

C-S-H gels in blended cements: Study by infrared spectroscopy

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Abstract

C-S-H gel is the main product in the Portland cement (PC) hydration. Of their structure and composition depends the cement properties (strength, durability...). The mixes of others materials with PC provides new cementitious materials with different properties. Understand the changes produces in the hydration products in these blends improves their use.

This work studies the changes produced in the C-S-H gel by means Fourier Transform Infrared Spectroscopy (FTIR). Several samples were studied, PC (as reference system), a system formed by PC and calcium aluminate cement (CAC) with a 75/25 ratio, and two system formed by PC, CAC and calcium sulfate (CS) with an 85/15 ratio of PC/CAC with 3 and 5% of CS. All samples were cured in two environmental; at the air and under water, in order to observe the influence of curing. The samples were studied at the 6 hours, 7 days, 12 and 32 months of age.

Results show in the PC, it changes to lower wavenumbers in the Q^2 units positions over time. This fact indicates a little transformation of structure like-tobermorite to structure like-jennite providing a C-S-H less compact. Addition of CAC in PC hydration decreases the migration of Q^2 units to lower wavenumbers indicating that C-S-H structure is more compact in this case. When CS is included in the system, this migration of Q^2 units is lower and the bands are sharper indicating the structure like-tobermorite presence.

Other effect visible in the spectra is the decrease of bands due to Q^1 units with the addition of CAC. The greater presence of aluminates in the system provides substitutions of Si^{4+} by Al^{3+} in the C-S-H structure. This fact produces longer chains reducing the units Q^1 . Different behaviors are observed in the cured conditions showing higher transformation towards structures like-jennite in the samples cured under water.

Several conclusions can be drawn of this work. First, it use of infrared spectroscopy as powerful tool in the cement chemistry field. Not only as characterization technique but also it can be used for obtain structural information about cement phases, both hydrated as anhydrous. Regarding addition of other hydraulic materials at PC, the study shows formation of C-S-H more compact that will provide better mechanical properties. Also the cured conditions have influenced about hydrated products structure.

Originality

This paper presents a study about C-S-H gel structure. Usually for this aim is used ^{29}Si RMN technique from where are obtained great results. This technique is a powerful tool but is very slow, since the resident time of the sample is large in the order of days. In this case we study the influence in the C-S-H formation of different hydraulic materials by means infrared spectroscopy. The results show changes in the Q units that provide information about C-S-H structure. Originality of this work reside in the use of the FTIR for obtain structural information, being faster and cheaper than other techniques.

Keywords: C-S-H, infrared spectrum, structure, blended cements

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1. Introduction

C-S-H gel is the main product in the Portland cement (PC) hydration. Cement properties (strength, durability...) will depend of C-S-H structure and composition. C-S-H structures are complicated of to study by means XDR due to low crystalline. It is consequence of ions incorporation in his structure (Mg^{2+} , Al^{3+} or Fe^{3+}) (Taylor H. F. W., 1990). C-S-H nanostructure will depend of Ca/Si ratio which can range from 1.2 to 2.1 (Grutzeck M.W., 1999).

C-S-H is amorphous, but it has a certain order. Exist two main models to describe of C-S-H structure:

- Proposed model by Taylor is based in layer 1.4 nm like-tobermorite blend with layer like-jennite (Taylor H. F. W., 1993,1986).
- Proposed model by Richardson and Groves based in structures like-tobermorite with layer of calcium hydroxide (Richardson I. G., Groves G. W., 2004, 1993).

Both models consider at the gel as disorderly structure in layers like-tobermorite and like-jennite, where each layer is formed by silicates chains.

In the Figure 1 are depicted schematically a C-S-H structure with their different structural units. The chain of SiO_4 tetrahedra in the upper part illustrates an octameric unit where two bridging SiO_4 tetrahedra (Q_B^2) connect three dimers, resulting in two SiO_4 end groups (Q^1) and four paired SiO_4 sites (Q_P^2). The lower part of Figure 1 shows the incorporation of Al in a bridging site and the corresponding two $Q^2(1Al)$ sites (i.e., a SiO_4 chain unit connected to one SiO_4 and one AlO_4 tetrahedron). Moreover, a defect in the tobermorite structure is illustrated by a missing bridging tetrahedron in the lower part, which results in two neighboring Q^1 sites (Skibsted. J., 2004).

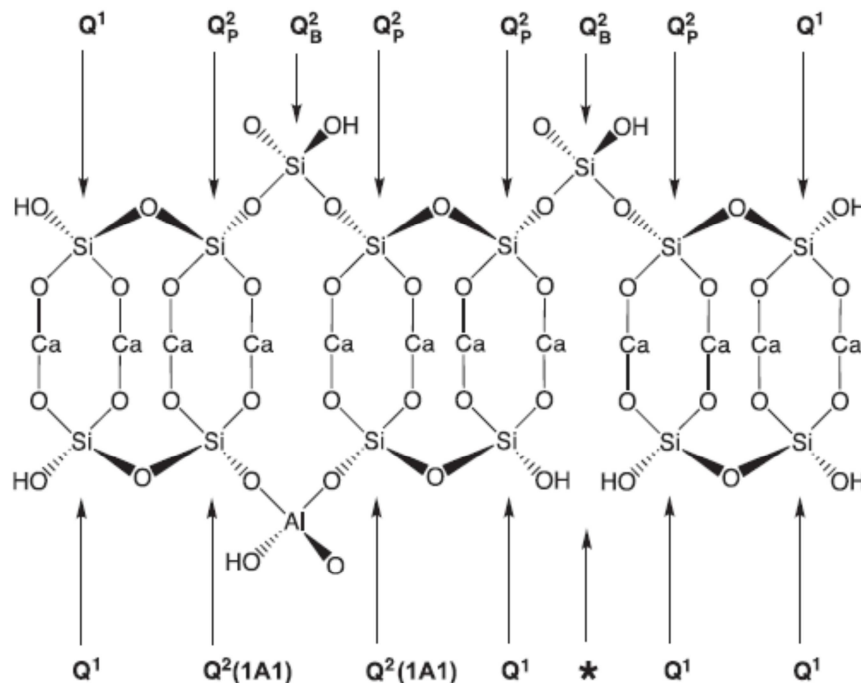


Figure 1 Schematic representation of a single layer in the crystal structure for a 14 Å tobermorite (Skibsted. J., 2004).

The composition of the C-S-H gel varies over time, with the additions, temperature... One most important characteristic in the gel composition is Ca/Si ratio, so gels more evolved and with chains longer or complexes seem to be poorer in Ca (Fuencisla I., 2012). The average ratio Ca/Si in the commercial cements varies between 2.3 and 0.7 (Thomas J. J. et al., 2006). In several gels there is a substitution of Si^{4+} by Al^{3+} , due to mixed with wastes or other cement kind as calcium aluminate cement (CAC). This fact leads to a decrease of Ca/Si ratio and to an increase of Al/Ca ratio.

A lot of works study the structure of C-S-H gel by means RMN technique with isotopes of ^{27}Al and ^{29}Si . In the literature there are few works that study the gel by infrared spectroscopy. Yu et al. performed a study where identified by FTIR (Fourier transform infrared spectroscopy) the different structures present in a C-S-H gel. These authors established the main bands of the gel and differentiating the vibrations between like-tobermorite structures and like-jennite structures. Infrared spectroscopy have become as a useful, non destructive technique to study the phase composition of initial and the hydration products. Moreover, by using this tool is possible the detection of crystalline but also the amorphous phases, as gel C-S-H. The infrared spectroscopy is used both gather information about the structure of compounds and as analytical tool to assess in qualitative and quantitative analysis of mixtures. (Fernández-Carrasco et al., 2012).

For generate new properties or improve some of them in PC, exist a great number of composites formed by one or more cements with several additions. The different combinations of materials produced variations in the hydrated phases that lead to changes in their structures (Torrens-Martin D., 2013). Adding new components as CAC or calcium sulfate (CS) both together or separately can improve certain properties of PC (Torrens-Martín et al., 2013). This type of mixed produced a blended building material that in the last years has increased their demand (Mainer S., 2008).

This work is focused in the study of changes produced in the C-S-H gel when is adding at hydration of PC different proportions of CAC and CS . Also was studied the influence of the cured in the C-S-H development using two cured different (water and air). The changes produced during of hydration in the gel were monitored by means of FTIR.

2. Experimental

2.1. Raw Materials

The materials used in this research were Portland cement type I 52.5R, Electroland calcium aluminate cement and a commercial calcium sulfate from Algiss. The X-ray fluorescence technique (XRF) was used to determine the chemical composition of the cements (Table 1). Both cements and the calcium sulfate were analyzed by X-ray diffraction (XRD) to verify their mineralogical composition (Figure 2).

Table 1 Chemical composition of raw materials/%

	CaO	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	SO ₃	MgO	TiO ₂	MnO	K ₂ O	P ₂ O ₅
CP	63.25	19.56	5.04	3.50	3.00	1.96	0.22	0.04	0.75	0.06
CAC	36.54	4.83	40.55	15.50	0.10	0.50	1.68	0.02	0.05	0.09

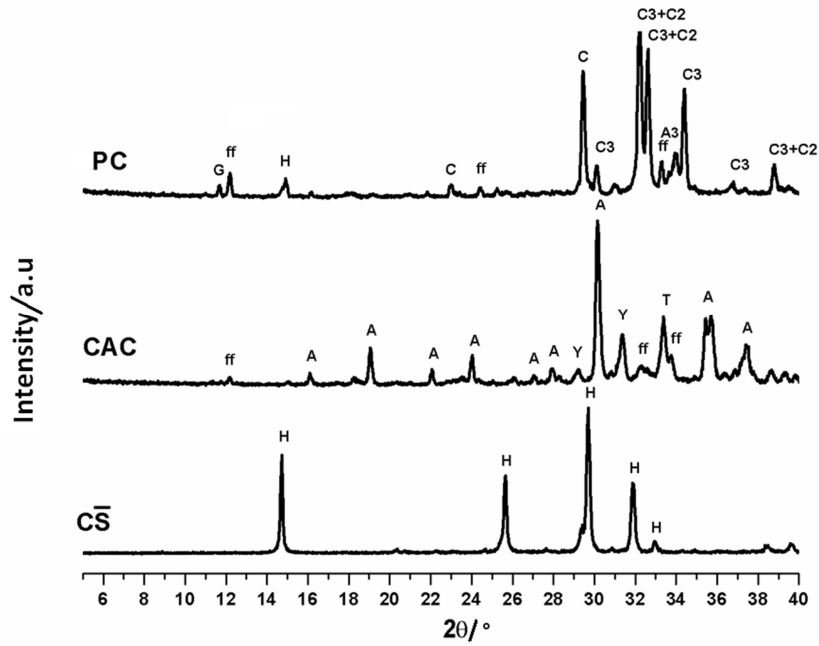


Figure 2 Diffraction patterns of raw materials
 C3:C₃S, C2:C₂S, A3:C₃A, ff:C₄AF, A:CA, Y:C₂AS, T:C₃FT,
 H:CaSO₄·0,5H₂O, G:CaSO₄·2H₂O, C:CaCO₃

2.2. Experimental Process

PC with different additions was studied, the proportion of raw materials used is shown in Table 2. It was studied one sample of PC for establish it as reference system. To see the influence of CAC was studied one sample with PC/CAC ratio of 75/25. 85/15 ratio with 3 and 5% of CS was studied to see the influence of sulfate in the C-S-H gel development. The water/cement ratio was kept constant at 0.4. The paste was cured for 6 h inside a curing chamber under the following conditions: 97% of relative humidity (RH) and 20°C. After this period, samples were cured under two different conditions: (i) in the chamber at 20°C and 97% RH (hereafter called dry curing) and (ii) immersed in distilled water at 20°C (wet curing). The selected ratio for the immersion was 2 ml of water per 1 g of cement paste. All samples were studied a different ages; 6 hours, 7 days, 12 and 32 months. The hydration stop was performed with the acetone/ethanol method (Zhang J., et al. 2011).

Table 2 Proportion of raw materials /% wt

Composition	%CP	%CAC	%CS
PC	100	0	0
75/25	75	25	0
85/15 3%	82.45	14.55	3
85/15 5%	80.75	14.25	5

The infrared spectroscopy analysis was carried with a Fourier transform infrared spectroscopy Nicolet 6700 with a He/Ne laser source, CsI beamsplitter and DTGS-CsI detector. The spectrums of the samples were registered in the region of mid-infrared (4000–400 cm⁻¹) with a spectral resolution of 4 cm⁻¹. The samples for FTIR were prepared using the pellets procedure (1 mg sample/300 mg KBr).

3. Results and Discussion

3.1. C-S-H Infrared Study in a Portland cement

Figure 3 show the study by FTIR in the zone due to Si-O vibrations ($1100-700\text{ cm}^{-1}$) for the PC. The spectra depicted are at 6 hours and for the two cured at 7 days, 12 and 32 months. There are not differences between the both cured, except a band due to carbonates, stronger in the sample dry.

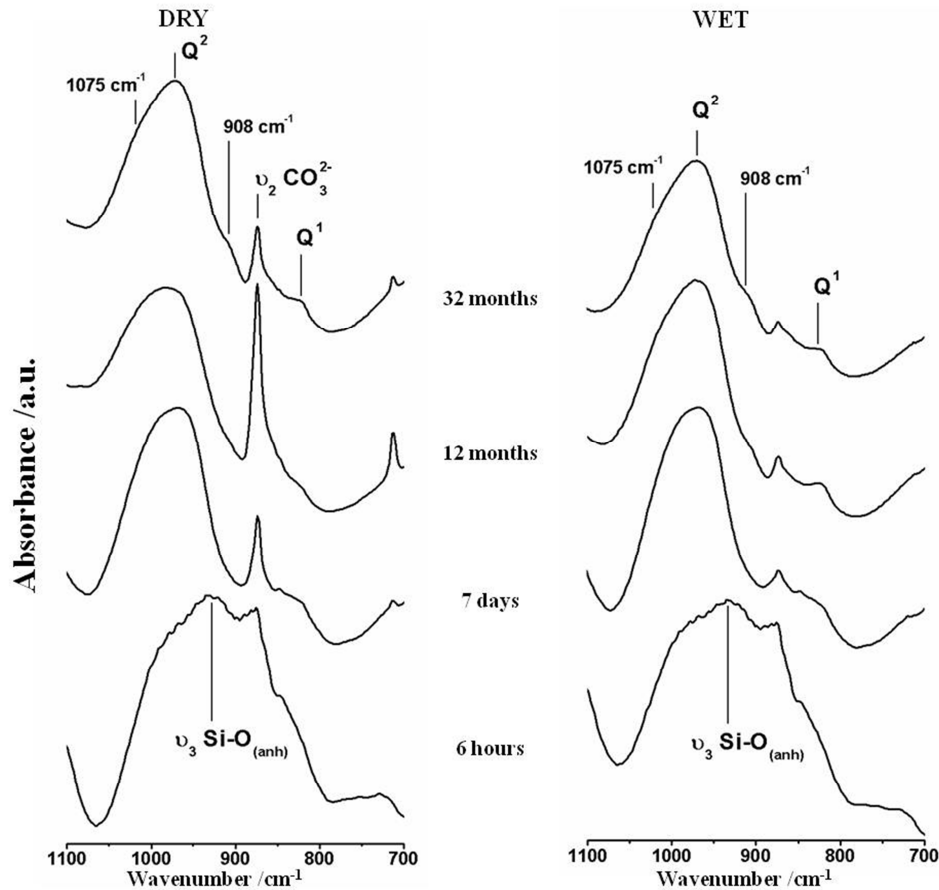


Figure 3 Infrared spectra for PC at 6 hours, 7 days, 12 and 32 months in the both cured; dry and wet.

At 6 hours the band is centered at 930 cm^{-1} , indicating that the band is composed mainly for vibrations due to anhydrous silicate (Fernández-Carrasco et al. 2012). These vibrations disappear when the hydration advances. Q^2 units are centered at 974 cm^{-1} moving to high wavenumbers at 12 months. According to Yu et al. (1999) this fact indicates a polymerization of gel toward like-tobermorite structure. To 32 months appear two shoulders at 1075 and 908 cm^{-1} and the Q^2 units down to lower wavenumbers. These changes could indicate that C-S-H gel is transformed in a like-jennite structure. The shoulders in the Si-O band vibration are more visible in the wet sample suggesting that the change is faster under water. On the other hand, Q^1 units, at 820 cm^{-1} , are detectable from 7 days, with more intensity in the wet sample.

3.2. Effect of aluminates in the C-S-H development

For to know the influence of aluminate presence in the C-S-H development was studied a sample with a 25% of CAC. It performed an infrared study in the Si-O vibrations zone in the same way as in the previously case. The spectra records are in the Figure 4.

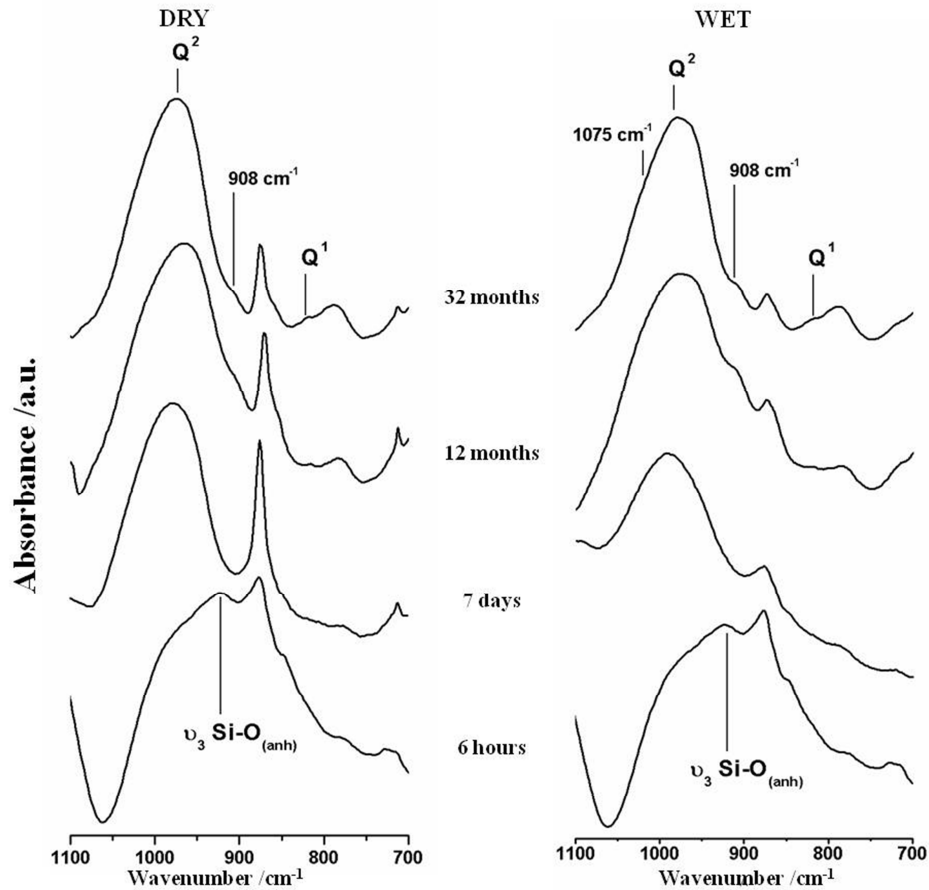


Figure 4 Infrared spectra for 75/25 sample at 6 hours, 7 days, 12 and 32 months in the both cured; dry and wet.

At 6 hours there are bands stronger due to anhydrous silicate though are overlapping with carbonates vibrations. This great presence of anhydrous silicate at early ages is due to a delayed in silicate hydration. Delay is produced by an ettringite layer around silicate grains which comes from the reaction between aluminates and sulfates preventing the normal silicate hydration (Gu P. et al. 1997, Torrens-Martin D., et al 2013).

When hydration time advances Q^2 units are centered at 977 cm^{-1} . The bands are sharper than in the PC sample. This fact indicates that the band is formed for less contributions (Nakamoto K. 1986), being the gel more homogeneous in their structure. According with Yu et al. (1999) these Q^2 units positions are due at a like-tobermorite structure. At 32 months the Q^2 units do not move to lower wavenumbers, though the shoulders appear with minor intensity towards 1075 cm^{-1} (wet) and 908 cm^{-1} (wet and dry). These two facts indicate a lower transformation to like-jennite structure.

Q^1 units towards 810 cm^{-1} show weak bands from 12 months. This is due at increase in the gel chains with respect at PC sample. Skibsted et al. (2003, 2004) observed by means of ^{27}Al and ^{29}Si NMR that more substitution of Al^{3+} for Si^{4+} in the C-S-H produces gels with chains longer. Therefore the presence of CAC in PC hydration leads to inclusion of Al^{3+} in the gel, generated gels more polymerized with chains more longer.

3.3. Effect of sulfates in the C-S-H development

Two percentages of CS (3 and 5%) was studied in a composition with PC/CAC ratio of 85/15. With this, the influence of sulfate will be observed in the development of gels formed by CP cements in the presence of aluminate. Increasing the proportion of sulfate will be obtained better view of the effect it produces. The spectra registered are in the Figure 5.

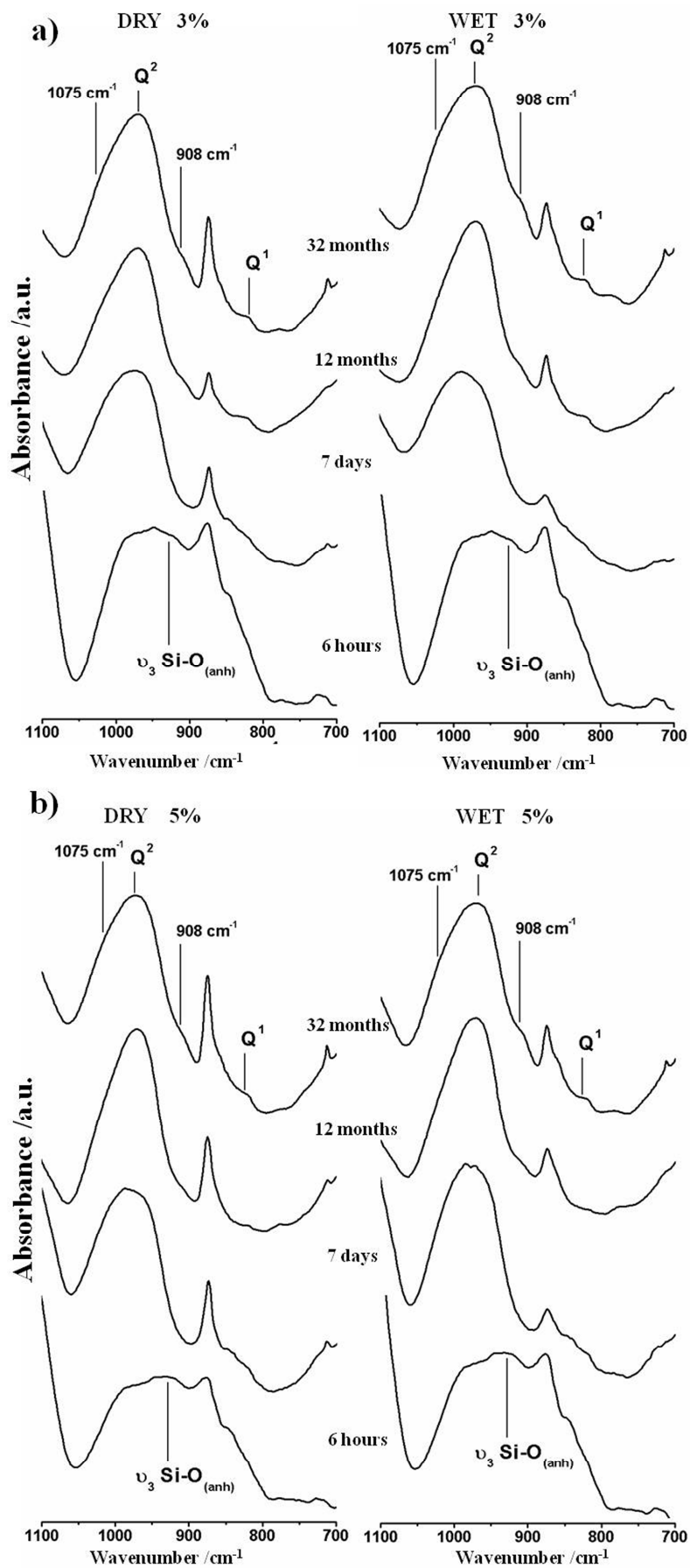


Figure 5 Infrared spectra for 85/15 sample at 6 hours, 7 days, 12 and 32 months in the both cured; dry and wet. a) with 3% of CS b) with 5% of CS.

Q^2 units are centered towards 972 cm^{-1} at 7 days, moving at lower wavenumbers when increases hydration time. At 32 months the main band is broader and appear two shoulders at 908 and 1075 cm^{-1} . The change in the wavenumbers and the appearance of shoulders can be interpreted as apparition a like-jennite structure. This fact in this composition is due at lower proportion of aluminates that produced gels less polymerized.

This fact is not produced in the same way in the different cured. The shoulders in the band due to Si-O vibrations, and particularly the centering in 908 cm^{-1} , have more intensity in wet samples. Therefore in the compositions cured under water the gel have more contributions of a like-jennite structure.

The contribution like-jennite structure is lower in the compositions with more proportion of $C\bar{S}$. So Q^2 units in the samples with 3% of $C\bar{S}$ are towards 977 cm^{-1} at 7 days, moving to 969 cm^{-1} at 32 months. On the contrary, Q^2 units in the cases with 5% of $C\bar{S}$ change from 981 cm^{-1} to 971 cm^{-1} , indicate higher presence of like-tobermorite structure. Also the shoulders due to like-jennite structure are weaker in the compositions with more $C\bar{S}$.

Q^1 units, towards 820 cm^{-1} , are more intense in the samples under water and with low proportion of $C\bar{S}$. Therefore the compositions dry and with more $C\bar{S}$ present longer chains. This fact can indicate that the presence of $C\bar{S}$ favors the incorporation of Al^{3+} in the C-S-H gel.

C-S-H gel structure developed for the PC will be a combination between like-tobermorite structure and like-jennite structure. At first hours, the majority will be like-tobermorite structure and when the hydration time advance will appears like-jennite structure. Adding CAC and $C\bar{S}$ will influence in this fact making it slower, producing gels with a more contribution of like-tobermorite structure. Increasing CAC and $C\bar{S}$ proportions also causes that the gels have longer chains. The cured will influence in the C-S-H formation, dry samples have a minor contribution of like-jennite structure with longer chains. In the Table 3 are the main vibrations observed for Si-O.

Table 3 Main Si-O vibrations
anh:anhydrous, s:sharp, w:weak sh:shoulder

	6 hours	7 days	12 months	32 months
CP	930 (anh)	820 Q^1	974 Q^2	969 Q^2 1075 (sh) stronger in wet cured 908 (sh) stronger in wet cured
CP+CAC	923 (anh)	977 Q^2 (s)	977 Q^2 810 Q^1	977 Q^2 1075 (sh, w) in wet cured 908 (sh, w) in dry and wet cured
3% $C\bar{S}$	920 (anh)	977 Q^2		969 Q^2 820 Q^1 stronger in wet cured 908 (sh) stronger in wet cured 1075 (sh)
5% $C\bar{S}$	925 (anh)	981 Q^2		971 Q^2 820 Q^1 908 (sh, w) 1075 (sh, w)

4. Conclusions

The following conclusions can be drawn from the present study:

- Adding aluminates to PC achieve gels more polymerized and with longer chains, due to incorporation of Al^{3+} in the gel.
- Adding $C\bar{S}$ is achieved gels with more contributions of like-tobermorite structures.
- Samples cured under water have a more contribution of like-jennite structure.
- Infrared spectroscopy is present as good tool for the structural analysis in the cement chemistry obtained results in less time.

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