Near-Infrared Spectroscopy Investigation of the Water Confined in Tricalcium Silicate Pastes

Francesca Ridi, Emiliano Fratini, Silvia Milani, and Piero Baglioni*

*Department of Chemistry and CSGI, University of Florence, via della Lastruccia 3,
50019 Sesto Fiorentino, Florence, Italy*

Near-infrared (NIR) spectroscopy has been employed to investigate the evolution of the vibrational spectrum of water entrapped in a tricalcium silicate paste. The overall free water, which decreases as a function of time due to the formation of the hydrated phases (portlandite, $Ca(OH)_2$, and hydrated calcium silicate, C-S-H) during the hydration reaction, is quantified by the decrease in the area of the NIR band at about 5000 cm^{-1}. The coexistence of two types of water in the hydrated phases (a "surface-interacting water" (type I) and a "bulklike water" (type II)) during the hydration is obtained by the analysis of the band at about 7000 cm^{-1}. The deconvolution of this band allows the quantification of the two water types. As the reaction advances, part of the "bulklike water" is converted to "surface-interacting water" in direct agreement with the C-S-H surface development. Finally, the $Ca(OH)_2$ formation can be concurrently monitored by NIR through the increase of a very sharp peak at 7083 cm^{-1}. Near-infrared spectroscopy allows determination in a very simple way of the most important features of the tricalcium silicate setting process.

Introduction

In the past years the study of water confined in restricted geometries has received increasing attention because of its relevance in many chemical and biological processes. The structure and the biological activity of the proteins, for example, are essentially determined by the presence of a few layers of water molecules, strongly interacting at the protein surface.[1] The influence of the surface hydrophilicity−hydrophobicity on the structural and dynamical properties of the water molecules (at the nanoscale level) has been extensively investigated in inorganic model systems such as carbon nanotubes [2,3] or silica gels. [4] In this regard, cementitious pastes are "*sui* generis" systems worth investigating, since they evolve continuously from both chemical and mechanical points of view. Cement develops its characteristics as a result of heterogeneous reactions between solid phases (calcium silicates and/or aluminates) and water. The final product of this process is a poorly porous material mainly constituted by hydrated calcium silicates (C-S-H), hydrated calcium aluminates, and by portlandite (calcium hydroxide). In the cement chemistry notation the tricalcium silicate and its hydrated form are abbreviated as C_3S and C-S-H, where $CaO = C$; $SiO_2 = S$, and $H_2O = H$. The dash in C-S-H refers to a not well-defined stoichiometry. The residual porosity, containing unreacted water, is one of the principal features affecting the mechanical resistance of cement.

The structure and the dynamics of water entrapped in a hydrating cement paste have been mainly studied by means of NMR[5,6] and neutron scattering.[7−13] These two techniques are complementary since NMR can discriminate between the types of water, present in a cement paste, through the analysis of the rotational relaxation times and the QENS technique mainly deals with the translational motion of the hydrogenated species. Near-

infrared (NIR) spectroscopy provides complementary information on the vibrational low harmonics modes of stretching and bending of hydrogen bonds. The absorption bands in the near-infrared region are known to be excellent markers of the state of water O−H bonds, since both the strength and the geometry of these bonds affect the frequency of the absorption peaks. The "state" of water molecules have been studied for different matrixes[14−16] as pure water, electrolytic solutions, and hydrogels. In particular, the first overtone band of the O−H stretching mode of water (∼7000 cm^{-1}) has been deeply investigated and structural models have been proposed to account for the peculiar vibrational spectrum of the water. According to a widely accepted model,[17] the absorption of water in this near-infrared region is due to two different classes of O−H oscillators, the so-called "weakly hydrogen bonded" (WHB) and "strongly hydrogen bonded" (SHB) water oscillator. While the SHB oscillator has a broad absorption at lower wavenumber, the WHB oscillator is sharper and centered at higher wavenumber. A significant increment of the WHB intensity is registered increasing the temperature[17] or increasing the confinement effects due to a solid matrix.[15]

In this work, we present a near-infrared spectroscopy investigation aimed at probing the state of water constrained in a cementitious porous matrix, and, in particular, in tricalcium silicate, C_3S, which is the major component of a cement paste, widely used as a model system for the study of the cement hydration reaction. To the best of our knowledge this is the first time that this approach has been used to investigate cementitious pastes in order to get information on the nature of the water contained in them.

We acquired the NIR spectra of a C_3S paste, following the kinetics of the hydration process. The deconvolution of the 7000 cm^{-1} band, characteristic of the liquid water molecules, revealed that at least two populations of water molecules differing in the O−H bond strength are present in the C_3S paste: a surface-interacting population (WHB) and a bulklike water population

* To whom all correspondence should be addressed. Phone: +39 055 457−3033. Fax: +39 055 457-3032. E-mail: piero.baglioni@unifi.it (www.csgi.unifi.it).
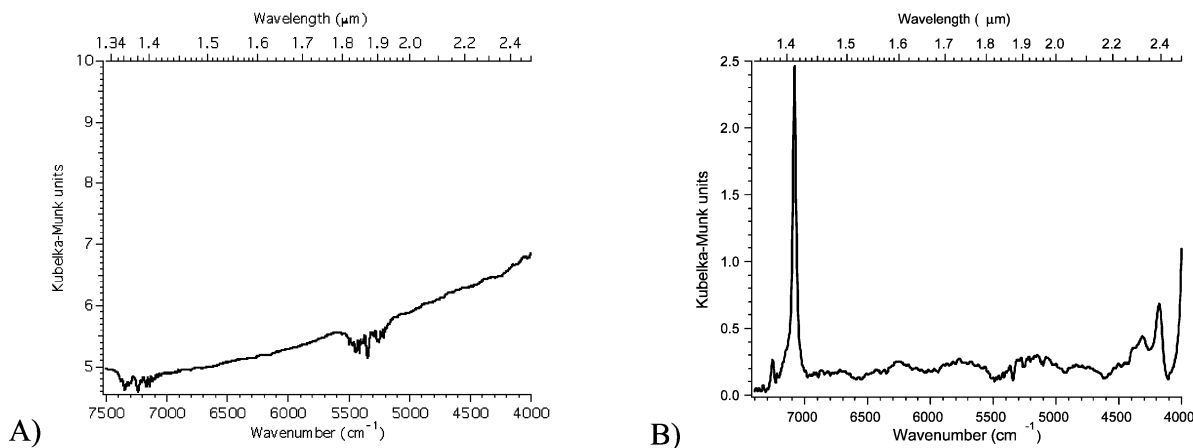
Water Confined in Tricalcium Silicate Paste

J. Phys. Chem. B, Vol. 110, No. 33, 2006 **16327**

Figure 1. NIR spectra (7600−4000 cm^{-1}) of (A) pure tricalcium silicate not corrected for the background contribution and (B) pure calcium hydroxide corrected for the background.

(SHB). The time evolution of these two populations along with the total amount of unreacted water has been monitored. Good agreement has been found between the water consumption as measured by NIR and the free water index as previously determined from differential scanning calorimetry (DSC) and neutron scattering experiments.[18] Moreover the WHB water fraction evolution compared with the C-S-H surface development as determined by NMR [19] has given a strong evidence that the WHB class accounts for surface-interacting water.

Experimental Section

Synthetic tricalcium silicate (C$_3$S) was a gift from CTG, Italcementi Group, with BET specific surface area of 0.44 ± 0.05 m^2/g and particle median radius of 5.75 μm. Water was purified by a Millipore Organex system ($R \geq 18$ MΩ·cm).

The sample for FT-IR measurements has been prepared with 0.4 water/solid ratio by mass. The silicate powder was mixed with water to obtain a paste that was stored in a Teflon mold, in a controlled moisture environment (~100%), at 20 ± 1 °C. The C$_3$S paste was removed for the FT-IR investigation from the storing Teflon mold at different times during the hydration process. The procedure to record an FT-IR spectrum took approximately 5 min: after the measurement the condition of controlled moisture was restored. The C$_3$S hydration was followed for approximately 1 month.

Near-infrared spectra have been acquired in the wavenumber interval 7600−4000 cm^{-1}, with a Nexus 870-FTIR (Thermo-Nicolet) and a FT-IR Continuμm microscope in diffuse reflectance mode (beam splitter: KBr; detector: MCT/A) with a resolution of 4 cm^{-1}, coadding 512 scans. To take into account the small part of the incident light transmitted by the sample, the obtained single beam spectra have been processed with a reference gold background using the Kubelka−Munk algorithm. The spectra of the pure powders (C$_3$S and Ca(OH)$_2$) have been acquired in diffuse reflectance mode following the same procedure used for the paste. To reduce the scattering contribution to the detected signal, some milligrams of the pure powders have been pressed into pellets.

In previous papers, we have already reported the methodology used for the DSC experiment.[18,20] NMR surface measurements were calculated using T_2 data [21] obtained for the same C$_3$S/water mixture and in the same time interval, according to the well-known Halperin's equation[22]

$$S = \frac{T_{2S}V}{\lambda T_{2i}}$$

where λ is the surface water layer thickness, V is the volume of mobile water in the pore system, T_{2S} is the characteristic spin−spin relaxation time for surface water, and T_{2i} is the experimentally measured spin−spin relaxation time for mobile water in the saturated paste. λ has been set to 0.3 nm, assuming that relaxation only occurs from the first surface layer, which may not be strictly true: surface areas could have been overestimated by perhaps 15% due to this hypothesis.[22] Nevertheless this choice is supported by the work of Hansen and co-workers,[23] who determined this thickness from NMR analysis of the freezing of water confined in mesoporous MCM-41 materials and found λ in the range 0.35−0.06 nm.

Results and Discussion

Addition of water to tricalcium silicate generates nearly amorphous calcium hydrosilicate, (CaO)$_x$(SiO$_2$)·(H$_2$O)$_y$, that is accompanied by crystalline calcium hydroxide, Ca(OH)$_2$, formation.

The overall hydration reaction can be summarized as follows:

$$\text{Ca}_3\text{SiO}_5 + (3 + y - x)\text{H}_2\text{O} \rightarrow$$
$$(\text{CaO})_x(\text{SiO}_2)\cdot(\text{H}_2\text{O})_y + (3 - x)\text{Ca(OH)}_2$$
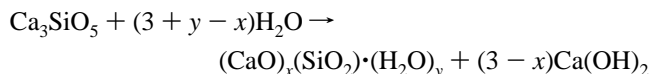
The NIR spectra at any time after water addition present three major components: C$_3$S, C-S-H, and portlandite. The deconvolution of the NIR spectra has been accomplished by using the featureless NIR spectrum of anhydrous tricalcium silicate for the correction of the background (see Figure 1A) and the calcium hydroxide spectrum that presents a well-defined sharp peak at 7083 cm^{-1} (see Figure 1B). The spectra registered for the hydrating tricalcium silicate paste present a very intense absorption below 4000 cm^{-1}, which dramatically affects the shape of the baseline in the region of interest: for this reason a baseline correction has been applied to the raw curves. To focus the attention on the two principal bands around 5000 and 7000 cm^{-1},[16] we used the same polynomial function for all the spectra. Furthermore, the noise produced by the environmental moisture in the two regions 7450−7050 cm^{-1} and 5500−5050 cm^{-1} has been estimated from the diffuse reflectance spectrum of anhydrous tricalcium silicate (Figure 1A) and subtracted to all spectra. The final subtracted baseline is shown in Figure 2A, together with some of the acquired raw curves; Figure 2B reports the spectra already corrected for the background. It is
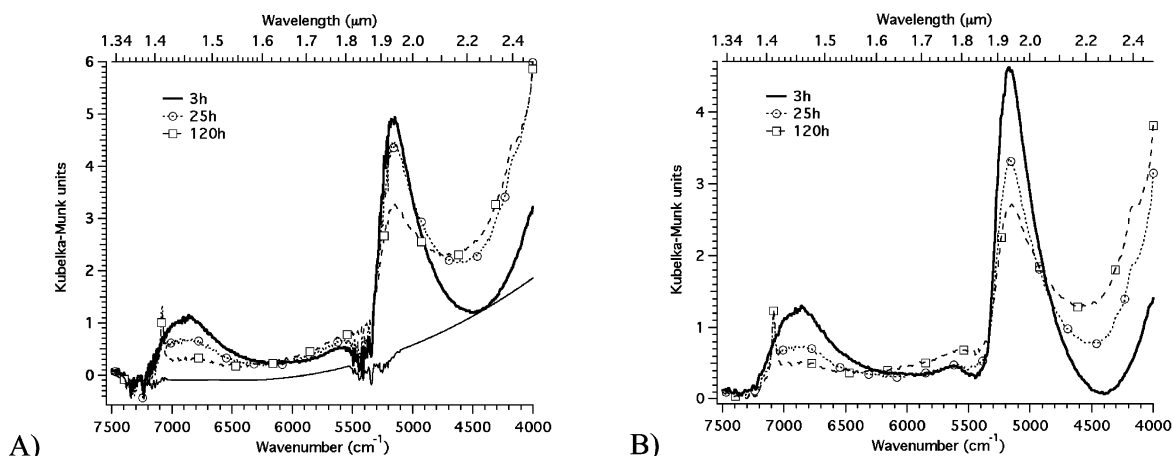
Figure 2. NIR spectra (7600−4000 cm^{-1}) registered at 3, 25, and 120 h after mixing for the C$_3$S/water paste (w/c = 0.4): (A) raw spectra, the curve used for baseline correction is also shown; (B) spectra corrected for the baseline.

TABLE 1: Assignment of the Principal Bands of the NIR Spectra of the Hydrating Tricalcium Silicate Paste[24] in the Region 7600−4000 cm^{-1}

wavenumber (cm^{-1})	assignment
7083	first O−H stretching overtone, Ca(OH)$_2$
∼7000	first O−H stretching overtone, water ($2\nu_1$, $2\nu_3$, $\nu_1 + \nu_3$)
∼5000	O−H combination band, water ($\nu_2 + \nu_3$)

evident that the moisture contribution has been completely subtracted out.

The mid-, near-, and far-infrared (IR) spectra of synthetic, single-phase calcium silicate hydrates (C-S-H) with Ca/Si ratios (C/S) of 0.41−1.85 (1.4 nm tobermorite, 1.1 nm tobermorite, and jennite) have been already analyzed and described elsewhere.[24] To follow the hydration reaction, we acquired the NIR spectra of a hydrating tricalcium silicate paste as a function of the hardening time. After 3 h from the mixing, the spectrum is dominated by the spectroscopic features of the liquid water, with two broad bands approximately at 7000 and 5000 cm^{-1} (Figure 2B), whose assignment is reported in Table 1. Previous calorimetric measurements[18] showed that at this time the hydration reaction is in the induction period and the water inside the paste has not reacted yet with the anhydrous powder, maintaining the physicochemical properties of the bulk liquid phase. During the hydration process the total intensity of the characteristic bands decreases, because of the conversion of the water into hydrated phases. Contextually the intensity of the sharp peak at 7083 cm^{-1}, due to the formation of portlandite,[24] increases.

To have a deeper insight on the state of water inside the C$_3$S paste and on its evolution during the hydration reaction, we performed a fitting using Gaussian components to deconvolve the 7000 cm^{-1} band. A similar approach has been applied to study supercooling phenomena of water entrapped in solid matrix as silica hydrogels.[15] We have chosen to deconvolve the 7000 cm^{-1} band since in this overtone region the intensities of the WHB O−H oscillators are enhanced as compared to those of the SHB population.[17] Five Gaussian functions (four to address the O−H stretching, one used to take into account the background contribution) have been used to fit the experimental data. Following the notation used in the literature[14,15] the components are denoted with Greek characters (α, β, γ, δ, and ϵ).

The parameters used for the Gaussian deconvolution were left free to vary except the frequency of the δ component (experimental background, mainly due to the KBr beam splitter)

centered at the fixed value of 6000 cm^{-1}, and, ϵ, that has been used to account for the very sharp peak at 7083 cm^{-1} coming from the overtone of the O−H stretching in Ca(OH)$_2$,[24] as shown in Figure 1B. The width of this peak has been extracted from the pure Ca(OH)$_2$ spectrum, reported in Figure 1B. This value has been then used throughout the following five Gaussian deconvolutions to avoid any contamination for the parameters of the α component. According to the existing literature[15] the Gaussian β and γ, respectively at 6600 and 6900 cm^{-1}, are referred to as coming from a continuum of strongly hydrogen bonded water molecules rather than attributed to a specific molecular class. The extra component δ, whose frequency has been kept fixed at 6000 cm^{-1}, was used to correct the background contribution due to the instrumental setup. Finally, the α Gaussian (around 7070 cm^{-1}), is attributed to a particular class of water molecules: this contribution to the first overtone absorption band has been assigned to the oscillation of weak O−H bonds. Angell and Rodgers[17] demonstrated experimentally that in bulk the "weakly hydrogen bonded" water population increases in intensity with increasing temperature. Furthermore a recent work[15] highlights that the geometric constrains imposed to the water phase by a solid matrix produce a similar increment of the high-frequency component of the 7000 cm^{-1} band of the NIR spectrum. The Gaussian deconvolution results for hydration time from 3 h to 27 days are shown in Figure 3. The data analysis provides evidence of the existence of two types of water molecules in the C$_3$S hydrating system: a fraction of water being in close contact with the pores surfaces (accounted for by the α Gaussian) and a second fraction practically unaffected by the solid matrix (Gaussian β and γ).

In the literature the combination band at ∼5000 cm^{-1} has been used in a quantitative way and for a variety of systems, such as the food, pharmaceutical, and medical sciences and polymer and textile industries, for the determination of total amount of water present in the sample.[25−27] We compared the trend of the free water index vs time, as obtained with the differential scanning calorimetry,[18] with the overall area of the ∼5000 cm^{-1} band, normalized to the area registered at the beginning of the hydration process

$$\mathrm{FWI}_{\mathrm{NIR}}(t) = \frac{A_{5000}(t)}{A_{5000}(t=0)}$$

Figure 4 shows that the hydration reaction can be successfully monitored considering the area of the 5000 cm^{-1} combination
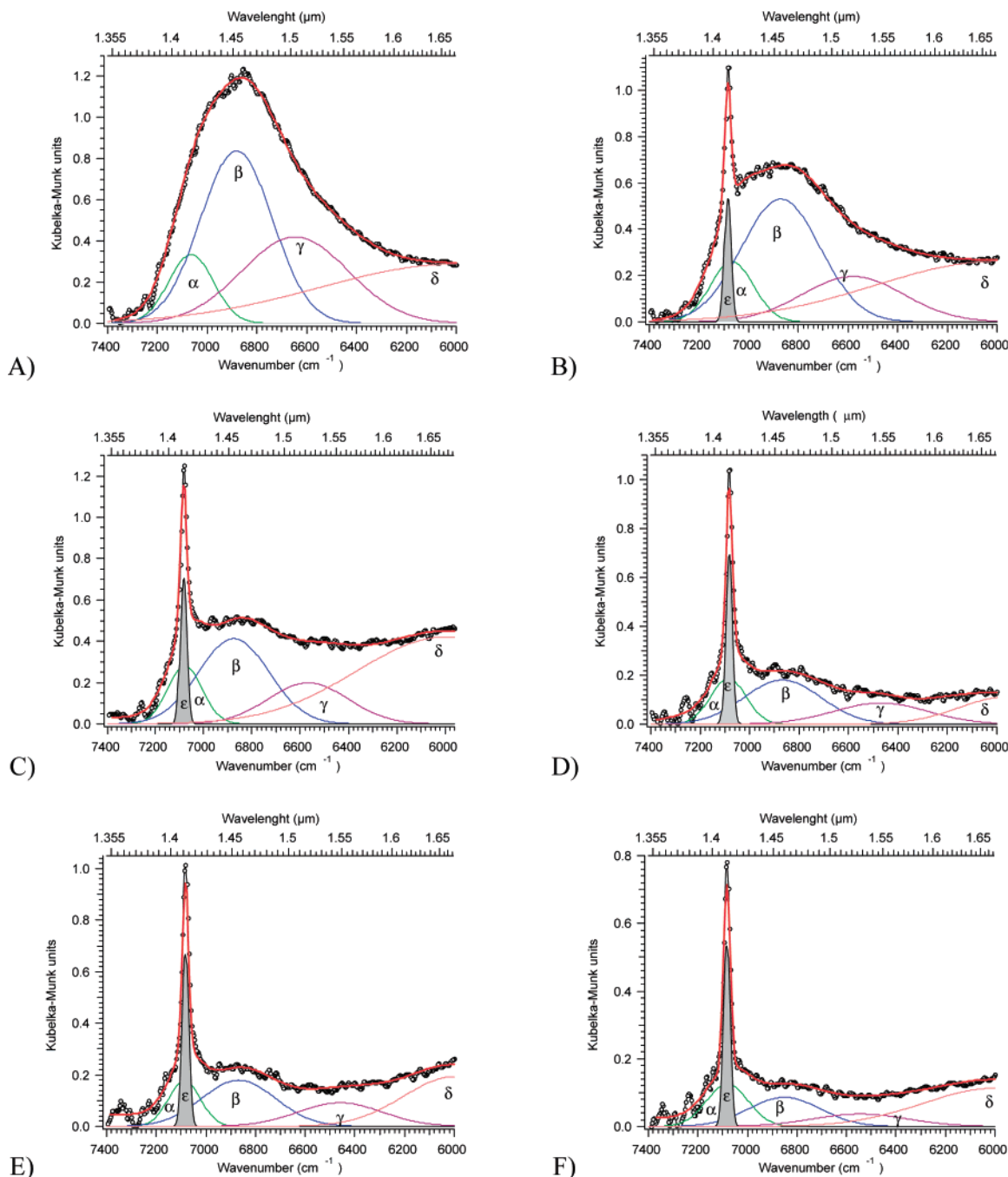
Water Confined in Tricalcium Silicate Paste

J. Phys. Chem. B, Vol. 110, No. 33, 2006 **16329**

Figure 3. NIR spectra (7400−6000 cm^{-1}) registered at increasing hydration times for the C$_3$S/water paste (w/c = 0.4): (A) 3 h, (B) 1 day (25 h), (C) 5 days (120 h), (D) 11 days (268 h), (E) 19 days (456 h), and (F) 27 days (648 h) after mixing. The components obtained from the Gaussian deconvolution of the band are also reported at each time.

band. Despite the conceptual difference between the two experimental techniques, an excellent agreement exists between this method and the differential scanning calorimetry approach.

The contribution of α, β, and γ components to the 7000 cm^{-1} band has been estimated by integrating the area of each peak. Since the unreacted water still present in the sample is proportional to the area of the 5000 cm^{-1} band, for each hydration time we normalized the area of the components to the $A_{5000}(t)$ value. Figure 5 reports the α, β, and γ contribution weighed over the total amount of water and shows the evolution of the areas of α, β, and γ as hydration time increases. It is evident that the contributions of β and γ components to the spectrum decrease in time, while α increases, suggesting that the water inside the pores is progressively converted from a "bulklike" (β and γ spectral contributions) to a "surface-

interacting" type water (the α peak, originating from the weakened hydrogen bonds). Moreover, the analysis of the α peak position (Table 2) shows that the wavenumber progressively increases, from 7065 to 7082 cm^{-1}. It is worth noting that in the literature a value of 7066 ± 3 cm^{-1} is reported for the α component of bulk water, while 7088 ± 2 cm^{-1} is typical of the same component in a dry silica hydrogel.[15] To be complete it is also important to stress that both the frequency and the width of components β and γ did not show any specific trend as a function of the hydration time.

Figure 6 shows the comparison between the increase of the surface-interacting water in the sample and the ratio of the surface area to weight of dry C$_3$S. This quantity has been determined from the surface-to-volume ratio, obtained from NMR spin−spin relaxation data[2] by estimating the pore volume
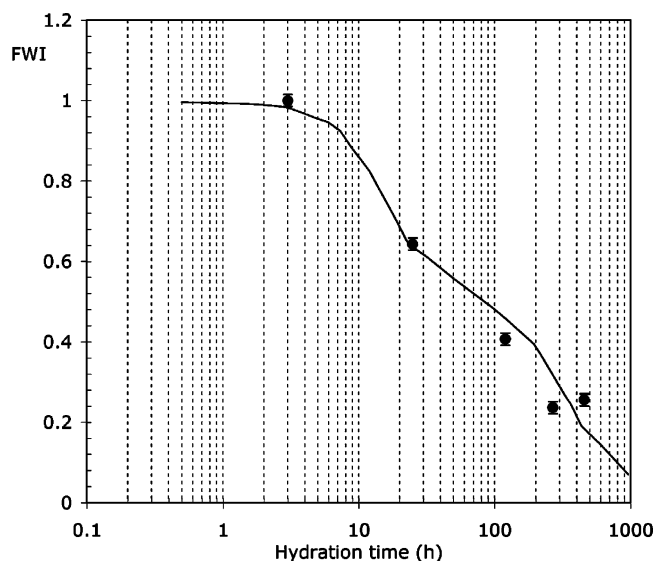
Figure 4. Comparison between the free water index (FWI) as obtained from calorimetric measurement[18] (continuous line) and the FWI obtained from the areas of the NIR band at 5000 cm^{-1} (●), normalized to unity.
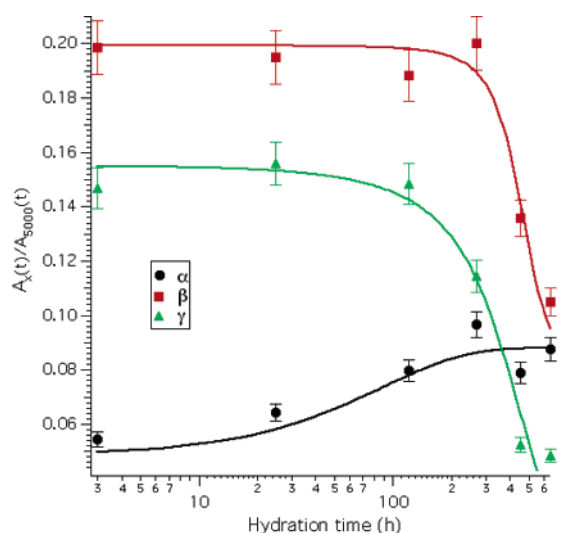

Figure 5. Areas of the (●) α, (■) β, and (▲) γ components vs hydration time obtained from the deconvolution of the NIR absorption (7400−6000 cm^{-1}). For each spectrum the areas have been normalized to the area of the 5000 cm^{-1} absorption that accounts for the total water. Reported error bars are directly estimated from the errors of the Gaussian parameters coming from the fitting of the NIR absorptions. The lines are drawn as guides for the eye.

TABLE 2: Peak Frequency (ν_α) and Width (σ_α) of the Gaussian α, as a Function of the Hydration Time[a]

time (h)	ν_α (cm^{-1})	σ_α (cm^{-1})
3	7065 ± 8	130 ± 16
25	7068 ± 8	125 ± 14
120	7077 ± 4	101 ± 4
268	7086 ± 4	101 ± 6
456	7086 ± 4	93 ± 5
648	7082 ± 8	119 ± 16

[a] Peak frequencies (ν_i), widths (σ_i), and relative Gaussian weights are defined by the mathematical form $R(\nu) = \sum_{i=\alpha,\beta,\gamma,\delta,E} M_i \exp[-(\nu - \nu_i)^2/\sigma_i^2]$, according to ref 14.

from the water content calculated from the calorimetric FWI data (continuous line in Figure 3). It is clearly evidenced in Figure 6 that the two quantities have the same trend.

We can conclude that the proposed Gaussian deconvolution approach clearly allows the quantification of the evolution of
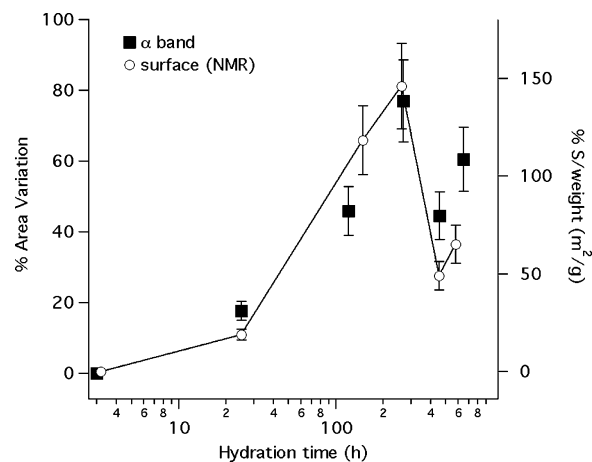

Figure 6. Comparison between the area of the α component obtained from the deconvolution of the NIR absorption (7400−6000cm^{-1}) and the surface-to-volume ratio, as obtained from NMR spin−spin relaxation data. It is evident that the α component is strictly related to the surface area developed during the setting process of C$_3$S.

the surface interacting water, being this quantity directly connected to the surface formation of the hydrated products.

Conclusions

The nature of the water inside a hydrating tricalcium silicate paste has been investigated by analyzing the vibrational spectrum in the near-infrared region. The absorption at 7000 cm^{-1} (O−H stretching, first overtone) has been evaluated in terms of five Gaussian components. According to a recent model,[13] the existence of two different populations of water has been proved to be present during the setting process of C$_3$S paste: a "surface-interacting" and a "bulklike" water. The evolution of these populations in time has been monitored. The percentage of "bulklike" water has been found to progressively decrease, with the concomitant increase of the "surface-interacting" water fraction, in agreement with the C-S-H surface development. The FWI can be easily accessed by the area of the 5000 cm^{-1} combination band, and it is in agreement with previous differential scanning calorimetry and quasi-elastic neutron scattering investigations.

We conclude that NIR analysis of water in the confined C-S-H growing matrix during the setting process provides reliable semiquantitative information on the water confined in the C$_3$S paste. The advantage in using NIR is mainly related to the simple data analysis and experimental procedure.

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