SYNTHESIS AND CHARACTERIZATION OF CEMENTITIOUS GELS (C-S-H AND N-A-S-H). COMPATIBILITY STUDIES

I. García-Lodeiro, A. Fernández-Jiménez, M.T. Blanco-Varela and A. Palomo
Eduardo Torroja Institute (CSIC). PO Box 19002. 28080 Madrid (Spain)

Abstract
C-S-H and N-A-S-H gels and combinations of the two were synthesized using a sol-gel procedure. The synthesis variables were the Ca/Si and Si/Al ratios and the (NaOH-regulated) system pH. The objective was to analyze the compatibility between the C-S-H and N-A-S-H gels formed during the alkali activation of aluminosilicate materials.
The following deductions were drawn from FTIR, SEM, and NMR-MAS studies:
- C-S-H gel Ca/Si ratios were consistently lower than the theoretical values. Upward of certain pH values, gel composition was constant.
- N-A-S-H gel composition likewise remained unchanged upward of certain pH values, irrespective of the initial Si/Al ratio.
- The results obtained from the joint synthesis of the two gels were not conclusive. With the techniques used it was not possible to distinguish whether the product formed comprised a mix of gels or a single product.

1. Introduction

Silica and silicate colloid chemistry research was pioneered by R.K. Iller **[1,2]**, among others. The fundamentals of silicic acid polymerization in aqueous solutions established by this author laid the groundwork for the modern techniques used to produce highly concentrated yet stable silica gels and precipitates.

Indeed, sol-gel chemistry has made it possible to develop mixed silica-alumina oxides with different Al/Si ratios. The properties of the oxides obtained are highly dependent upon sol-gel synthesis parameters such as the type and concentration of precursor molecules, solvent used, temperature, amount of water for hydrolysis, pH and so on **[3,4]**.

The last few years have witnessed the advent of a new family of inorganic polymeric materials based on related aluminosilicate units. Referred to as geopolymers by some authors **[5]** and alkaline inorganic polymers by others **[6-10]**, these compounds are characterized by physical and mechanical properties that make them viable alternative raw materials for conventional cement and ceramic manufacture. And because it involves lower temperatures, their synthesis is more energy-efficient and environmentally friendly than many other traditional materials **[5-9]**.

These inorganic polymers are usually synthesized via the reaction between an active aluminosilicate (metakaolin, fly ash or similar) and an appropriate proportion of an alkaline metal (Na, K, Ca) in a very basic medium in which the water content is strictly controlled. Temperature and curing time are other important processing factors **[6-10]**, although the more efficient use of soluble silicate solutions has gradually lowered the former to ambient levels **[11-12]**. Ikeda et al **[12-13]** have successfully used this procedure in recent years to synthesize mullite from sodium aluminosilicate gels under acidic conditions. In subsequent research, Vallepu and Fernández-Jiménez **[14-15]** divided these

gels into two groups depending on the potassium- or sodium-based composition of the aluminosilicate, and proceeded to their sol-gel synthesis. The main nanostructural characteristics and the effect of the pH on gel chemical composition were then studied.

In a parallel line of study, the ability of "type F fly ash – OPC clinker – alkaline component" systems to yield good cement was first proven in 1974 [16]. Research conducted at the Eduardo Torroja Institute [17-18] and the University of Melbourne [19] has shown C-S-H (main hydration product in Portland cement systems) and N-A-S-H (main reaction product in type F fly ash activation) gels to be compatible.

The potential social and industrial benefits of developing blended cements with both a high fly ash content and the excellent strength and other properties of normal Portland cement prompted the present exploration of a common procedure for simultaneously synthesizing a mixture of the two cementitious gels (C-S-H+N-A-S-H). A better understanding of the pure components should help to develop new cements in the near future.

2. Experimental procedure

2.1 Initial reagents
The following working materials were used: laboratory grade calcium nitrate, aluminium nitrate and sodium silicate supplied by PANREAC, S.A.

The sol-gel method was used throughout to synthesize the working gels (C-S-H and N-A-S-H). The synthesis variables studied were pH and the initial Ca/Si and Si/Al ratios for the respective types of gel. A 1M NaOH solution prepared from NaOH pellets and de-ionized, de-carbonated water was used as a buffer.

2.2. C-S-H gel synthesis
The C-S-H gels were synthesized under the following conditions: a sodium silicate (Na_2SiO_3) solution with a pH of 11.1 was used as the source of silicon and calcium nitrate $Ca(NO_3)_2.4H_2O$ as the source of calcium. One-molar solutions were prepared from both compounds. The procedure deployed consisted in the following: a pre-defined volume of 1M $Ca(NO_3)_3.4H_2O$ was added, drop by drop, to the sodium silicate solution (to which an appropriate amount of NaOH buffer had been added). The entire process was conducted at laboratory temperature with continuous stirring. A whitish gel precipitated immediately. The two phases obtained at the end of the process were: the solid precipitate (the gel) and a supernatant liquor. After measuring the pH of the liquor, the gel was filtered and washed with de-ionized and decarbonated water to a neutral pH. Finally, the gel was dried in a desiccator at ambient temperature and characterized using FTIR, SEM, and ^{29}Si NMR techniques. The synthesis conditions are listed in Table 1.

2.3 N-A-S-H gel synthesis
The procedure followed to synthesize this type of gels was the same as for the C-S-H gels. A 1M sodium silicate solution was used as the source of silicon and a 1M solution of aluminium nitrate ($Al(NO_3)_3.9H_2O$) for the aluminium. The gels obtained were likewise characterized using FTIR, SEM, ^{29}Si and ^{27}Al NMR-MAS analysis. The synthesis conditions are listed in Table 2.

Table 1. C-S-H gel synthesis conditions

	C-S-H gel	NaSiO$_3$[1] (ml)	Ca(NO$_3$)$_2$[2] (ml)	NaOH[3] (ml)	Si (Mol)	Ca (Mol)	Na (Mol)	Ca/ Si	pH [4]
Ca/Si ratio = 1 pH = variable	C1	50	50	-	0.05	0.05	-	1	8.72
	C2	50	50	10	0.05	0.05	0.01	1	9.26
	C3	50	50	20	0.05	0.05	0.02	1	10.10
	C4	50	50	25	0.05	0.05	0.025	1	11.14
	C5	50	50	50	0.05	0.05	0.05	1	11.73
	C6	50	50	70	0.05	0.05	0.070	1	12.20
Variable Ca/Si ratio	C7	50	40	65	0.05	0.04	0.065	0.8	12.25
	C8	50	55	65	0.05	0.055	0.065	1.1	12.04
	C9	50	70	95	0.05	0.07	0.095	1.4	11.97
	*C10	50	90	120	0.05	0.09	0.120	1.8	11.90
	C11	50	100	140	0.05	0.10	0.140	2	11.93

Table 1. N-A-S-H gel synthesis conditions

	N-A-S-H gel	NaSiO$_3$[1] (ml)	Al(NO$_3$)$_2$[5] (ml)	NaOH[3] (ml)	Si (Mol)	Al (Mol)	Na (Mol)	Si/ Al	pH [4]
Si/Al ratio = 1 pH = variable	N1	50	50	150	0.05	0.05	0.15	1	8.67
	N2	50	50	170	0.05	0.05	0.17	1	10.54
	N 3	50	50	200	0.05	0.05	0.20	1	11.43
	N4	50	50	225	0.05	0.05	0.20*	1	12.51
	N5	50	50	250	0.05	0.05	0.25	1	12.74
	N6	50	50	275	0.05	0.05	0.20*	1	12.87
	N7	50	50	300	0.05	0.05	0.30	1	12.90
	*N8	50	50	400	0.05	0.05	0.40	1	13.26
Variable Si/Al ratio	N9	50	33	225	0.05	0.033	0.225	1.5	13.02
	N10	50	25	200	0.05	0.025	0.200	2	13.09
	N11	50	16.67	180	0.05	0.016	0.180	3	13.16

Table 3. Mixed gel synthesis conditions

	NaSiO$_3$[1] (ml)	Ca(NO$_3$)$_2$[2] (ml)	Al(NO^3)$_2$[5] (ml)	NaOH[3] (ml)	Si/Al	Ca/Si	pH [4]
*M2	50 ml	25ml	25ml	50	2	0.5	**13.10**
M 7	50 ml	50 ml	25ml	200	2	1	**12.87**

*In all tables: (1) initial volume of 1M sodium silicate; (2) initial volume of 1M calcium nitrate; (3) volume of 1M NaOH added to original silicate solution during synthesis; (4) average pH in supernatant liquor after precipitation of the gel; (5) initial volume of 1M aluminium nitrate; *Samples selected for NMR and SEM characterization.*

3. Results and discussion

3.1. FTIR results

C-S-H gels Figure 1(a) shows the FTIR spectra for the C-S-H gels synthesized with the same theoretical Ca/Si ratios but different pH values (samples C1 to C6). Table 4 gives the FTIR spectrum band assignments for gels C2 and C4. As system alkalinity increased, the main band, attributed to Si-O bond asymmetric stretching vibrations, shifted to lower frequencies, although this shift ceased to be significant upward of a certain pH value (approximately 11)

(see Figure 2). The gels obtained were very similar to the gels synthesized with other experimental procedures and described in the literature **[20-21]**.

(a) C-S-H Gels
Ca/Si Theoretical= 1

(b) C-S-H gels
Ca/Si=variable
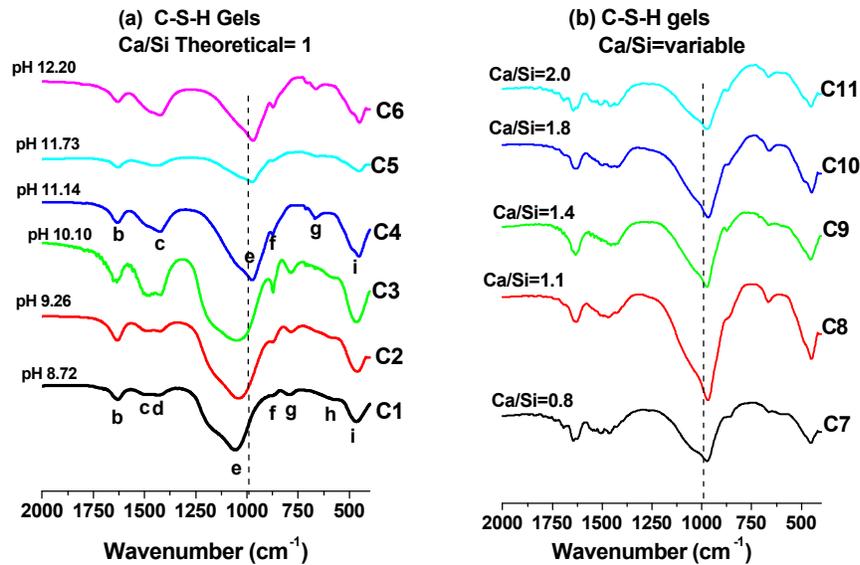
Figure 1. FTIR spectra for C-S-H gels with (a) the same theoretical Ca/Si ratio; (b) differing Ca/Si ratios

Table 4. Gel C2 and C4 band assignments

Band	Gel C2 (cm^{-1})	ASSIGNED TO	Gel C4 (cm^{-1})	ASSIGNED TO
a	3434	νOH stretching	3429	ν OH (H_2O)
b	1632	δOH bending	1632	δ OH (H_2O)
c	1486	ν_3 CO (CO_3^{2-})	1444	ν_3 CO (CO_3^{2-})
d	1428	ν_3 CO (CO_3^{2-})	----	----
e	1041	Si-O asymmetric stretching	**975**	ν Si-O asymmetric stretching **(C-S-H gel)**
f	874	Narrow vaterite band ν_2 CO (CO_3^{2-})	875	δ_2CO (CO_3^{2-})
g	784	δSi-O-Si bending	662	δ Si-O-Si
h	578	δSi-O-Si bending	-	-
i	464	δ SiO (SiO_4 Td)	452	δ Si-O (Td)

The main ν_3 Si-O band on the spectra for the gels synthesized at pH < 11 was wider and centred at a higher frequency (around 1041 cm^{-1}, see gel C2, Table 4) than in other C-S-H gels, an indication of a higher SiO_2 content and degree of polymerization in the former **[22-23]**. Such more intense average polymerization of the silicates may reflect the presence of Q^3 and Q^4 sites on the SiO_2 gel. In the FTIR spectrum of the gel synthesized at pH>11 (gel C4), however, the Si-O stretching band appeared at around 975 cm^{-1}, i.e., at a considerably lower frequency than on the gel C2 spectrum. This is an indication that C4 incorporated calcium in its structure (as in conventional C-S-H gel). According to Kirkpatrick et al **[23]**, this band can be assigned to the Si-O bond stretching vibrations in the Q^2 tetrahedra. It shifts toward lower frequencies as the C/S ratio rises to values ≤ 1.2, a sign of progressive depolymerization of the silicate chains. In other words, the higher the synthesis

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pH, the greater is gel Ca content and therefore the lower is its degree of polymerization.

It may also be inferred from these results that despite the use of de-ionized and decarbonated water, these gels carbonated fairly readily.

Figure 1(b) shows the FTIR spectra of the gels prepared with different theoretical Ca/Si ratios but similar pH values (~12). Changing theoretical Ca/Si ratios in the gels was observed to have no significant effect on band position. The Si-O bond stretching vibration band appeared at 970 cm^{-1} (typical of a C-S-H gel) on the spectra for all these gels, while the C-S-H gel Si-O-Si bending band was positioned at 660-670 cm^{-1}. The intensity of this band was higher for gel C8, where the theoretical C/S ratio was 1.1. According to the literature on C-S-H gels, this band is more intense in tobermorite-type gels with C/S ratios $\cong 0.88$ [23]. Its intensity tends to decline for gels with C/S ratios >0.88, a finding that is consistent with depolymerization and laxer structural order. The band at 450 cm^{-1} is likewise characteristic of bending vibrations in C-S-H gel SiO$_4$ tetrahedra [23]. There is every indication, then, that the product of this synthesis procedure was always the same C-S-H gel, regardless of the initial Ca/Si ratios. In short, pH was found to play a more relevant role than the theoretical Ca/Si ratio in C-S-H-type gel synthesis.
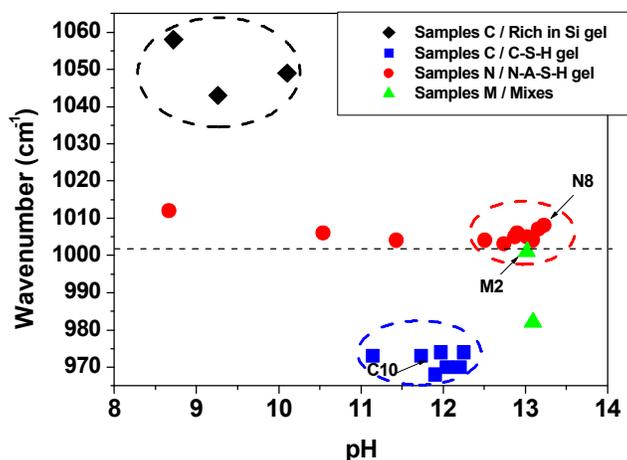
Figure 2. Shift in the T-O band versus pH for the gels synthesized

**N-A-S-H gels** Figure 3(a) shows the FTIR spectra for a series of N-A-S-H gels synthesized with the same theoretical Ca/Si ratios but different pH values (see Table 2) and Figure 3(b) the spectra for another group of gels, synthesized at the same pH but with different Si/Al ratios in the initial systems. The position of the main band in these spectra (corresponding to T-O (T=Si or Al) bond asymmetric stretching vibrations) was observed to change slightly as system pH rose to a given value (~12.5), upward of which the spectra of the gels synthesized with the same theoretical Si/Al ratios were essentially identical. Indeed, at pH values of about 12.5 the main band appeared at around 1006 cm-1 (see Figure 2). For low pH values, the FTIR spectra were observed to have very wide and poorly defined bands. Here the main band was positioned at around 1012 cm^{-1}.

A higher Si/Al ratio in the synthesized gels might initially be expected to shift the position of the main band on their spectra (to higher frequencies),

indicating a gel richer in silicon – but this proved not to be the case. The sol-gel procedure would appear to have limitations in respect of the production of very Si-rich gels, perhaps because of their particularly slow formation kinetics.
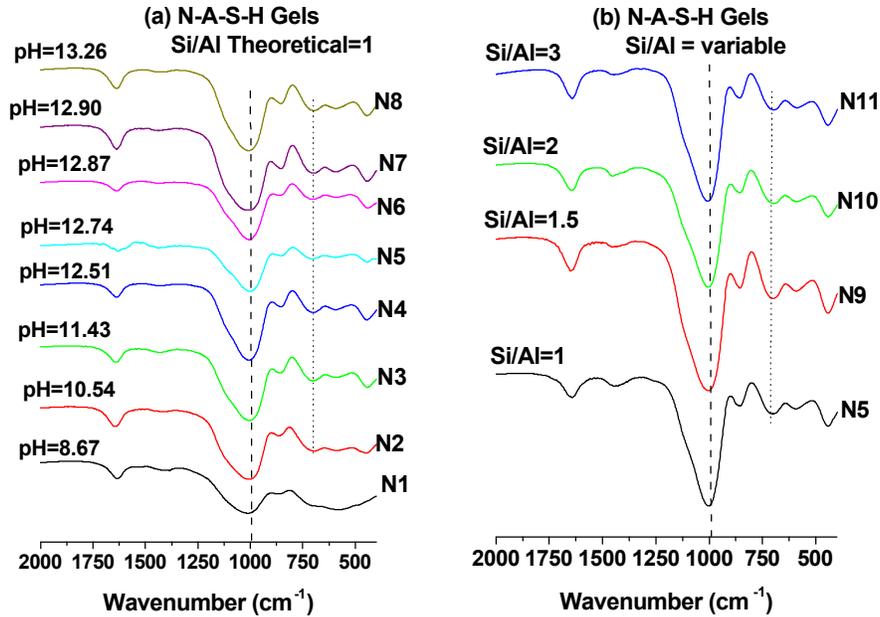
Figure 3. FTIR spectra for N-A-S-H gels with (a) the same theoretical Si/Al ratio; (b) differing Si/Al ratios.

Close observation of any of the FTIR spectra in Figure 3 for gels synthesized at high pH reveal that these materials had nanostructures very similar to the structures of the gels resulting from the alkali activation of fly ash **[10]**. Hence, the band corresponding to T-O bond asymmetric stretching vibrations, positioned in this study at 1006 cm^{-1}, may be compared to the band characteristic of activated ash T-O stretching vibrations, which usually appears at around 1000 cm^{-1} **[10]**.

On the sample C (C-S-H-type gels) spectra, a single band (~660-670 cm^{-1}) appeared in the 800-500 cm^{-1} zone, whereas two were observed in the sample N spectra: one at 690-700 and the other at around 594 cm^{-1}. According to aluminosilicate theory **[10,24,25]**, these bands are associated with vibrations in the tetrahedra that form the so-called **secondary building units (SBU)** and fragments of the aluminosilicate network. Also known as **bands due to pseudo-lattice vibrations of structural units,** they are characteristic of the double or single rings that depend on the structure of the material, and/or TO$_4$ tetrahedral bonds. Hence, changes prompted by the formation of three-dimensional structures as the result of inter-ring connections generate variations in the number, shape and position of the bands in this zone. Variations in the Si/Al ratio also change this area of the spectrum. While the former band is associated with TO$_4$ internal symmetric bending vibrations, the latter is associated with external vibrations; more specifically, the band between 650 and 500 cm^{-1} is associated with the presence of double rings.

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The band appearing at 445 cm^{-1}, assigned to internal T-O bond bending vibrations, remained essentially unchanged, for its intensity does not depend on the degree of crystallization. Finally, these gels were found to carbonate less extensively than the C-S-H gels.

3.2.- Mixed gels (C-S-H + N-A-S-H)

All the mixed gels were synthesized at pH values of over 12.5 to ensure precipitation of both C-S-H and N-A-S-H. Like the other two gels, the mixed gel was analyzed with FTIR technology (see Figure 4).
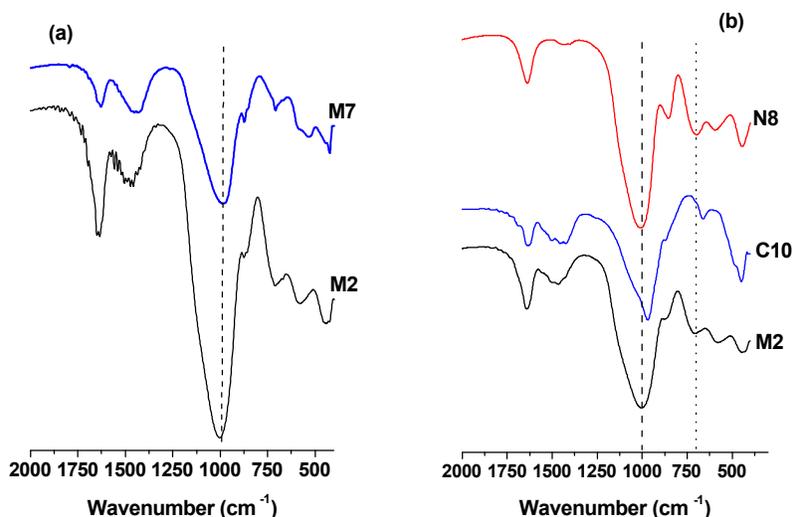
Figure 4. (a) FTIR spectra for mixed gels (b) comparison of FTIR spectra for samples C10, N8 and M2

The shape of the IR spectrum and position of the gel M2 bands (synthesized at a high pH (13.1) with an initial theoretical Ca/Si ratio of 0.5 and Si/Al ratio of 2) were more reminiscent of an N-A-S-H than a C-S-H gel. The gel M7 (synthesized with theoretical ratios of Si/Al = 2 and Ca/Si = 1), spectrum however, showed a central band at around 980 cm^{-1} that matches the stretching vibration band observed in C-S-H gels quite well (see Figure 2).

Figure 4(b) compares representative spectra for each of the three gels synthesized: C10, N8 and M2. In gels N8 and M2 the asymmetric stretching vibration band appeared at clearly higher frequencies, indicating greater degrees of polymerization than in sample C10, an observation consistent with the possible formation of N-A-S-H-type gels. Moreover, in the 800-500 cm^{-1} zone, both gels N8 and M2 had two bands associated with the vibrations of the tetrahedra that constitute the so-called ***Secondary Building Units (SBU)*** and fragments of the aluminosilicate network. This denotes highly polymerized and possibly three-dimensional structures in these gels.

3.2 SEM/EDX results

Gels C10, N8, M2 and M7 were selected for elemental SEM/EDX analysis to contrast the theoretical Si/Al and Ca/Si ratios with the experimental values.

Figures 5 and 6 show the morphology of these gels and the EDX microanalytical findings. The morphology of gel C10 (Figure 5(a)) was very

similar to type I (tobermorite-type) C-S-H gel morphology [22]. The experimentally measured Ca/Si ratio was slightly lower than the theoretical value. It was, however, similar to the reading reported by other authors for C-S-H gels, obtained via OPC hydration or synthesis under different conditions than in the present study [20-21].

Figure 5(b) shows the morphology and elemental analysis of gel N8. This gel contained Al, Si and Na in its composition, although the Si/Al ratio was, surprisingly, found to be higher than the theoretical value; this would signify that part of the aluminium was not taken up in the structure. From the morphological standpoint, this gel was more powdery and had a finer particle size than gel C10. A comparison with other N-A-S-H-type gels described in the literature [26] revealed that both its morphology and composition were quite similar to the product of the alkali activation of metakaolin in the presence of caustic salts (but not soluble silica).

Table 5 Comparison of theoretical and SEM/EDX theoretical values

Gel	pH	Ca/Si ratio		Si/Al	
		Theoret.	Experimental	Theoret.	Experimental
C10	11.89	1.8	0.87	-	-
N8	13.26	-	-	1.0	1.22
M2	13.1	0.5	0.48	2	1.56
M7	12.87	1	0.84	2	1.18

Finally, Figure 6 gives both the morphological and the SEM/EDX microanalytical findings for mixed gels M2 and M7. Gel M2 was observed to be more like N8 and M7 more like C10. The Al content was somewhat high in gel M2, which may explain the intense polymerization reflected in the shift in its T-O bond ν_3 band (see Figure 4(a)). Here also the gel was powdery and resembled sodium aluminosilicate. Gel M7, in turn, had a high Ca content, which concurred with the FTIR findings; this gel was less intensely polymerized and looked more like a C-S-H gel. It might actually be considered to be an A-S-C-H-type gel, a calcium aluminosilicate.
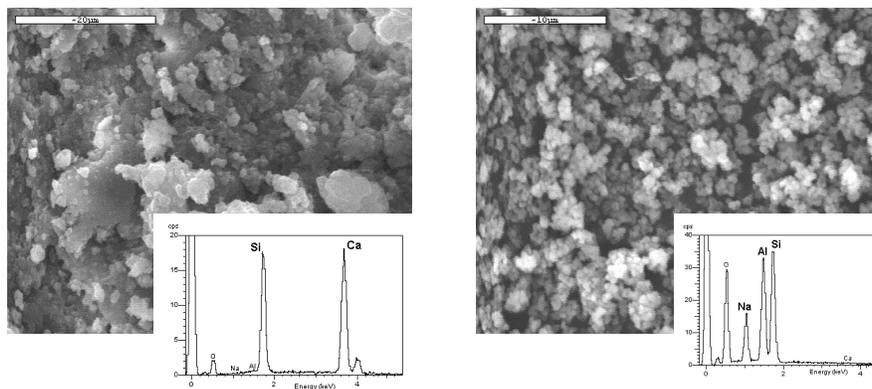
Figure 5. Gel morphology and microanalysis for (a) C10 and (b) N8
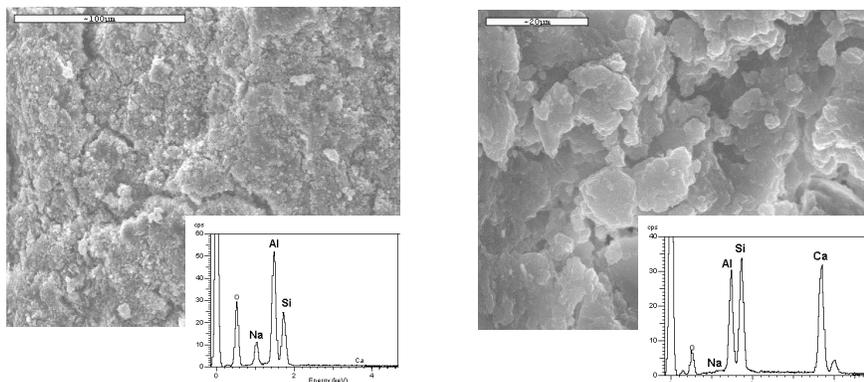
Figure 6. Gel morphology and microanalysis for (a) M2 and (b) M7

3.2 NMR results

Finally, a short series of representative gels prepared in this study were also analyzed with ^{29}Si and ^{27}Al NMR; the respective spectra are shown in Figure 7.

The spectrum for **_gel C10_** (which had a theoretical Ca/Si ratio of 1.8 and an experimental ratio of 0.87) exhibited three well-defined peaks located at -79.8, -83.8 and -85.8 ppm. These three signals were assigned to dimers or to the silicon tetrahedra in terminal positions on the chain (end-of-chain Q^1 site – signal at -79.8) and mid-chain tetrahedra (Q^2 sites – signal at -85.85) **[27,28]**. More intensely polymerized gels would have wide bands across a variable interval of from -90 to -100 ppm, associated with Q^3 tetrahedra. But as the Ca/Si ratios rose the degree of polymerization declined, producing spectra with sharper and better resolved peaks.
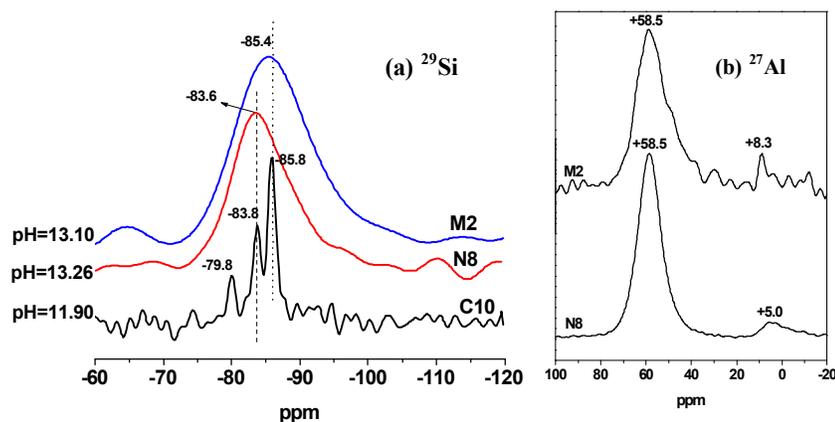
Figure 7. (a) ^{29}Si and (b) ^{27}Al NMR-MAS spectra

The signal appearing at around -83.8 ppm, in turn, might have denoted the presence of a sodium silicate impurity in the gel, but the SEM/EDX results showed that these gels had no sodium in their composition. The literature is helpful in this regard: Faucon distinguished between two types of Q^2 signals, which he associated with two different environments **[29]**: one, corresponding to mid-chain tetrahedra, at approximately -85 ppm and the other to Q^2 bridge

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sites (bridge tetrahedra in the chain), appearing at around -82.5 ppm. The signal detected here may be associated with such sites.

In short, the type of NMR spectrum shown in Figure 7 (highly defined and containing these specific peaks), along with the Ca/Si ratios observed in the microscopic analysis, appear to suggest that the C-S-H gels synthesized constitute a type I (tobermorite) C-S-H gel [22].

Gel N8 was selected as representative of the N-A-S-H gels (see Figure 7). Unlike the C-S-H gels, these gels generated spectra with a very wide and asymmetric signal peaking at -83.6 ppm. When deconvoluted (see Figure 8(a)), this wide signal was found to comprise four components at positions -78, -83.6, -89.3 and -94.5 ppm. The signal at -78 ppm was associated with end-of-chain Q^1 sites. Assignment of the other three signals (83.6, -89.3 and -94.5 ppm) was more complex, however, inasmuch as they may be attributed to Q^2, $Q^3(nAl)$ or $Q^4(nAl)$ sites [28]. In light of the high percentage of Al detected in these gels and the higher degree of polymerization observed with FTIR, these signals are more likely due to the presence of $Q^3(nAl)$ or even $Q^4(nAl)$ sites in the gel. Considering also the papers published on N-A-S-H-type gels [11,13,14] and knowing that very similar ^{29}Si NMR-MAS spectra are obtained for gels produced in metakaolin and fly ash alkali activation [7,9,28], it may be deduced that these signals may be associated with $Q^4(4Al)$, $Q^4(3Al)$ and $Q^4(2Al)$ sites, respectively. Assuming these assignments, the $(Si/Al)_{NMR}$ ratio found with Engelhard's equation for this gel was 1.07, which is very much in line with the theoretical value and the EDX analysis.

The ^{27}Al NMR-MAS results (see Figure 7(b)) may also provide support for assigning these signals as suggested. The Al in these gels appeared as tetrahedral Al positioned at around +60/+58 ppm. This signal is associated with the existence of aluminium tetrahedra surrounded by four silicon tetrahedra, a configuration characteristic of Al in zeolite precursors ($AlQ^4(4Si)$ environments) [28].
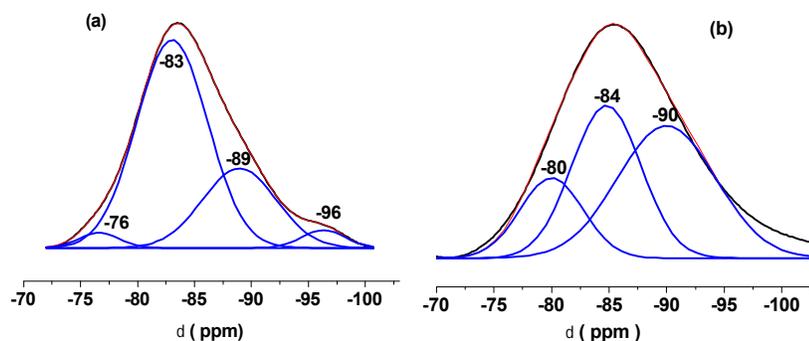
Figure 8. Deconvolution of the ^{29}Si NMR-MAS spectra for gels (a) N8 and (b) M2

The ^{29}Si NMR-MAS spectrum for *gel M2* also contained a wide and asymmetric signal peaking at -85 ppm, which is typical of Q^2 sites (see Figure 7). The deconvolution of this signal, however (Figure 8(b)) revealed the presence of three peaks positioned at -80, -84 and -90.54 ppm. Assignment was not obvious in this case, either: indeed, the substantial amount of Ca (in addition to Si and Al) present in this gel leads to wider-ranging chemical shifts

(to less negative values) when the adjacent Si is replaced by an Al, because the Ca^{2+} interacts more intensely than Na^{2+} with the O atoms in Si-O-Al. In light of these data, the first signal may be associated with the presence of $Q^2(2Al)$, $Q^3(3Al)$ or even $Q^4(4Al)$ sites. The second may be assigned to Q^2, $Q^3(2Al)$ or $Q^4(3Al)$ sites and the third to $Q^3(1Al)$ or even $Q^4(2Al)$ sites. As in the case of sample N8, given the presence of Al_T in positions around +58.5 ppm (see Figure 7(b)), these signals are more likely to correspond to the highly polymerized $Q^3(nAl)$ or $Q^4(nAl)$ sites. Nonetheless, the data presently available do not provide sufficient grounds for an unequivocal assignment.

In summary, the sol-gel technique can be used to synthesize both C-S-H and N-A-S-H gels. The results obtained to date with respect to the possibility of jointly synthesizing a mix of the two gels are not conclusive, however. With the techniques used it is difficult to distinguish whether the product formed comprises a mix of gels or a different gel: a calcium silicoaluminate. A series of additional studies is therefore planned to determine more precisely whether this method is suitable for the synthesis of mixed gels.

4. Conclusions

The results reported in this paper describe a simple procedure for synthesizing two different types of gels at laboratory temperature: C-S-H-and N-A-S-H-type gels.

In both cases, while the initial chemical composition of the system was found to play an important role, the pH of the resulting mix was identified as the critical factor in determining both the intensity of polymerization and the composition of the final product.

The results obtained to date on the viability of this method to jointly synthesize the two gels (C-S-H and N-A-S-H) are not conclusive, due in part to the difficulty in distinguishing them – assuming that both are formed – with the characterization techniques used.

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