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Early-hydration of β-Ca_2SiO_4 followed by FTIR/ATR spectroscopy

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Ca_3SiO_5 and β-Ca_2SiO_4 are the major components of ordinary Portland cement. β-Ca_2SiO_4 presents many intrinsic advantages over Ca_3SiO_5 because its preparation demands less raw material and energy consumption. Recent works have dealt with its synthesis [1–3], hydration [4, 5] and its use as a major component in cement-based materials [6, 7].

It is well known that β-Ca_2SiO_4 exhibits a slower hydration rate when compared to Ca_3SiO_5 and this behavior is attributed to differences in crystalline structure and thermodynamic stability [4, 8, 9].

In recent papers [1, 2] the synthesis of β-Ca_2SiO_4 and related materials was described. In those works, silica was obtained from rice hull ash, an agricultural waste. Briefly, after heating the rice hull at 600 °C, silica was obtained and mixed together with calcium oxide and barium chloride in an ultrasonic bath, keeping the ratio $(Ca + Ba)/Si = 2$. Barium chloride was used in small concentrations to help the stabilization of the β-phase. The synthesis was carried out at 700–800 °C.

The work presented here deals with the use of Fourier Transform Infrared Attenuated Total Reflectance (FTIR/ATR) as a tool to study the hydration of β-Ca_2SiO_4 obtained from rice hull ash. This is a powerful technique to study initial stages of cement hydration. In many hydration studies such as the determination of $Ca(OH)_2$, chemically-bound water or the use of TGA/DSC techniques, the hydration process is somehow affected by the experimental procedure. The overall effect of this kind of manipulation is still unclear. Unlike transmission FTIR spectroscopy, ATR offers the opportunity for *in situ* analysis of the fresh paste without the need of sample manipulation.

The synthesis of β-Ca_2SiO_4 from rice hull ash has been described earlier [1, 2]. The hydration of β-Ca_2SiO_4 was studied at different water/cement ratio (w/c), varying from 0.40 to 0.70, using distilled, and freshly-boiled water to avoid carbonation. Water was added to β-Ca_2SiO_4 immediately before the measurements. In all cases, 1 g of β-Ca_2SiO_4 was used to prepare the pastes. To avoid excessive water evaporation, the paste was protected with a plastic cover without physical contact between them. Spectra were obtained at 19–22 °C and relative humidity between 40–50 %.

A FTIR spectrometer (model Spectrum One, Perkin-Elmer) was used. The ATR accessory was introduced directly into the sample chamber. The experiments were conducted using ZnSe as an internal reflection element having an angle of light incidence of 45 ° and a DTGS detector. The spectra were recorded using 64 accumulations. The ATR software correction was applied to all samples [10, 11].

Fig. 1 shows several spectra of a paste ($w/c = 0.50$), recorded at different times. The spectra were displaced for better visualization. The major bands corresponding to water absorption are 3400 cm^{-1} (O—H stretching), 2125 cm^{-1} (water association) and 1645 cm^{-1} (HOH bending mode). The major peak of β-Ca_2SiO_4 is located at 1000 cm^{-1} (Si—O—Si asymmetric stretching).

Fig. 2a details the spectral region around 1000 cm^{-1}, showing the behavior of the peak attributed to Si—O—Si stretching as a function of time. The intensity rises continuously as time proceeds, and this behavior can be associated to the hydration progress. According to Mollah [12, 13] the broadening of the peak located at 1000 cm^{-1}, as well as its shifting, gives information about the development of hydration and polymerization of the silicate. Using FTIR/ATR it is possible to monitor directly and continuously the intensity of this peak, and we assume that its intensity may be associated to the hydration process.

Fig. 2b presents the variation of the band located at 1645 cm^{-1} for the same sample. During an initial period, the band does not show any appreciable area variation. After a certain period of time (each sample presents a particular behavior) a continuous contraction in area is observed. For the sample displayed, this process starts after about 60 min. The important assumption here is that band at 1645 cm^{-1} is proportional to free water in the system.

In a simple way, the hydration process is followed by monitoring the area of the peak in the region of 1000 cm^{-1} (β-Ca_2SiO_4) and the band at 1645 cm^{-1} (water).

Fig. 3 shows the area of the peak located at 1000 cm^{-1} as time proceeds for samples having w/c ratio varying from 0.40 to 0.70. It becomes clear that hydration is strongly dependent on the w/c ratio, as would be expected. The hydration of β-Ca_2SiO_4, monitored by FTIR/ATR, can be divided into two stages. In the first stage, a rapid variation of the area attributed to silicate absorption is observed. The peak area rises sharply in the initial stage, regardless of the w/c ratio. As hydration takes place, the area variation tends to be less intense and eventually reaches a pseudo-plateau.

It seems reasonable to relate the behavior observed in Fig. 3 to commonly accepted ideas about hydration mechanism. Hydration proceeds in two steps: the first one is related to the initial hydrolysis of cement and is chemically-controlled. This is a relatively fast process

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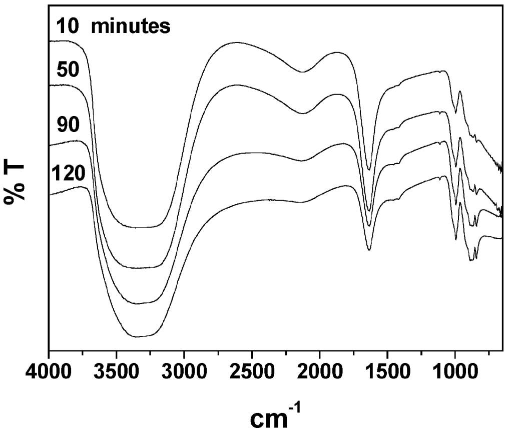

Figure 1 Selected FTIR/ATR spectra of freshly-hydrated β-Ca_2SiO_4 having a water/cement ratio = 0.50. Spectra were recorded from 5 to 240 min.

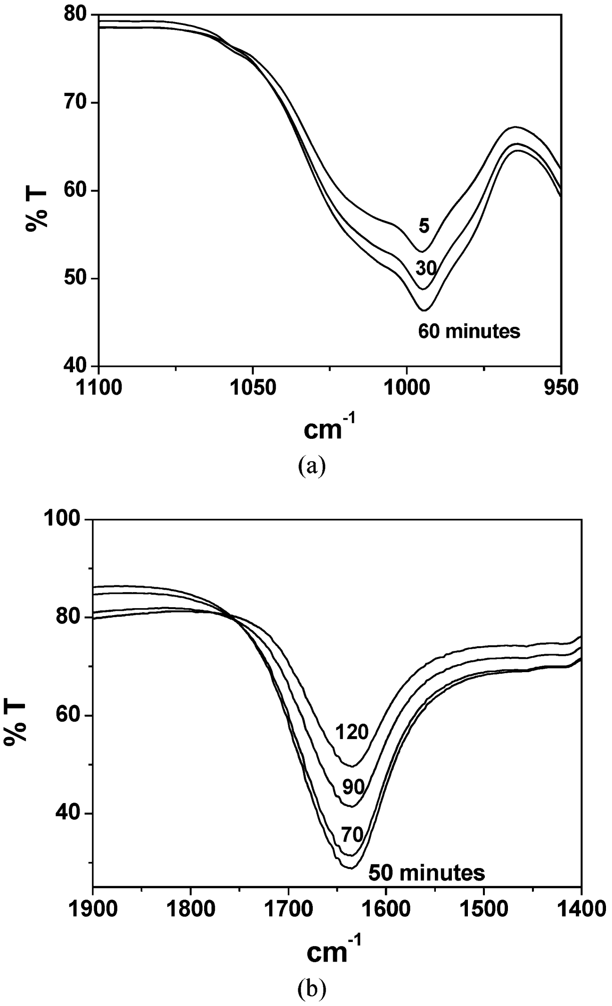

Figure 2 Detailed FTIR/ATR spectra of hydrated β-Ca_2SiO_4: (a) silicate absorption peak and (b) water absorption band.

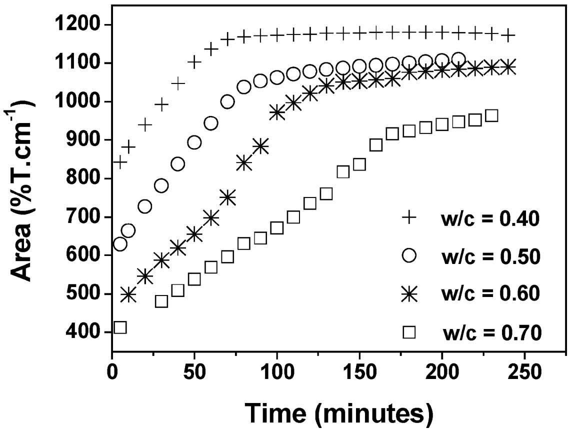

Figure 3 FTIR/ATR spectra of β-Ca_2SiO_4 having different *w*/*c* ratios: variation of the silicate peak (1000 cm^{-1}) as a function of time.

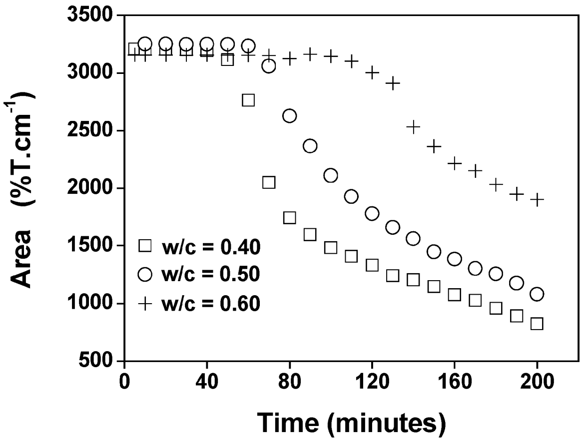

Figure 4 FTIR/ATR spectra of β-Ca_2SiO_4 having different *w*/*c* ratios: variation of the water band (1645 cm^{-1}) as a function of time.

[8]. In Fig. 3, it corresponds to the first stage. The second step is limited by water diffusion into cement grains (diffusion-controlled process), and is slower than the initial one. It corresponds to the second stage observed by FTIR/ATR spectroscopy, which is presented in Fig. 3.

Coherent to these observations, the variation of the peak located at 1645 cm^{-1} (HOH bending) follows the inverse behavior. Fig. 4 presents the variation of the band area as time proceeds. Once again, considering that water concentration is related to the area of the band, we observe two stages. In the initial stage, the water content is almost constant; however, after hydration occurs to some extent, the amount of water presents a sharp fall, constituting the start of the second stage. Following the hydration mechanism, this behavior is attributed to water penetration into the cement grains (diffusion-controlled stage). Since water penetrates into cement, its "concentration" in the medium falls. The results are presented in Fig. 4, showing that the second period starts earlier in samples with lower *w*/*c* ratios, as expected. (The sample having *w*/*c* ratio of 0.70 has been omitted for the sake of clarity).

Another important observation is the determination of this transition period, or the transition between the chemical and diffusion-controlled process, using both the silicate peak (1000 cm^{-1}) and water band (1645 cm^{-1}) as parameters. Table I shows the transition period obtained from mathematical analysis of curves presented in Figs 3 and 4. There is relatively good agreement between these measurements.

It seems that the actual transition period is best determined following the silicate absorption peak (1000 cm^{-1}), since it is more sensitive to changes in the concentration than the water absorption band.

TABLE I Transition period between chemical and diffusion-controlled hydration of β-Ca_2SiO_4

w/c ratio	Transition (min) peak at 1000 cm^{-1}	w/c ratio	Transition (min) band at 1645 cm^{-1}
0.40	60	0.40	50
0.50	80	0.50	60
0.60	120	0.60	110
0.70	170	0.70	160

Finally it should be emphasized that FTIR/ATR spectroscopy, applied to the study β-Ca_2SiO_4, offers important insights on its earlier-hydration behavior. It can be easily applied to investigate the mechanism and effectiveness of many accelerators and even help to design new ones. Also, it may be extended to commercial cements and may give valuable information on more complex systems.

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