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Effect of alkalis on fresh C–S–H gels. FTIR analysis

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ABSTRACT

The present study addresses the effect of different concentrations of Na_2O on the structure of a composition of fresh C–S–H gels. The gels were synthesized from laboratory reagents, using calcium nitrate as the source of calcium and a sodium silicate solution for the silicon. A 10-M solution of NaOH was used to maintain a pH of over 13 throughout. The synthesized gels were exposed to different amounts of 8-M NaOH to determine their chemical stability and subsequently characterized with Fourier transform IR spectroscopy. The results showed that the addition of different concentrations of sodium leads to C–S–H gel modification even in the very short term.

1. Introduction

For every tonne of Portland cement manufactured, approximately one tonne of CO_2, in addition to other greenhouse gases, is released into the atmosphere. In light of the adverse impact of the accumulation of these gases on the environment [1], acceptance of the use of alternative binders to replace Portland cement is growing. One such alternative is alkali-activated cement.

The use of fly ash to replace part of the Portland cement in traditional concrete has been shown to have a beneficial effect on durability [2–4]. Moreover, if part of the Portland cement can be replaced by waste materials, e.g. fly ash, the amount of cement needed and therefore the amount of CO_2 released into the atmosphere can be reduced. Proposals for using alkali-activated cement-ash blends (with high ash content) have been supported by findings reported in the recent literature [5,6]. Consequently, the effect of a high alkaline content on the respective reaction products merits attention.

The two principal products of Portland cement hydration are crystalline portlandite and an amorphous material known as C–S–H gel. The composition of this latter phase varies depending on factors such as pH, temperature and so on [7–10]. Most of the present knowledge about C–S–H gel structure has been gleaned from the study of the structure of 1.4-nm tobermorite- and jennite-type crystalline calcium silicate hydrates and has been reviewed recently by Richardson [11].

Tobermorite has a dreierkette-like structure [10] in which the same pattern of silica tetrahedra is repeated every three units on both sides of a central sheet of Ca–O. Two silicon tetrahedra (called tetrahedral pairs) share two oxygen atoms with the CaO, while a third (bridging tetrahedron) shares oxygen atoms with the pairing tetrahedra. Water molecules and additional calcium cations occupy the interlayer. The Ca/Si ratio is 0.83, but this value varies readily in less crystalline forms. Like tobermorite, jennite is structured around a central layer of CaO flanked by two rows of (dreierkette-type) silicates with calcium atoms and water molecules in the interlayer [10]. The chief difference between the two structures is that in jennite some of the silica tetrahedra in the simple dreierkette chain are replaced by OH groups, causing substantial undulation in the CaO layer. In C–S–H gels synthesized from alkaline silicates and calcium salts, the product generally formed is an imperfect version of 1.4-nm tobermorite (C–S–H gel I), whose Ca/Si ratio ranges from 0.67 to 1.5 [10].

This gel interacts with other cement components, and it is well known that sodium and aluminium oxides play a significant role in Portland cement reaction mechanisms and hydration kinetics [12–18]. In this paper, we address the effects of alkali at room temperature; the effect of alkaline oxides (Na_2O) on calcium silicate hydrates has been studied previously but essentially on gels synthesized at high temperatures or after lengthy reaction times [12–17]. Nelson, for instance, in gels synthesized hydrothermally (180–250 °C), found pectolite, a calcium sodium silicate, to be a stable phase that may co-exist with other calcium silicates typical of cement hydration, such as tobermorite and xonolite [13]. Blakeman et al. also mentioned the co-existence of these phases following hydrothermal reactions [14]. Sung-Yoon Hung et al. [15] reported that C–S–H gels, reacting with various concentrations of NaOH and KOH, undergo a change in composition (Ca/Si ratio) and by analyzing cation adsorption and desorption on the gel, concluded that alkali-gel bonds are weak [15,16]. Nocún-Wczelick [17] showed that the presence of alkali hastened the formation of calcium silicate hydrate but this was poorly crystallized in comparison and that in some mixtures the transformation of this intermediate product into a higher order crystalline structure may be interrupted by the presence of alkalis.

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Fig. 1. Photograph of the apparatus used to synthesize C–S–H gels.

These combined findings of the above authors [12–17] confirm that calcium silicate hydrate formation and properties are affected by the presence of alkalis. If a response to sustainable cement binders is to consider hybrid Portland cement-activated aluminosilicate systems, a need is therefore identified (and this would be the primary objective of the present study) to explore the short-term (72 h) behaviour of fresh C–S–H gels in highly alkaline media.

2. Experimental

2.1. C–S–H gel synthesis

Four C–S–H gels with a target Ca/Si ratio of 1.9, chosen to best represent the composition anticipated in Portland cement pastes, were prepared by identical procedures as follows [18]: $Ca(NO_3)_2 \cdot 4H_2O$ 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 under 5 °C; the experimental apparatus is depicted in Fig. 1. 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 water to remove the excess sodium and nitrate ions.

The mixture was stirred at laboratory temperature for a further 24 h and again left to stand until two phases appeared, after which the supernatant water was removed. This supernatant was used to measure gel pH.

A small amount of each slurry was analyzed with FTIR to verify the formation of C–S–H gel. This involved filtering the slurry removed through a Büchner funnel under vacuum and then washing the filtrate with large volumes of distilled water (to remove any residual sodium and nitrate). The filtrate was then vacuum-dried on a watch glass in a desiccator at ambient temperature (20–25 °C). All the preceding operations were conducted in a nitrogen atmosphere inside an AtmosBag, to minimise the carbonation risk. The rest of the C–S–H gel slurry was divided and stored in four separate containers at ambient temperature until sodium was added. X-ray diffraction and SEM/EDX were carried out on samples to confirm product compositions.

2.2. Mixing C–S–H gels with 8-M NaOH: effect of alkalis

NaOH (8 M; BDH 'Convol') was added to three of the four slurries to study the effect of sodium on the structure of these fresh gels. The fourth gel was used as a control (N0). The 8-M NaOH solution was added to the other three in amounts that would generate target Na_2O/SiO_2 ratios of 2, 4 or 10 (gels N2, N4 and N10, see Table 1). The gels were mixed with the alkaline solution inside an AtmosBag. After all the sodium had been added, the mixtures were agitated on a rotating mixer for 72 h, after which a sample of the mixture was taken, filtered in a Büchner funnel (in an N_2 atmosphere) and subsequently vacuum-dried in a desiccator. Samples for FTIR analyses were prepared by mixing 1 mg of sample with 300 mg of KBr and spectra were obtained using an ATIMATT-SON FTIR-TM series spectrophotometer at a resolution of 1 cm^{-1}, over the range from 4000 to 400 cm^{-1}. Finally, a JEOL JSM 5400 scanning electron microscope equipped with a LINK-ISIS energy dispersive (EDX) analyser was used for micro-structural characterization of the samples.

2.3. C–S–H gel dissolution: Takashima attack (separation with methanol/salicylic acid)

All the gels were subjected to a selective chemical attack with methanol and salicylic acid (Takashima attack [19,20]), initially designed to separate the aluminate and ferrite from the siliceous phases of Portland cement clinkers, to obtain a deeper understanding of the phases precipitating during C–S–H gel synthesis and the effect of alkalis on their structure. The procedure is based on the formation of a soluble calcium complex. The phases containing calcium dissolve in the salicylic acid/methanol (SAM) medium, whereas those with no calcium in their composition form an insoluble residue after the attack. The gels were subjected to this attack. For this, a sample of each gel (1 g) was mixed with salicylic acid (6 g) and methanol (40 ml) for 1 h. The insoluble residue obtained after the attack was filtered, dried and finally analysed by FTIR.

3. Results

3.1. Effect of adding NaOH to C–S–H gels: FTIR and SEM/EDX analysis

All the results of FTIR characterization of the four C–S–H gels synthesized were reproducible. The vibration bands appearing in the FTIR spectra were the same for all the gels, and concurred with the signals characteristic of C–S–H gels previously described in the literature [21–26]. By way of example, Fig. 2 shows the FTIR spectrum for one of the gels (the control, N0), synthesized from laboratory reagents to a target Ca/Si ratio of 1.9. Table 2 gives the FTIR spectrum frequencies and band assignments for this gel (band assignments annotated 1–12). The FTIR spectrum shows a main narrow band at around 966 cm^{-1} (band 6), typical of the Si–O asymmetric stretching vibrations generated by Q^2 units, as well as a signal at 815 cm^{-1} (band 8) typical of Q^1 units [21,23]. Some authors point out that the presence of Q^3 and Q^4 units are possible in C–S–H gels with low C/S ratio [21,26,27] or in mature and partly carbonated samples [28], but no Q^3 units were detected by this technique (i.e. at 1200 cm^{-1}) during this study. The series of bands in the 450–650 cm^{-1} range is characteristic of Si–O–Si deformation vibrations (see Table 2). The intense narrow

Table 1
Raw material proportions for gel synthesis

Gel	Ca/Si(1)	NaOH 8 M(2) (ml)	Na_2O/SiO_2(3)	pH(4)
N0	1.9	–	–	13.13
N2	1.9	5	2	13.20
N4	1.9	10	4	13.17
N10	1.9	25	10	13.15

(1) Target Ca/Si ratio in initial gels; (2) volume of 8-M NaOH added to C–S–H gel slurries; (3) target Na_2O/SiO_2 ratios in gels after adding sodium in the form of 8-M NaOH; (4) gel pH measured in the supernatant liquor using a pH meter, once the gel has been synthesized. We have to consider pH value can change during reaction.

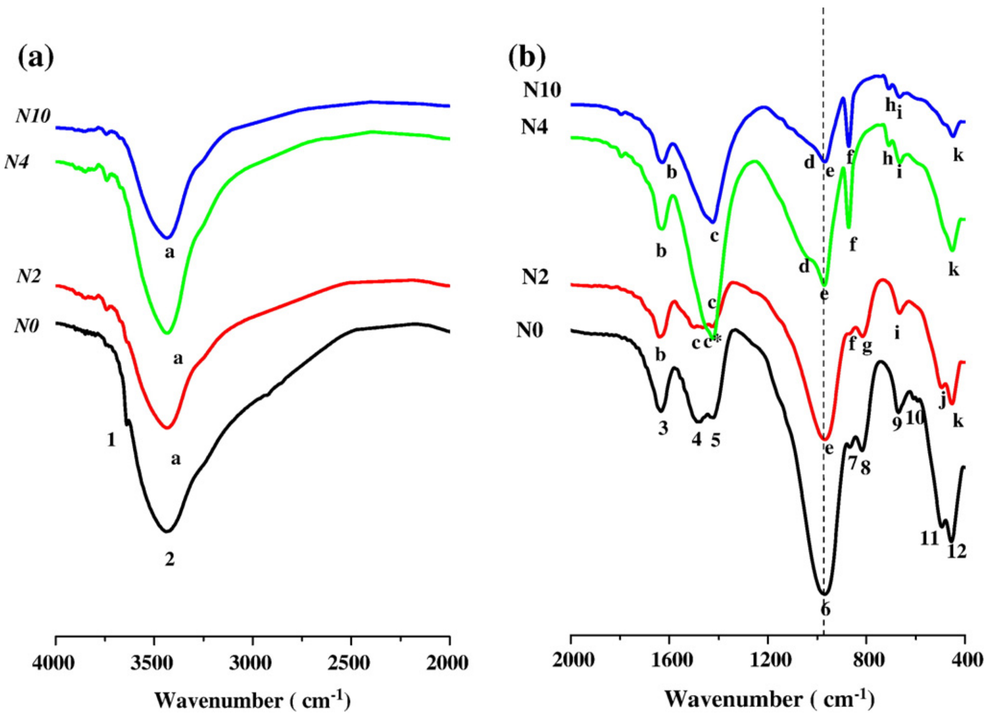

Fig. 2. Effect of 8 M NaOH on C–S–H gels. FTIR spectra for gels N0, N2, N4 and N10 (a): in the 4000–2000 cm^{-1} range. (b): in the 2000–400 cm^{-1} range.

band at 3635 cm^{-1} on this spectrum is characteristic of the stretching vibrations generated by the O–H bonds in portlandite ($Ca(OH)_2$), from which it may be inferred that due to the high initial Ca/Si ratio (1.9) in these gels, a certain amount of portlandite precipitated with the C–S–H gel.

The signals appearing at around 1400–1450 cm^{-1}, typical of C–O stretching vibrations, may be attributed to calcium carbonates (see Fig. 2). The obvious deduction is that despite the precautions taken, sample carbonation took place during the experimental stage, probably as samples were dried in the desiccator or during subsequent gel characterization.

Fig. 2(a) and (b) also shows the FTIR spectra for the C–S–H gels after 72 h of exposure to different concentrations of alkalis, in the ranges 4000–2000 cm^{-1} and 2000–400 cm^{-1}, respectively. The spectra show a series of significant changes even at a very early stage (see Fig. 2). The peak corresponding to portlandite (narrow band at around 3635 cm^{-1} typical of O–H stretching vibrations), for instance, disappeared after the NaOH was added. The intensity of the bands attributed to carbonates (calcite) [29] was also found to rise when the Na_2O/SiO_2 ratio was ≥4 (see Fig. 2(b), spectra N4 and N10). Normally, it would be expected that increasing the alkali content would promote portlandite precipitation due to the common ion effect, but this does not appear to happen; portlandite is not observed either by XRD or by FTIR (no band is observed at 3635 cm^{-1}). An alternative explanation proposed here is that Ca is redistributed on the surface of a modification product or products of the C–S–H gel or onto N–S–H gels to satisfy surface charges. It is suggested that either sodium silicate gels form under the influence of increased NaOH concentrations or that C–S–H itself is modified to higher degrees of silicate polymerisation by the effect of NaOH addition. In either case, new gel surfaces are likely to provide the necessary sites for cation adsorption.

Further, the spectra show that the various concentrations of sodium caused no shift in the position of the main band corresponding to Si–O stretching vibrations; for Na_2O/SiO_2 ratios ≥4, however, the shape and intensity of this peak varied perceptibly, from narrow and intense to broad and less intense, with the appearance of shoulders at 1033 cm^{-1} (in gel N4) and 1109 cm^{-1} (in gel N10), neither of which was

Table 2
Gel N0, N2, N4 and N10 band assignments [21,23]

Band	Gel N0 (cm^{-1})	Assigned to	Band	Gel N2 (cm^{-1})	Gel N4 (cm^{-1})	Gel N10 (cm^{-1})	Assigned to
1	3635	ν OH ($Ca(OH)_2$)					
2	3439	ν OH (H_2O)	a	3432	3436	3438	ν OH (H_2O)
3	1631	δ OH (H_2O)	b	1635	1630	1626	δ OH (H_2O)
4	1470	ν_3 CO (CO_3^{2-})	c	1489	1424	1424	ν_3 CO (CO_3^{2-})
5	1417	ν_3 CO (CO_3^{2-})	c*	1463	–	–	ν_3 CO (CO_3^{2-})
–	–	–	d	–	1033	1109	ν Si–O
6	966	ν Si–O (C–S–H) Q^2	e	966	970	968	ν Si–O (C–S–H) Q^2
7	865	ν_2 CO (CO_3^{2-})	f	867	872	871	ν_2 CO (CO_3^{2-})
8	815	ν Si–O (C–S–H) Q^1	g	813	–	–	ν Si–O (C–S–H) Q^1
9	667	δ Si–O–Si	–	–	–	–	–
		–	h	–	709	710	ν_2 CO (CO_3^{2-})
10	590	δ Si–O–Si	–	–	–	–	–
–	–	–	i	664	665	666	δ Si–O–Si
11	491	δ Si–O–Si	j	491	–	–	δ Si–O–Si
12	453	δ Si–O (SiO_4 Td)	k	452	453	449	δ Si–O (SiO_4 Td)

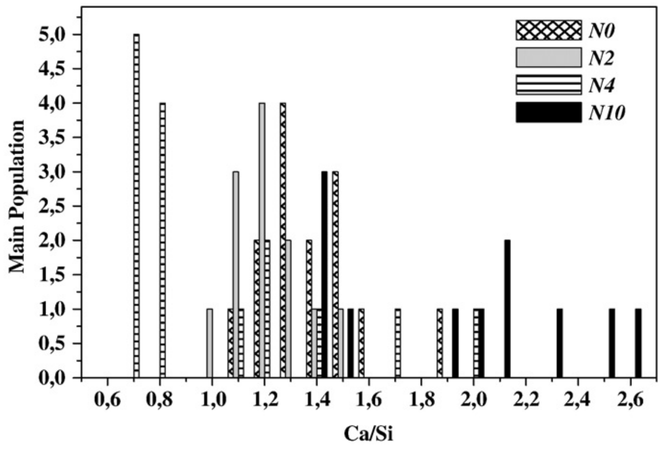

Fig. 3. Histogram of the Ca/Si ratio in gels.

Table 3
EDX analyses of gels

	N0		N2		N4		N10	
Analyses	C/S(1)	N/S(2)	C/S(1)	N/S(2)	C/S(1)	N/S(2)	C/S(1)	N/S(2)
1	1.224	0.017	1.207	0.004	1.108	0.001	3.065	1.865
2	1.592	0.014	2.383	0.023	0.797	0.005	2.025	0.623
3	1.099	0.004	1.114	0.015	0.648	0.004	3.167	0.033
4	1.205	0.014	3.471	0.006	8.608	0.124	4.342	0.071
5	1.410	0.009	1.109	0.000	2.465	0.024	1.126	0.020
6	1.222	0.024	0.962	0.027	1.985	0.024	1.069	0.015
7	1.102	0.000	4.285	0.000	0.671	0.015	2.584	1.261
8	1.314	0.006	1.037	0.017	1.604	0.000	1.649	0.063
9	1.211	0.006	1.175	0.021	7.498	0.035	2.470	0.137
10	1.490	0.000	1.494	0.033	0.692	0.000	1.004	0.042
11	1.142	0.020	1.194	0.020	0.784	0.006	2.974	0.019
12	1.423	0.006	1.280	0.010	0.727	0.013	3.890	0.132
13	1.396	0.014	1.394	0.015	0.616	0.001	2.277	0.087
14	1.808	0.008	1.063	0.011	0.629	0.000	1.554	0.065
15	–	–	1.035	0.002	1.360	0.030	2.929	0.008
16	–	–	–	–	0.704	0.010	2.016	0.012
17	–	–	–	–	1.198	0.024	1.067	0.032
18	–	–	–	–	1.070	0.002	–	–

(1) C/S: CaO/SiO_2 (2) N/S:Na_2O/SiO_2.

visible on the control sample spectrum (see Table 2). These changes are associated with the possible formation of a silicon-rich gel with some sodium in its composition, as discussed below.

Another feature to be highlighted is that despite the precautions taken to prevent carbonation, the gels experienced some carbonation. Fig. 2(b) shows, moreover, that the intensity of the carbonate bands (at around 1460 cm^{-1}, assigned to calcite) increased with the alkaline content in the gels. Gels N4 and N10, with target Na_2O/SiO_2 ratios of 4 and 10, respectively, were the ones most intensely carbonated. In cement pastes, carbonation is largely controlled by the alkaline content of the solution in the pores and increased pH (the addition of NaOH has been shown to hasten concrete carbonation) [30]. In addition to the speed and degree of sample carbonation, alkali content also impacts on carbonation depth [30,31]. Consequently, one possibility that must not be ruled out is that sample carbonation may generate a residue in the form of an amorphous silicate, with a higher degree of polymerization than the C–S–H gel [32,33].

The gels were also analysed by SEM/EDX (Fig. 3 shows a histogram of Ca/Si values). Table 3 shows the range of compositions for all gels; N0 (control sample) and N2, N4 and N10, samples with extra sodium. The EDX analyses of gel N0 shows Ca/Si ratios ranging from 1.1–1.8 but with the main grouping of analyses around 1.4. No carbonates were detected in this sample, but portlandite was observed and explains the deviation from the target value of 1.9. The analysis of sample N2 shows a significant spread in compositions in the range $0.98<Ca/Si<4.55$, the highest values again likely due to interference from precipitated $Ca(OH)_2$; most of the compositions have $Ca/Si<1.9$. With higher NaOH loadings, more significant variations in composition were observed. Again, precipitated $Ca(OH)_2$ or $CaCO_3$ is likely to influence the analysis at the higher Ca/Si values, but significantly, for the N4 set, the lower limits of Ca/Si ratio extends down to around 0.6, below that which represents the lower limit of Ca/Si for C–S–H gels in a Na_2O-free system. Finally, the N10 system shows two different kinds of gels; a C–S–H gel containing small amounts of sodium (up to $Na_2O:SiO_2$ of 0.012) and analogous to the other gels observed, and a gel having considerably higher levels of sodium with the indicative composition $N_{1.86}C_{3.16}SH_x$. It is not yet clear how representative this composition is of precipitated gels in this system, considering the influences of other phases present, and further investigation is required.

3.2. Results of selective chemical attacks

A selective chemical attack with methanol/salicylic acid [19,20] was conducted to confirm the hypotheses explored in this study, with respect to the phases that precipitate during C–S–H gel synthesis and the formation of possible new phases when sodium is added to the gels.

Fig. 4(a) shows the FTIR spectra of the insoluble residues remaining after chemical attack on the control C–S–H and the sodium-containing gels. Fig. 4(b) shows the FTIR spectra generated when those spectra were subtracted (with the aid of computer software) from the spectra of the original samples. The spectra for the insoluble residue remaining after the attack contain, in addition to the bands characteristic of carbonates (around 1450 cm^{-1}), a broad signal at a frequency higher than the position of the band typical of

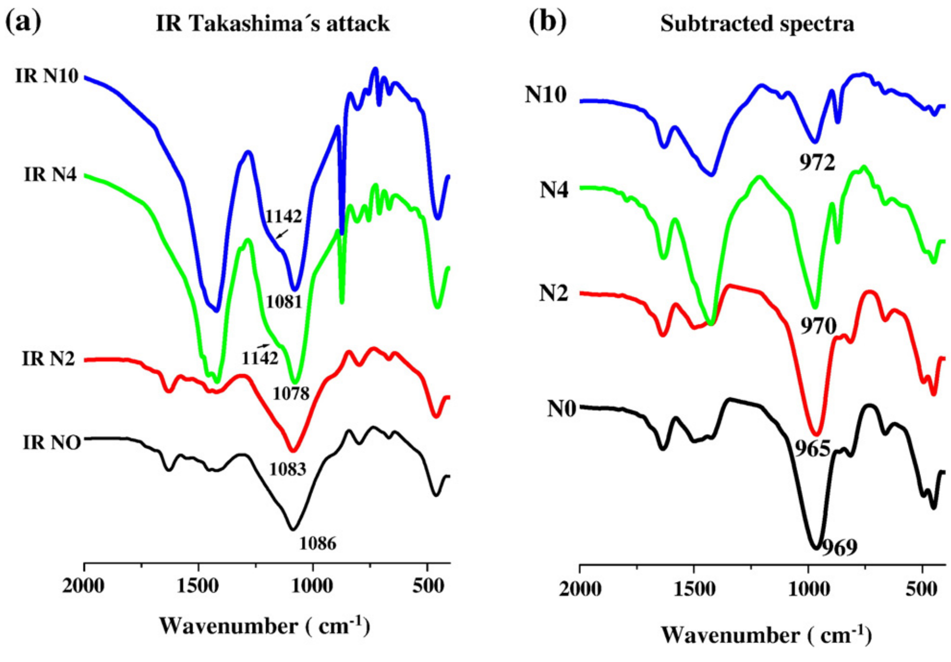

Fig. 4. FTIR spectra (a) for insoluble residue (IR) after Takashima attack and (b) spectra resulting from subtracting the spectra in (a) from the spectra for gels N0, N2, N4 and N10.

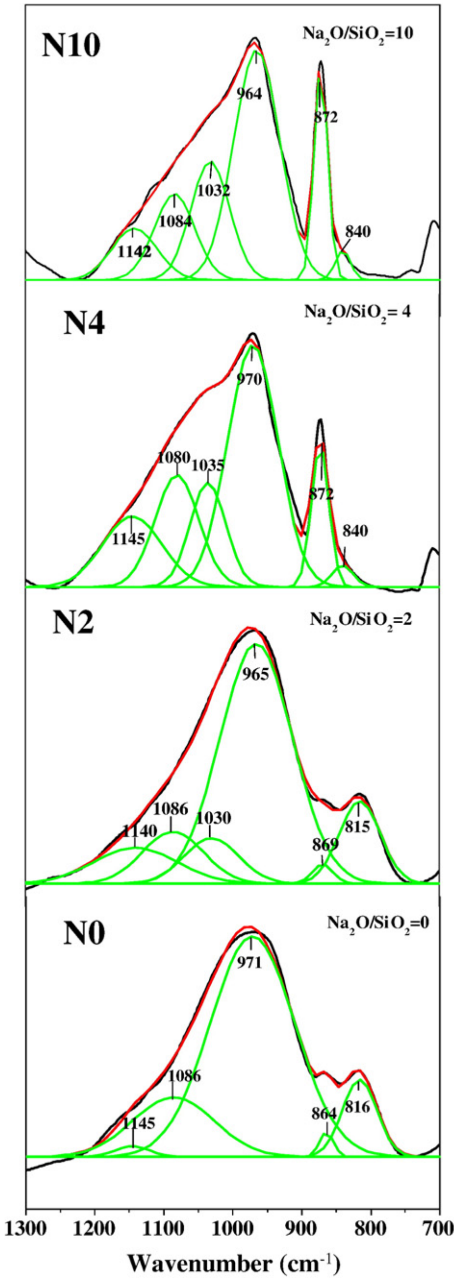

Fig. 5. Deconvolution of the Si–O asymmetric stretching band in C–S–H gels (FTIR).

C–S–H gels. This band appears at around 1086 cm^{-1} (in the spectrum for the residue corresponding to gel N0). In all other cases, the same band appears at lower frequencies, and has a shoulder at 1142 cm^{-1}; again, these signals would correspond to Si–O stretching vibrations in a silicon-rich gel. The downward shift in this main band may mean that the silicon-rich gel took up sodium in its structure, but not calcium. These kinds of gels, which do not include calcium in their composition are not affected by the methanol/salicylic acid attack [23].

All the spectra obtained by subtracting the insoluble residue from the original sample spectra (Fig. 5(b)), which correspond, therefore, to the part of the gel that dissolves in the methanol/salicylic acid solution, contain the bands typical of C–S–H gels [21,23]: a main signal at around 970 cm^{-1}, corresponding to the Si–O asymmetric stretching bands in Q^2 units, a band at 810 cm^{-1} typical of the Si–O symmetric vibrations in Q^1 units, and a series of signals in the 650–450 cm^{-1} range, typical of δ Si–O–Si deformation vibrations. There is a strong similarity between these spectra and the FTIR spectrum of the control sample (gel N0, see Fig. 2). This could be an indication that Takashima's attack dissolves the C–S–H gel.

4. Discussion

The effect of alkalis on calcium silicate hydrate composition and morphology is a subject that should be given careful consideration in the future. The present FTIR study of certain C–S–H gels revealed substantial changes in gel structure after exposure to a highly alkaline solution. The frequency of the main band appearing on the spectrum for the control C–S–H gel (N0) does not change when sodium is added, but the variation in its shape is a possible sign of the precipitation or appearance of new phases that are not typical components of C–S–H gels. A band at around 670 cm^{-1} potentially furnishes information on the structural order of the gel [21] but, whilst the apparent decrease in intensity of this band in the present study could be indicative of C–S–H gel degeneration or alteration due to exposure to high concentrations of sodium , it is more likely to be due to dilution of the sample by precipitated $CaCO_3$. In fact, carbonation was observed by FTIR in gels taking up high concentrations of sodium but this was found to be a consequence of exposure of sub-samples during FTIR analysis [34]. The disappearance of the portlandite band from FTIR spectra for sodium-containing samples could also be attributed to carbonation but portlandite also disappeared in the main samples which were less susceptible to carbonation effects. Therefore, the possibility of Ca being redistributed on silicate-rich gel surfaces remains an alternative mechanism for the loss of portlandite as sodium hydroxide content increases.

The results of the chemical attacks (with methanol/salicylic acid) generated valuable information. The presence of an insoluble residue confirmed that other phases precipitated together with the C–S–H gel or that the products formed were modified during chemical attack. In gels N0 (control) and N2 ($Na_2O/SiO_2=2$), the residue after the attack accounted for 2 and 2.8% of the original sample masses, respectively. Consequently, nearly all the control gel may be regarded to comprise C–S–H; and in the case of gel N2, the addition of a relatively low concentration of sodium would not appear to cause massive degeneration of the C–S–H gel, at least during the first 72 h.

The FTIR analyses of the insoluble residues remaining after the chemical attack on gels N0 and N2 contain a wide band at around 1086 cm^{-1}, characteristic of the Si–O stretching vibrations in a silica gel [21,23]. Based on these results, and given that the percentage of insoluble residue remaining after these gels were attacked was very low, it might be thought that together with the original C–S–H gel, a silica-rich gel with little calcium in its composition may have been formed (due to an excess of starting reagent). Such a possibility has been addressed in the literature [14,21–23,30,35,36].

It is known that even in Na_2O-free C–S–H, the degree of silicate polymerisation is dependent on Ca/Si ratio [37,38], with higher degrees of condensation being evident in gels with $Ca/Si<1.25$. It is also acknowledged [15] that the introduction of NaOH to C–S–H can result in a lowering of the Ca/Si ratio. It is not clear if the effect of Na_2O addition is sufficient in this study to suppress Ca/Si ratios to such a level that polymerisation effects in the silicates are induced [39], but if so, it could be expected that a higher insoluble residue could be expected with a higher degree of silicate polymerisation (based on the

Table 4
% IR (insoluble residue) after Takashima attack

Gel	% IR
N0	2.07
N2	2.68
N4	73.73
N10	68.82

chemistry of the SAM treatment [19]). If such a model is correct, the Na_2O-induced suppression of Ca/Si ratio may be insufficient to promote silicate polymerisation with $Na_2O:SiO_2 \leq 2$. This would be consistent with the low levels of insoluble residue following SAM treatment of gels with target $Na_2O:SiO_2 \leq 2$.

However, the SAM treatment on gels N4 and N10 (with Na_2O/SiO_2 ratios of 4 and 10, respectively) generated residues amounting to over 50% of the total original masses (see Table 4). This may be an indication that for Na_2O/SiO_2 ratios ≥4, C–S–H gels undergo significant modification, forming one or several phases either not susceptible to or only partially reactive to the SAM treatment. The FTIR data are also consistent with a more polymerised silicate; the residue for gel N4 generated an intense band at around 1078 cm^{-1}, with a shoulder at 1140 cm^{-1}, likely to be due to the Si–O asymmetric stretching bands in a silicon-rich gel [21]. The shift of this band on the residue spectrum to frequencies lower than the signal appearing in the gel N0 residue spectrum (from 1086 to 1078 cm^{-1}) may mean that the silicon-rich gel has taken up sodium in its structure. The spectrum for the residue from gel N10 exhibits the same bands as the N4 residue spectrum.

The main band corresponding to the Si–O bond asymmetric stretching vibrations in Q^2 units was examined more thoroughly to acquire a fuller understanding of the effect of sodium on these fresh C–S–H gels. This involved deconvoluting the signal generated in the 700 to 1300 cm^{-1} range of the spectrum with computer software that fits the theoretical curve (comprising a series of the overlaid peaks) to the original spectrum. The band was deconvoluted taking account of the frequencies of the C–S–H gel bands in the FTIR spectra (Fig. 2) and the band positions on the spectra for the insoluble residue remaining after the gels were attacked with methanol and salicylic acid. The deconvolution results for the control gel (with no additional sodium, sample N0) and gels N2, N4 and N10 are reproduced in Fig. 5.

As the figure shows, gel N0 (control C–S–H gel) has five distinct components. The first, appearing at around 815 cm^{-1}, would correspond to Si–O symmetric stretching vibrations, while the component appearing at around 970 cm^{-1} would correspond to asymmetric stretching vibrations (ν_3 Si–O, Q^2 units) in the C–S–H gel [21,23]. A smaller component is visible at around 864 cm^{-1}, which would correspond to the presence of carbonates. The two components appearing at around 1090 cm^{-1} and 1140 cm^{-1} could be equated to the bands characteristic of the Q^3 and Q^4 silicon tetrahedra in a silica-rich gel [15,22,23]. In other words, the deconvolution of this main band in the sample may be suggesting that a small amount of a silica gel precipitated with the C–S–H gel during synthesis.

When these gels were mixed with caustic NaOH in amounts corresponding to Na_2O/SiO_2 ratios ranging from 2 to 10, slight changes were observed in both the vibration frequencies and the areas of the respective peaks in the deconvoluted components. On the one hand, the main component (Si–O asymmetric stretching vibrations) shifted to slightly lower frequencies than observed in the control (without sodium); furthermore, the area of this component reduced (see Fig. 5).

The band corresponding to Si–O symmetric stretching vibrations (appearing at around 815 cm^{-1} in the control gel) practically disappeared at target Na_2O/SiO_2 ratios ≥4 (moreover, with such high ratios the shape of the deconvoluted band varied considerably). This may be interpreted to mean that exposure to high concentrations of NaOH brings about significant short-term alteration in C–S–H gels.

In addition, a new component was observed to appear at around 1030 cm^{-1}, which could not be fitted to the control gel N0 spectrum and is consequently attributed to the binding of sodium onto a silicate-based gel. The area of this component rose with NaOH concentration (see Fig. 5). The components with frequencies of around 1145 cm^{-1} and 1080 cm^{-1}, attributed to a more highly condensed silica-rich gel, appear in all the deconvoluted spectra, suggesting the incomplete reaction of starting materials in N0 but the change in the peak shape for the other gels confirms that NaOH addition strongly modifies the C–S–H gel. The mechanism involved in this process has still not been determined, however. The two possible explanations are not mutually exclusive, but may actually be complementary. The first would be based on gel carbonation. C–S–H gel is highly prone to react with atmospheric CO_2, resulting in carbonation. Gel carbonation, which is enhanced by high alkalinity, favours silicate polymerization [30–33]. However, the degree of carbonation must be sufficient to reduce Ca/Si ratios in the gel to around 1.25 or below. The presence of components at around 1080 and 1140 cm^{-1} confirm the precipitation of a silica-rich gel, but it should be acknowledged that these features would also be present for a sodium silicate-like gel also. The second, and more likely hypothesis is that the addition of high concentrations of alkali to fresh C–S–H gels directly promotes gel modification, specifically silicate polymerisation and a redistribution of Ca to surface sites, even in the short term.

Fig. 6 shows the standardized area percentages of the deconvoluted signals depicted in Fig. 5. Note the significant decrease in the area corresponding to the C–S–H gel component (appearing at around 970 cm^{-1}) with the increase in the amount of sodium in the medium, and the virtual disappearance of the component at 816 cm^{-1}, confirming the modification of the C–S–H. In addition to those corresponding to C–S–H gel components, two new bands appear at 1080 cm^{-1} and 1145 cm^{-1}, which are consistent with the vibrations of a silicate-based gel. The presence of this gel was confirmed by the results of the FTIR analysis of the insoluble residue remaining after the selective attack on these gels with methanol and salicylic acid. Finally, a further new component, not present on the gel N0 spectrum, was observed at around 1030 cm^{-1}. Fig. 6 clearly shows that its area increases with the alkaline concentration in these gels, providing further evidence of the appearance of a new phase when the gel is exposed to such highly alkaline media.

5. Conclusions

The following conclusions may be drawn from the results of the present research:

- High NaOH concentrations in fresh C–S–H gels brings about gel modification, even in the very short term (72 h).
- C–S–H gel carbonation is enhanced by alkali content.
- The alteration of these gels in the presence of high concentrations of NaOH may be due to two factors:
  - gel carbonation (enhanced by high alkalinity) leading to silicate polymerization, generating a silicate-rich gel residue.

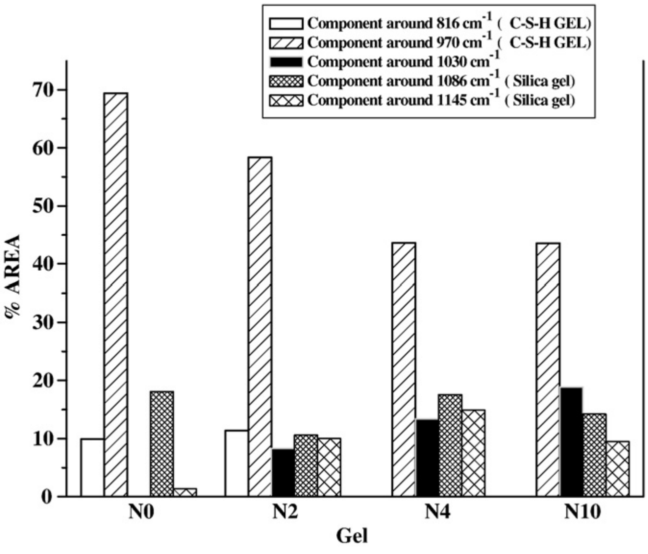

Fig. 6. Variation in the areas of deconvoluted components for gels N0, N2, N4 and N10.

- alkali-induced modification of the original C–S–H gel, favouring the formation of a Ca-containing N–S–H gel.

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