72 h).

2. Experimental

2.1. C-S-H gel synthesis

Three C-S-H gels were prepared with target Ca/Si ratios of 1.9. This ratio was chosen to be typical of Ca/Si in C-S-H in Portland cement

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hydration products. $Ca(NO_3)_2 \cdot 4H_2O$ solution (200 ml of a 0.19 M) was added drop by drop to a solution of $Na_2SiO_3 \cdot 5H_2O$ (200 ml; 0.1 M) and NaOH (20 ml;10 M); deionized, decarbonated water was used throughout. The solution was stirred constantly during synthesis at a temperature of <5 °C. Pure nitrogen was streamed through the flask during synthesis to prevent carbonation. After the gel precipitated, the mix was stirred for 24 h. It was then left to stand at laboratory temperature, 20–25 °C (for about 2 h), until two clearly differentiated phases formed; a precipitate and a supernatant solution. The supernatant was removed and replaced by the same volume of fresh deionized, decarbonated water to remove the excess sodium and nitrate ions. All the preceding operations were conducted inside an AtmosBag,[1] i.e., in a controlled nitrogen atmosphere to prevent possible carbonation.

2.2. C-S-H gel with 8-M NaOH and $Al(NO_3)_3$. Effect of simultaneously adding sodium and aluminium

The effect on C-S-H of the simultaneous addition of sodium and aluminium was studied in two of the three gels synthesized; the third gel was used as the control (gel NC). NaOH (8M) and $Al(NO_3)_3$ (0.4 M) were mixed with the C-S-H gels in a controlled nitrogen atmosphere within an AtmosBag for 24 h. The volumes of solution (see Table 1) were calculated to ensure that the SiO_2/Al_2O_3 ratio was kept constant at 1 and the Na_2O/SiO_2 ratio was either 2 or 4 (gels NA2 and NA4, respectively). Nitrates were removed by rinsing products with freshly deionised, decarbonated water for a further 24 h. Seventy two hours after adding the alkali and aluminium solutions, a sample of suspended solid was filtered through a Büchner funnel (in an N_2 atmosphere) and vacuum-dried in a desiccator prior to analyses.

2.2.1. Analyses

The FTIR spectra were obtained with an ATIMATT-SON FTIR-TM series spectrophotometer on specimens prepared by mixing 1 mg of sample with 3000 mg of KBr. Spectral analysis was performed at a resolution of 4 cm^{-1}, over the range from 4000 to 400 cm^{-1}.

A JEOL 200EX TEM microscope was used for the TEM studies, while EDX analysis was performed with a LINK AN10/855 analyzer. XRD data were obtained using a Bruker D8 Advance powder diffractometer. A Bruker Avance-400 NMR spectrometer was used for NMR studies with TMS and $Al(H_2O)_6^{3+}$ as references for ^{29}Si and ^{27}Al respectively. The ^{29}Si resonance frequency was 79.5 MHz and the spinning rate was10 KHz. Spectra were obtained after irradiation of samples with a π/2 pulse (5 μs). The ^{27}Al resonance frequency was 104.3 MHz and the spinning rate 10 KHz.

3. Results and discussion

3.1. Effect of simultaneously adding alkali and aluminium to C-S-H gels. FTIR analysis

Prior to aluminate and alkali additions, the three C-S-H gels synthesized were characterized with FTIR techniques. Spectrum analysis showed that the three were identical, exhibiting the same vibration bands, primarily the absorbances characteristic of C-S-H gels. The vibration bands for gel NC (control sample) are shown in Fig. 1. The bands found for this gel are consistent with spectra characteristic of C-S-H gels as reported in the literature [18–20].

Fig. 1 also shows the FTIR spectra for gels NA2 and NA4, with SiO_2/Al_2O_3 ratios = 1 and Na_2O/SiO_2 ratios of 2 and 4, respectively. Table 2 gives the vibration frequencies and assignments for all of the gels studied.

Table 1
Gel synthesis.

Gel	Na_2SiO_3[a] (ml)	$Ca(NO_3)_2$[b] (ml)	10-M NaOH[c] (ml)	Ca/Si[d]	8-M NaOH[e] (ml)	Na_2O/SiO_2[f]	$Al(NO_3)_3$[g] (ml)	SiO_2/Al_2O_3[h]	pH[i]
NC	200	200	20	1.9	–	–	–	–	13.13
NA2	200	200	20	1.9	5	2	50	1	11.29
NA4	200	200	20	1.9	10	4	50	1	12.50

[a] Initial volume (ml) of 0.1-M sodium silicate.
[b] Initial volume of 0.19-M calcium nitrate.
[c] Volume of NaOH added to original silicate solution to regulate alkaline conditions.
[d] Target Ca/Si ratio in starting gels.
[e] Volume of 8-M NaOH added to C-S-H gels after synthesis.
[f] Target Na_2O/SiO_2 ratios of the gels after adding 8-M NaOH.
[g] Volume of 0.4-M $Al(NO_3)_3$ added to the C-S-H gels.
[h] Al_2O_3/SiO_2 ratios of gels after adding 8-M NaOH and aluminium in the form of $Al(NO_3)_3$.
[i] Average gel pH as measured in supernatant.

The spectrum for control gel NC shows an intense narrow band at around 970 cm^{-1}, which, according to Yu et al. [19], contains a contribution from the asymmetric Si–O stretching vibrations generated by Q^2 units. The signal at around 815 cm^{-1} is typical of Si–O (Q^1) symmetric stretching vibrations. It is interesting to comment at this stage on the relative intensities of these Si–O absorptions. The greater intensity of the 970 cm^{-1} absorption seems inconsistent with expected Q^2/Q^1 ratio for silicates in C-S-H with such high Ca/Si ratio (Ca/Si = 1.6). Consequently, the prospect of other bonding vibration modes being active in this range might be considered. For example, Lazarev [21] notes the occurrence of silanol bending modes at 1085 and 1187 cm^{-1} and these could account in part for the relatively high intensity of the band at around 970 cm^{-1} in Fig. 1.

The series of bands observed in the 650–450 cm^{-1} range are typical of δ Si–O–Si [19] deformation vibrations (see Fig. 1). The bands visible in the 1450–1400 cm^{-1} region are typical of the C–O stretching vibrations in carbonates. Despite the inert atmosphere, the gels underwent slight carbonation during characterisation. The intense narrow band at 3635 cm^{-1} (see Fig. 1(a)) on this spectrum is characteristic of portlandite, which is expected to appear as a result of the high target Ca/Si ratio at the outset (Ca/Si = 1.9) and its occurrence accounts for the lower observed Ca/Si of 1.6.

As in the first part of this study on the effect of sodium hydroxide alone [8], the portlandite band in these spectra, visible in the control sample (at around 3635 cm^{-1}), disappeared in the samples containing both sodium and aluminium. Here also, the explanation may be due to: (i) sample carbonation, (ii) to a reduction in $Ca(OH)_2$ crystallinity [22], (iii) to the pH reduction permitting $Ca(OH)_2$ solubility and/or (iv) to a redistribution of Ca adsorbed onto surfaces of a modification product, e.g. a sodium aluminosilicate hydrate (N-A-S-H) gel. Note that it is shown later, by XRD and TEM, that calcium carbonate is not present in samples prior to FTIR measurement implying that carbonation occurred during FTIR analyses so option (i) can be discounted.

A narrow band is also visible at around 1380 cm^{-1} (characteristic of N–O stretching vibrations) typical of nitrates, an indication that the gel was not sufficiently washed after the addition of the $Al(NO_3)_3$.

The spectra for the gels with added sodium and aluminium were modified with respect to the control C-S-H gel (NC). The main band, corresponding to the Si–O stretching vibrations in the C-S-H gel, became somewhat rounder in shape and appear broader, particularly in the case of gel NA2 (a small shoulder is also evident in the spectrum of gel NA4) at higher wavenumbers. This is interpreted as arising from the formation of Si–O–Al cross-linkages from what was previously Si–O–H or Si–O–Ca groups. The more acidic Al^{3+} ion (relative to H^+ or Ca^{2+}) draws electron density away from the neighbouring Si–O bond, weakening it and resulting in a peak shift to lower wavenumbers. However, the remaining Si–O bonds in what were previously the pairing silicate tetrahedra may experience an increase in strength due

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[1] Aldrich.

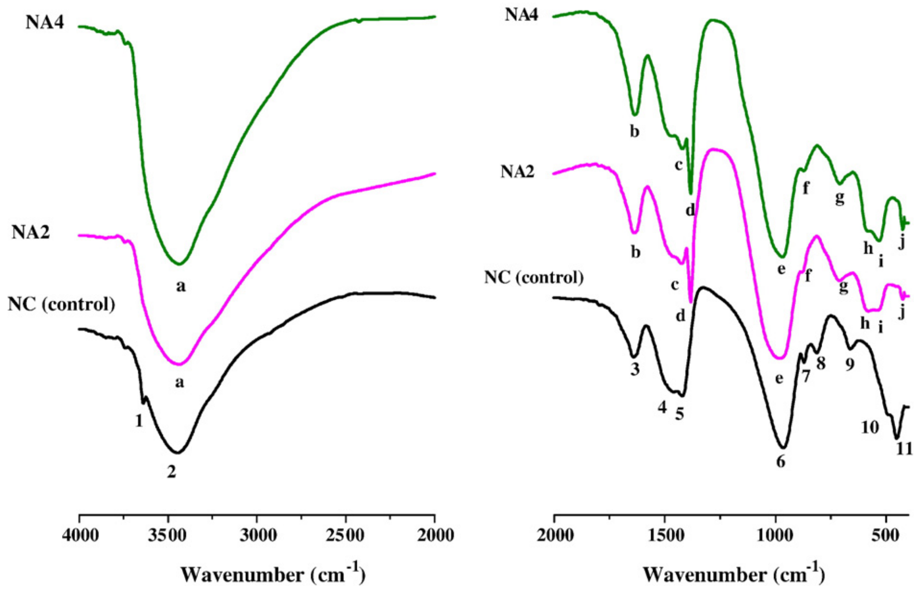

Fig. 1. FTIR spectra for samples NC (control), NA2 and NA4. (a) In the 4000–2000 cm^{-1} range. (b) In the 2000–400 cm^{-1} range.

to the resulting change in polarisation at the O on the Si–O–Al linkage, leading to higher wavenumber contributions to the main Si–O band and consequent broadening of the band around 970 cm^{-1}. For further interpretation of absorption bands from aluminosilicates, the reader is referred to references [21,23].

Analysis of pH (measured in the supernatant after sodium and aluminium addition) showed a reduction to 11.2 and 12.5 for gels NA2 and gel NA4 respectively. The relatively low values may be a consequence of the use of the nitrate salt of aluminium but also, potentially, of consumption of OH$^-$ in the hydrolysis of Si–O–Si linkages in the original C-S-H by the mechanism identified by Glasser et al. [24]. This pH reduction may additionally offer a possible explanation for the absence of crystalline $Ca(OH)_2$ in either sample.

Further, the bands typical of Si–O–Si deformation vibrations and characteristic of C-S-H gels, appearing between 670 and 450 cm^{-1}, practically disappeared in the gels following sodium and aluminium additions, while a new group of bands, which were absent from the spectrum for the control sample, appeared in the 580–500 cm^{-1} range (see Fig. 1(b)). These observations are also consistent with the formation of Si–O–Al linkages [20,21,23,25].

This results show that pH plays an important role not only in phase formation or modification, but in polymerization as well [26–29], an effect enhanced by the availability of Al. Initially high pH is likely to promote hydrolysis of available silicates (as in the C-S-H starting material) but the subsequent reduction in alkalinity is more likely to support condensation (polymerisation) of (alumino)silicates available from solution or surface sites, the counter ions (Ca^{2+}, Na^+ and possibly H^+ depending on local pH conditions) playing an essential charge balancing role on gel surfaces. The pH reduces when aluminium nitrate is added but the more highly polymerized phases arising are likely to arise from the available Al which is known to form bridges between silicate tetrahedral. The more extensively connected aluminosilicate gel has a reduced Ca/Si ratio because in this case, there is limited availability of Ca, the residual surface sites being taken up by Na.

3.2. TEM/EDX, XRD and NMR analysis

The TEM/EDX analysis of gel NC showed a homogeneous gel (Fig. 2(a)) with a Ca/Si ratio of 1.6, lower than the target value due to precipitation of $Ca(OH)_2$. No carbonates were detected in the TEM/EDX analysis of this gel (conducted prior to the FTIR scan), suggesting that carbonate observed by FTIR arises from exposure to air during FTIR analysis.

The micrograph in Fig. 2(b) of gel NA2, shows two distinct zones: a light coloured calcium aluminosilicate plates and a darker aluminium-containing C-S-H gel. No portlandite or gibbsite nanocrystals were detected, nor was sodium identified in this sample.

Fig. 3 gives compositional information for the gel phase (C in Fig. 2(b)). Analyses (30 points) reveal essentially two groups of compositions: the group of points with $0.08 < Al/Ca < 0.32$ and $0.5 < Si/Ca < 0.7$, is likely to correspond to aluminium-substituted C-S-H gel. Here, a trend line is evident indicating the relationship between the level of aluminium substitution and Ca/Si ratio, i.e. as Ca content of gels reduces, the level of aluminium substitution increases

Table 2
Gel NC, NA2 and NA4 band assignments.

Band	Gel NC (cm^{-1})	Assigned to	Band	Gel NA2 (cm^{-1})	Gel NA4 (cm^{-1})	Assigned to
1	3640	ν O–H ($Ca(OH)_2$)	a	3432	3437	ν O–H (H_2O)
2	3441	ν O–H (H_2O)	b	1637	1632	δ O–H (H_2O)
3	1639	δ O–H (H_2O)	c	1425	1421	ν C–O (CO_3^{2-})
4	1458	ν_3 C–O (CO_3^{2-})	d	1383	1383	ν N–O (NO_3^-)
5	1422	ν_3 C–O (CO_3^{2-})	e	982	970	ν Si–O (C-S-H)
6	966	ν Si–O (C-S-H) Q^2	f	877	873	ν C–O (CO_3^{2-})
7	865	ν_2 C–O (CO_3^{2-})	g	710	710	ν C–O (CO_3^{2-})
8	815	ν Si–O (C-S-H) Q^1	h	584	585	δ Si–O–Si//Si–O–Al
9	664	δ Si–O–Si	i	535	531	δ Si–O–Si//Si–O–Al
10	490	δ Si–O–Si	j	425	425	δ Si–O (SiO_4 Td)
11	452	δ Si–O (SiO_4 Td)				

ν: Stretching vibrations ; δ: deformation vibrations.

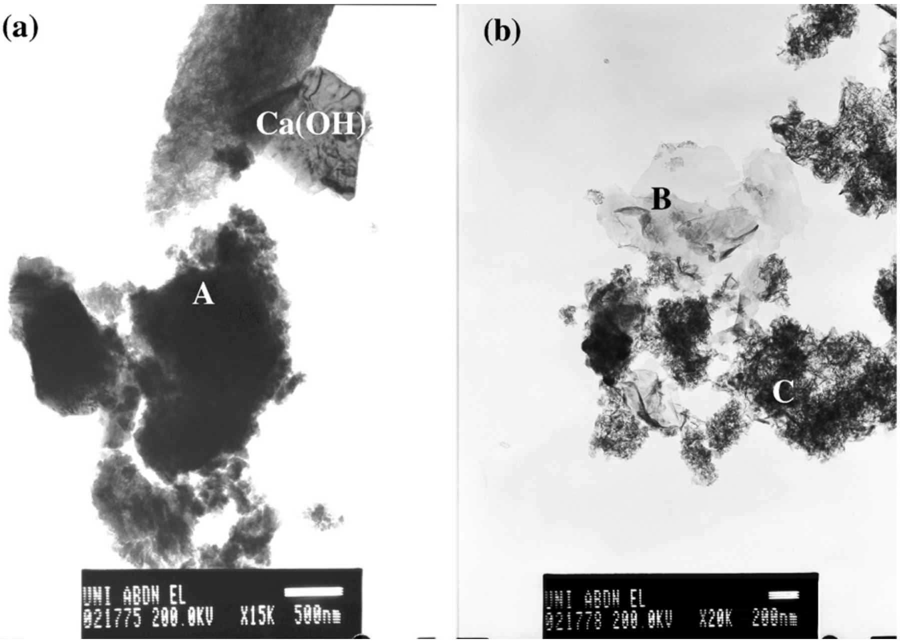

Fig. 2. Micrograph of (a) gel NC (A: C-S-H gel) (b) gel NA2 seen under TEM (B: aluminium-rich phase; C: silicon-rich gel).

as observed by De Silva and Glasser [30]. The second group of compositions has a considerably higher aluminium content ($0.6 < Al/Ca < 0.9$) than the first and would appear to be closer in composition with the more crystalline phase indicated in Fig. 2(b).

X-ray diffraction from sample NA2 and NA4 (Fig. 4) identified a series of peaks (at 21.15, 31.11, 36.10 and 38.03° 2θ) in addition to peaks characteristic of C-S-H gel [4] which were also observed from the control sample (NC). The additional peaks are consistent with strätlingite (JCPDS-80-1579) but the composition derived from analytical electron microscopy ($0.6 < Al/Ca < 0.9$ and $0.52 < Si/Ca < 0.64$) indicates a Si-rich composition with respect to the ideal strätlingite stoichiometry (C_2ASH_8; Ca:Al:Si = 2:2:1). Sodium analysis by EDX is unreliable due to volatilisation but no significant sodium signal was detected to account for the slightly lower than expected Al/Ca ratios for this phase. In fact, the observed Si-rich compositions suggest the possibility of solid solution between strätlingite and C-(A)-S-H gel, the characteristics of which are not yet known.

Finally all samples were analysed by NMR. In Fig. 5(a) and (b), the ^{29}Si and ^{27}Al NMR spectra for NC (control sample) and NA2and NA4 gels are shown. The two peaks at −78.31 and −83.62 ppm on the ^{29}Si spectrum of the control (NC) are assigned to tetrahedral end-of-chain Q^1 silicates, and, mid-chain, Q^2 silicates respectively. The smaller signal at −89.60 ppm is assigned to Q^3 silicate (assumed to be from silica gel arising as a carbonation product or as a consequence of disequilibrium in the gel products).

The spectra for samples NA2 and NA4 show a wide and asymmetric signal around −84 ppm. The contributions to the overall signal can be estimated by deconvolution as shown in Fig. 5(a). The first three peaks (at −78, −81 and −84 ppm) are consistent with Q^1, Q^2 (1Al) and Q^2 silicates respectively [11,31] in the gel phase but, in the present system, strätlingite also contributes to the spectra. According to Kwan et al. [32], the peaks at −81 and −84 are also consistent with Q^2 (2Al), Q^2 (1Al), respectively in strätlingite, which also consists of Q^2, and Q^3 (2Al) silicates with peaks at −87 and −91 ppm respectively.

The corresponding ^{27}Al NMR spectra show peaks at around 62 ppm and 9.9 ppm assigned to Al[4] and Al[6], respectively. Only the strätlingite phase contains aluminium in tetrahedral and octahedral coordination [32].

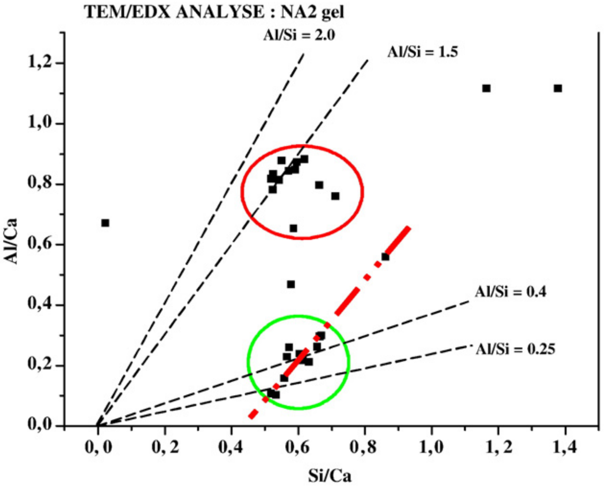

Fig. 3. EDX data on gel NA2 (from TEM). Al/Ca and Si/Ca exp ratio calculated in different points of the NA2 gel.

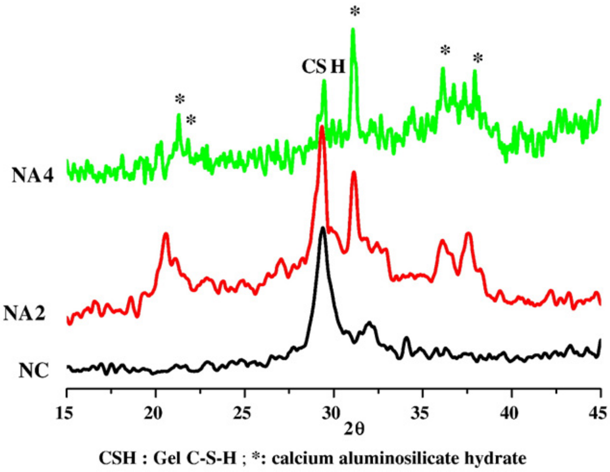

Fig. 4. Diffractograms for gels NC, NA2 and NA4.

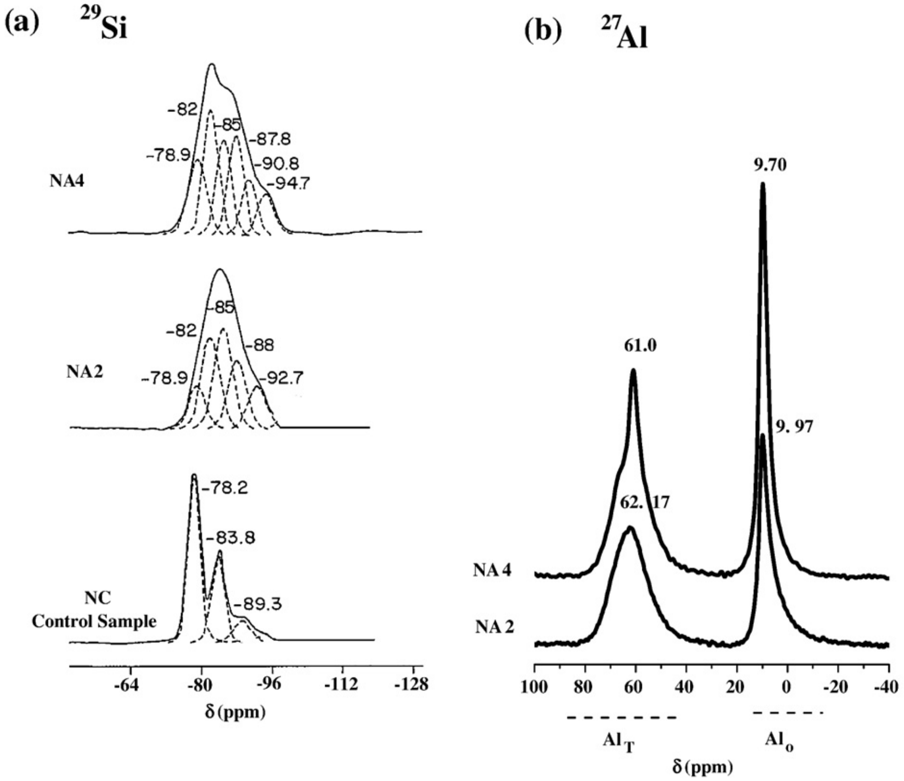

Fig. 5. (a) ^{29}Si-NMR spectra of NC, NA2 and NA4 gels (b) ^{27}Al-NMR spectra of NA2 and NA4 gels.

The appearance of a strätlingite-like phase in these short-term studies is indicative of the reactivity and modification of C-S-H gel in the presence of soluble aluminates at increased pH. It is further noted that the composition of strätlingite may be variable; the range of compositions observed here ranging from $1.5 \leq Al/Si \leq 1.6$; $0.52 \leq Si/Ca \leq 0.64$, indicating a more Si-rich composition than the idealised composition would suggest. Kwan et al. also found a strätlingite-type alkaline aluminosilicate together with aluminium-substituted C-S-H and silica gel [32], as did Sun et al. [11] and Nonat et al. [33] also recently report its appearance in aluminium-substituted C-S-H systems in even lower alkaline environments (no sodium hydroxide). It should be noted also that strätlingite-type phases are also commonly associated with the hydration of slag-containing or aluminium-enriched cements [33–35].

4. Conclusions

This study has to some extent confirmed earlier findings, i.e. that:

- C-S-H structure undergoes modification in the presence of aluminium at high pH, to increased degrees of polymerisation in (alumino) silicates, and
- A strätlingite-like phase crystallises in this system.

But the study has also shown that these changes are effected at very young ages and have relevance to early hydration chemistry of heavily extended alkali-activated blends of Portland cement with aluminosilicates (e,g, fly ashes). The structural modifications themselves are similar to those previously observed for alkali-activated slags; these systems have sufficient calcium availability to produce aluminate-substituted C-S-H, similar to those produced here, and the enhanced degree of cross-linking that is facilitated by aluminates at high pH. However, this enhanced cross-linking appears to be limited; no silicate connectivities higher than Q^2 (possibly Q^3) are indicated in the present study and the co-ordinating role of Ca^{2+} must be considered key in this respect.

The conditions of the present study have favoured through-solution processes and consequently reflect the tendency towards equilibrium phase relations.

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