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Ettringite and calcium sulfoaluminate cement: investigation of water content by near-infrared spectroscopy

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Abstract Calcium sulfoaluminate (CSA) cement is a sulfate-based binder whose high-performance hydraulic behavior depends on the rapid formation of ettringite, when grinded clinker is hydrated in presence of gypsum. Ettringite is a calcium aluminum sulfate mineral characterized by high water content, estimated as 32 water molecules per formula unit. Three examples of utilization of near-infrared (NIR) spectroscopy are here shown. First of all, information on water distribution in pure ettringite was deduced and compared with infrared analyses. Then its thermal behavior has been followed up to 400 °C, allowing to improve the knowledge about water loss and thermal decomposition of this hydrated phase. Finally, the obtained results have been employed in order to follow hydration of CSA cement sample, demonstrating thus that NIR spectroscopy, being highly sensitive to water amount and distribution, can be an extremely useful tool for hydration studies.

Introduction

Calcium sulfoaluminate (CSA) cement was mentioned for the first time in a French patent in the 1930s [1], but it was only in the 1970s and 1980s that its production started to become important [2]. Differently from the well-known family of ordinary Portland cements, its main clinker minerals are not silica based but are sulfate phases produced by burning gypsum, bauxite, and limestone in a conventional rotary kiln at 1300 °C. The production of this kind of binder demonstrates many advantages when compared with ordinary cement, among which a reduced environmental impact, due to the lower burning temperature and lower CO_2 emissions, can be highlighted. Moreover, cements produced from CSA clinker show better performance: high early compression strength, high frost resistance, high corrosion resistance, etc. [2–4].

The main minerals of CSA cement are tetracalcium trialuminate sulfate, or yeelimite $\left(C_4A_3\bar{S}\right)$, dicalcium silicate or belite (C_2S) and calcium sulfate or anhydrite $\left(C\bar{S}\right)$; minor phases such as tricalcium aluminate (C_3A), tetracalcium aluminoferrite or brownmillerite (C_4AF), dodecalcium heptaaluminate or mayenite ($C_{12}A_7$) and dicalcium aluminum silicate or gehlenite (C_2AS) can also be present.[1]

Hydration of CSA cement essentially results in the rapid formation of ettringite $\left(C_6A\bar{S}_3H_{32}\right)$ from yeelimite and calcium sulfate (anhydrite or gypsum), according to the following reaction schemes [2]:

$$C_4A_3\bar{S} + 2C\bar{S} + 38H \rightarrow C_6A\bar{S}_3H_{32} + 2AH_3$$

or

$$C_4A_3\bar{S} + 2C\bar{S}H_2 + 34H \rightarrow C_6A\bar{S}_3H_{32} + 2AH_3$$

Ettringite is the most important mineral of the group of AFt phases (Al_2O_3–Fe_2O_3–tri), hydrated phases that commonly form in small amounts in hydrated ordinary cements: the general extended formula is $[Ca_3(Al,Fe)(OH)_6 \cdot 12H_2O]_2 \cdot X_3 \cdot$

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[1] Note that standard cement nomenclature is followed here, whereby $C = CaO$, $S = SiO_2$, $A = Al_2O_3$, $F = Fe_2O_3$, $\bar{S} = SO_3$, and $H = H_2O$.

nH$_2$O, where $n \leq 2$ and X is a singly or doubly charged anion (carbonate, sulfate, etc.) [5]. In an ettringite with ideal composition, no substitution Fe^{3+}–Al^{3+} is present and X is $[SO_4]^{2-}$: the corresponding chemical formula is $Ca_6[Al(OH)_6]_2(SO_4)_3 \cdot 26H_2O$. From the crystallographic point of view, ettringite is characterized by a trigonal structure formed by hexagonal columns running parallel to c-axes ($a_0 = 11.24$ Å; $c_0 = 21.45$ Å; SG = P31c) [6–8]. In these columns, $[Al(OH)_6]^{3-}$ octahedra alternate with triangular groups of edge-sharing CaO_8 polyhedra, with which they share OH^- ions; each calcium atom is also coordinated by four water molecules, the hydrogen atoms of which form the nearly cylindrical surface of the column. For each channel, there are two $[SO_4]^{2-}$ tetrahedra pointing upwards, followed by one pointing down, and then followed by a site containing three water molecules. Summarizing, we can individuate the following types of water:

- inter-channel water (three molecules per formula unit);
- Ca-coordinated water (four molecules for each calcium atom);
- Al-coordinated OH groups (shared with calcium atoms).

In Portland cement, variously substituted ettringite can form in low amounts during the early hydration, but tends to be fragile and easily decomposes to AFm phases (Al_2O_3–Fe_2O_3–mono, general formula $[Ca_2(Al,Fe)(OH)_6] \cdot X \cdot nH_2O$) or to undergo the gradual substitution of sulfate with carbonate groups.

In commercial CSA cement, calcium sulfate (gypsum or hemihydrate) is added and ground with the clinker in order to control the growth of ettringite [9]: in fact, depending on its microstructural characteristics, ettringite can influence the setting time of the cement and can be responsible for very high early strength, high sulfate resistance, and low shrinkage [10].

Apart from the kind of binder being considered, the chemistry of cement is essentially ruled by the study and comprehension of its hydraulic properties. The development of the mechanical characteristics of cement mainly depends on three main factors: the mineralogical composition of the powder, the fineness of grinding of the clinker, and the water content of the paste. Well-developed investigation techniques are available to analyze the first two factors: mineralogical composition can be determined and quantified by X-ray diffraction (XRD), while laser granulometers for fineness measurements are present in most cement laboratories. Determination of water amount has always been more problematic: water content is usually regulated only during the initial mixing but compositional variability of the binder can highly influence the water distribution, the growth of hydrated phases, and the formation of more or less developed porosity. Therefore, investigation techniques that are able to follow variations in water amount and distribution are most welcome.

Even if in situ hydration studies are generally performed by time-solved XRD analysis, this technique does not provide full information for this kind of investigation: first of all, water can be entrapped, especially in the first stages of hydration, in amorphous structures that XRD is not able to reveal; secondly, crystal structures containing large amounts of water are characterized by a low x-ray scattering activity that does not make their individuation easy.

Thermal methods are more diffuse to investigate the water amount and distribution in a sample: nevertheless they require sampling of a specimen, they are destructive and time consuming, having a low scan rate necessary for good resolution analysis.

Nuclear magnetic resonance spectroscopy is a very powerful technique for the investigation of water content as it allows the study of hydration and/or hardening kinetics on the basis of H-1 relaxation activity of cement pastes. On the other hand, this technique still remains mainly academic, as it is difficult to perform, requires a qualified operator, results are difficult to interpret, and it is moreover very expensive.

In our study, we present an investigation of water content in synthetic ettringite based on near-infrared (NIR) spectroscopy, from which information on the vibrational low harmonic modes of stretching and bending of hydrogen bonds can be obtained. Similar investigations have already been successfully performed on hydrated silica-based cement materials [11–13], revealing that NIR spectroscopy can be helpful in following the state of the hydration of water and the microstructure development of a cement paste. For interpretation of NIR ettringite spectrum, infrared investigations (mid-infrared) have also been performed.

The evolution of NIR spectrum in the function of temperature was followed up to 400 °C and was found useful in understanding the water distribution and thermal behavior of this phase: due to a loss of crystallinity that happens in the first step of heating, main studies on thermal behavior of ettringite rarely go beyond 150–200 °C.

Finally, the obtained results have been applied for investigation on samples of CSA cement at different aging times, in order to follow the evolution of water in the cement paste and the advancing of hydration (mainly due to the formation of ettringite).

Materials and methods

Ettringite was synthesized following the Mylius procedure, as indicated by Taylor [5]. To this end, a solution containing the desired calcium and sulfate content ($Ca(OH)_2$ and $CaSO_4 \cdot 2H_2O$ dissolved in distilled water) was mixed with another one providing the necessary aluminum amount ($Al_2(SO_4)_3 \cdot 18H_2O$ dissolved in distilled water). The resulting solution was homogenized on a magnetically shaken plate, vacuum filtered with a WHATMAN GF/C 1.2 mm filter and finally stored in a desiccator with silica gel and soda lime. After filtration and drying, the precipitate was ground in an agate mortar and sieved in the particle size range of 0.425–0.600 mm. Purity of the synthesized ettringite was checked by XRD using a Bruker AXS (Karlsruhe, DE) D4 Endeavor diffractometer working in Bragg-Brentano geometry, equipped with a ceramic X-ray tube KFF (Cu Kα radiation) and a SOL-X energy dispersive detector. Measurement was performed in the scan range 5–55° at a scan rate 1.2°/min. Refinement for semi-quantitative analyses was conducted by Rietveld method using the Topas 2.0 package (commercially supplied by Bruker AXS): structural models for all the phases were taken from the software database. 10% in weight of calcium carbonate was detected in the sample, revealing quite extensive carbonation; 5% of non-reacted calcium sulfate was also detected.

For thermal investigation on ettringite, a specimen of synthetic sample was treated at different increasing temperatures in a ventilated oven: at each step the specimen was placed in the oven for 30 min, then removed, cooled at room temperature in a desiccator with silica gel, and analyzed. Thanks to the observation that thermal decomposition of ettringite is not a reversible process [14], the obtained data are comparable to a set of isothermal analyses.

$Al(OH)_3$ and $Ca(OH)_2$ analyzed as reference were pure reagent grade supplied by Merck (Germany).

CSA cement was prepared mixing CSA clinker (specific surface = 0.50 m^2/g) and gypsum (specific surface = 0.12 m^2/g) in 9:1 proportion; both materials were supplied by Buzzi Unicem S.p.A., together with hemihydrate and anhydrite. Preparation and XRD characterization of hydrated calcium–sulfoaluminate cement samples have been already reported in a previous publication [15].

Mid-infrared spectra were collected in an Equinox 55 Bruker Optics FT-spectrometer; the samples were mixed and ground uniformly with KBr and pelletized and 100 scans at a rate of 2 cm^{-1} resolution were collected for each sample.

Near-infrared analyses were performed using a Bruker MPA FT-spectrometer working in diffuse reflectance. As operative conditions 32 scans at a rate of 2 cm^{-1} resolution were chosen. No sample treatment was performed: powdered samples of both ettringite and hydrated CSA cement were placed in special flat-bottomed vials and directly analyzed in diffuse reflectance.

Results and discussion

Near- and mid-infrared spectra of ettringite

NIR spectrum of ettringite is shown in Fig. 1: the main features are two wide and intense bands centered, respectively, around 6900 and 5100 cm^{-1}. Both of them arise from the presence of a large amount of water in various coordination states: the first band is assigned to the first O–H stretching overtone ($2\nu_1$, $2\nu_3$, and $\nu_1 + \nu_3$); the second one is an O–H combination band of water ($\nu_2 + \nu_3$) [10–12]. Minor bands can be observed at 4492 and 5588 cm^{-1}, their assignment will be discussed later.

The MIR spectrum of ettringite has been collected in order to allow a deeper interpretation of the NIR spectrum and is shown in Fig. 2a, b. Low-frequency MIR bands (Fig. 2a) are assigned as follows [14]: the strong and sharp peak at 1115 cm^{-1} is due to $[SO_4]^{2-}$ vibrations, the peak centered at 1650 cm^{-1} is due to the bending vibration of water molecules and two additional bands appear centered at 870 and 1460 cm^{-1}, imputable to $[CO_3]^{2-}$ vibrational modes of residual calcium carbonate present as an impurity in the sample.

The wide band ranging from 3000 to 3750 cm^{-1} (Fig. 2b) is due to stretching vibrations of O–H groups and water molecules. Its asymmetrical shape suggests that this band is the result of the convolution of different bands due to different vibrational modes: first of all there is a well-defined peak rising at 3640 cm^{-1}; secondly, a hump can be identified around 3550 cm^{-1}. Assignment of these bands can be argued on the basis of the crystal structure of ettringite, in which we can identify Ca-bonded and Al-bonded O–H groups: IR spectra of calcium hydroxide and aluminum hydroxide, collected in the 2500–4000 cm^{-1} frequency region, confirm this hypothesis as they actually

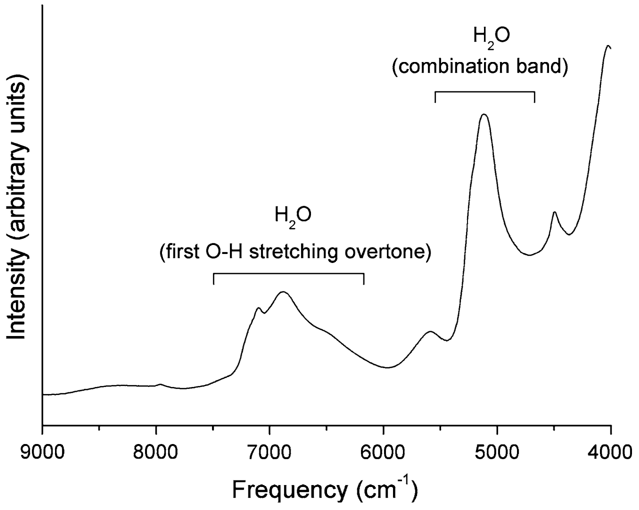
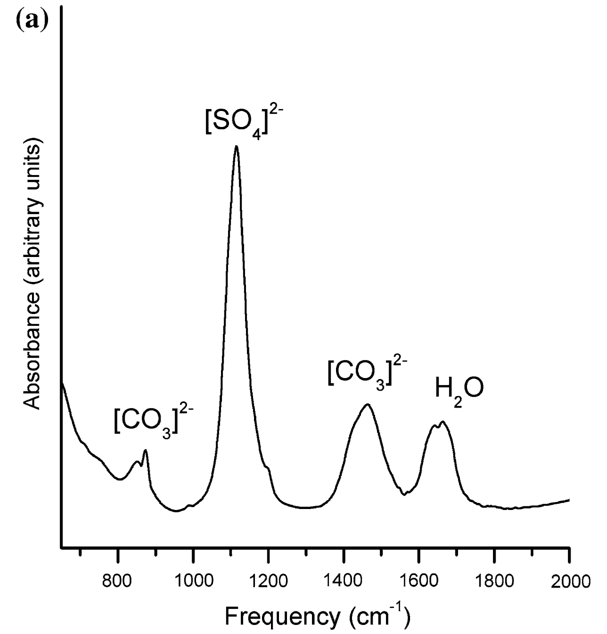


Fig. 1 NIR spectrum of ettringite



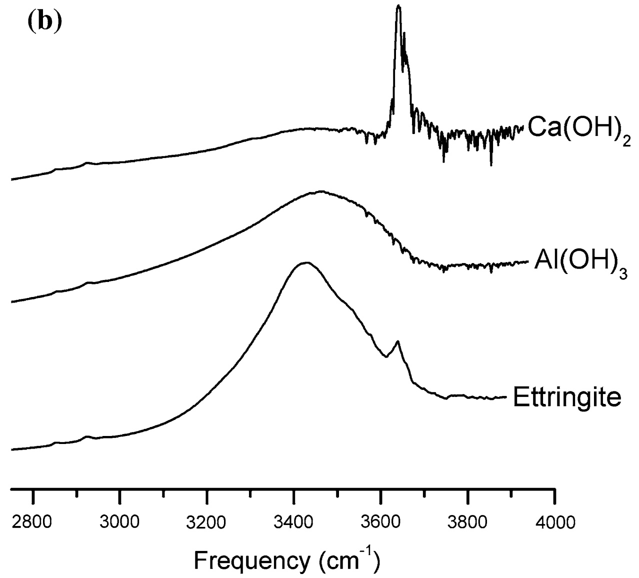


Fig. 2 IR spectrum of ettringite (**a**); IR spectra of $Ca(OH)_2$ and $Al(OH)_3$ in the 2800–4000 cm^{-1} region (**b**) are also shown

exhibit their O–H stretching vibration band centered at 3640 and 3550 cm^{-1}, respectively (Fig. 2b).

Turning our attention back to the NIR spectrum of ettringite, we can now perform a more detailed assignment of its bands. The wide band ranging between 7500 and 6000 cm^{-1} is an overtone band of O–H stretching vibrations and, similarly to the corresponding mid-infrared band (fundamental vibration) centered at 3420 cm^{-1} is clearly composed from different overlapped modes. At least three bands can be individuated: two strongly overlapped low-frequency bands, around approximately 6600 and 6900 cm^{-1} and a high-frequency band at 7100 cm^{-1}. This last can be easily attributed to the overtone of the Al-bonded OH groups vibrations, observation based both on its frequency (twice the IR frequency value of 3550 cm^{-1}) and on the presence of this band in the aluminum hydroxide spectrum. The two low-frequency bands occupy two positions that are well known in literature [16–18] and are typical of water molecules with different extents of hydrogen bonds; they do not represent a well-defined molecular class, but rather they account for spectral contribution probably originating from a continuum of strongly bonded water molecules.

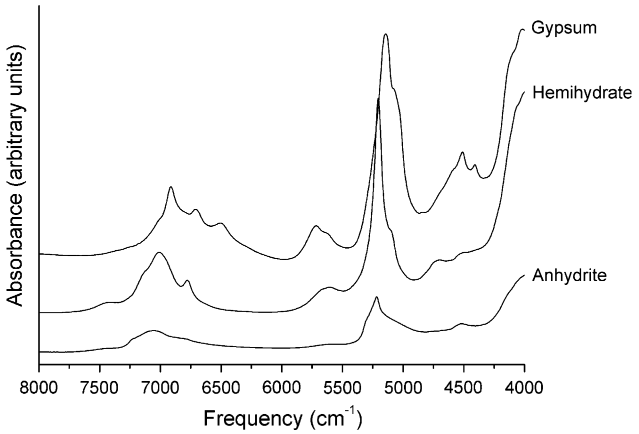


Fig. 3 NIR spectra of calcium sulfate phases

The 5588 cm^{-1} band is present in water containing sulfatic structures (Fig. 3, gypsum and hemihydrate), therefore it is probably due to the combination modes of sulfate-interacting water.

The 4492 cm^{-1} is presumed to be a combination band of the O–H and the Al–OH stretching mode, similarly to the band at 4567 cm^{-1} detectable in the presence of Si–OH bonds [11].

Thermal decomposition of ettringite

Selected NIR spectra of ettringite after treatment at different temperatures are shown in Fig. 4, allowing some well-defined dehydration steps to be distinguished.

Between room temperature and 90–100 °C, we can notice a general decrease in intensity of all NIR bands due to the loss of water molecules even if the shape of the spectrum is not modified at this stage, suggesting that the lost molecules consist of non-structural water. As a matter of fact, this modification lead to the formation of a partially dehydroxilated product known as *metaettringite*, in which the columnar structure is preserved [19].

A second step begins over 100 °C: at this stage the overtone band undergoes a consistent decrease in intensity of its low-frequency components, indicative of a collapse of the structure. Some interesting information can be

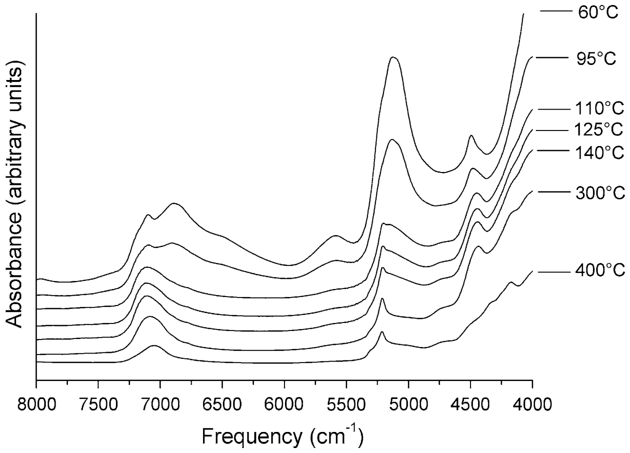


Fig. 4 Thermal decomposition of ettringite followed by NIR spectroscopy

gained from the observation of the combination band at 5000 cm^{-1}: over 100 °C this band starts decreasing and assumes a strongly asymmetrical shape. The two components that constitute it are centered, respectively, at 5205 and 5140 cm^{-1}. In this temperature range, ettringite decomposes to calcium alumino-monosulfate (AFm phase) and hemihydrate, whereas gypsum may form as an intermediate phase [20]: in agreement with this interpretation, in our investigation we found that as the temperature increases, the band component corresponding to gypsum (5140 cm^{-1}, Fig. 4) decreases. Over this band, a sharp peak centered at 5214 cm^{-1}, corresponding to hemihydrate (Fig. 3), begins to appear: as the temperature increases, over 140–150 °C, the overall area of the band decreases and this peak becomes much clearer, attesting to the gradual conversion of sulfate structures to hemihydrate and anhydrite.

When the temperature reaches 300 °C, the 5214 cm^{-1} band has become a sharp peak completely identical to the one of anhydrite. The overtone band is still broad and wide due to residual water in the structure, probably Al-bonded –OH groups originating from the decomposition of monosulfate, as also suggested by the residual band at 4450 cm^{-1}, still present even if shifted from its original position. In order to explain this shift, the twofold nature of these bands has to be taken into account: in ettringite this band is due to –OH groups bonded both to sulfate and to aluminum; when, due to increased temperature, the sulfate structures decompose, their contribution to the band starts decreasing until it completely disappears, leaving just the lower frequency combination band of Al–OH stretching mode.

The final transition from 300 to 400 °C causes a significant decrease in the overtone band and the disappearance of the 4430 cm^{-1} band: also strongly Al-bonded water has finally left and the final spectrum is highly similar to the spectrum of anhydrite.

Summarizing, on the basis of the observation of NIR spectrum modifications of ettringite, the following decomposition steps can be proposed:

- first step, from room temperature to 90–100 °C: loss of non-structural water and conversion to *metaettringite* (no structural modification);
- second step, from 100 to 150 °C: collapse of the structure and gradual decomposition of ettringite to a mixture of alumino-monosulfate and variously hydrated calcium sulfate phases;
- third step, from 150 to 300 °C: aluminum-hydrated structures take the place of alumino-monosulfate, while sulfate phases evolve toward anhydrite;
- fourth and last step, aluminum-bonded water leaves the sample.

Formation of ettringite in CSA cement

Selected spectra of samples of CSA cement at different degrees of hydration are shown in Fig. 5; corresponding variations of main mineralogical phases as detected by semi-quantitative Rietveld analyses [15] are summarized in Fig. 6.

After 1 h of hydration, the cement is still in its induction period and no chemical reactions have occured. The corresponding NIR spectrum reveals the characteristic features of gypsum, which are the strong band at 5140 cm^{-1} and a minor peak at 4510 cm^{-1}. The spectrum of CSA clinker is substantially featureless: its only characteristic is the pronounced slope given by the dark color of the ground material that, increasing the background, covers the characteristic triple band of gypsum (Fig. 3) in the range of 7000–6000 cm^{-1}.

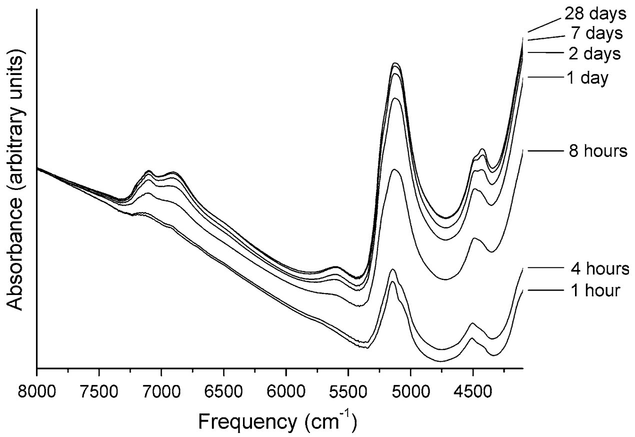


Fig. 5 Selected NIR spectra of hydrated CSA cement samples at different hydration times

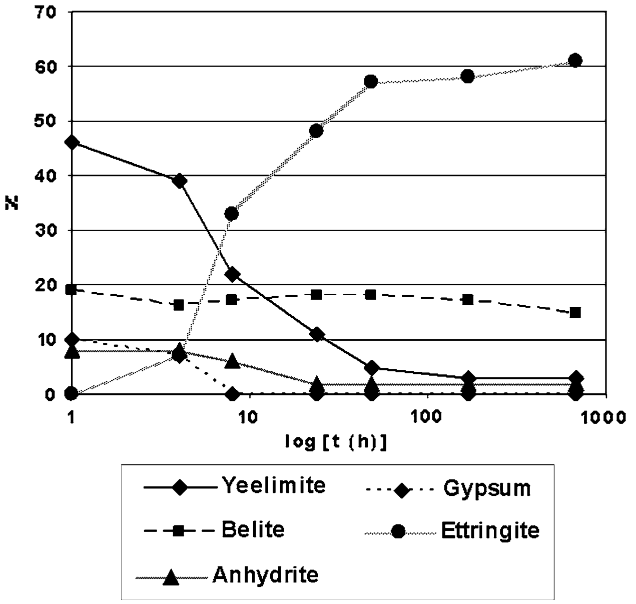


Fig. 6 Variation of main mineralogical phases of CSA cement during hydration detected by semi-quantitative XRD analyses (wt%)

In the first 4 h, only minor variations are observed, mainly regarding the formation of small amounts of ettringite: the NIR spectrum baseline is slightly shifted at higher intensities but there is neither a corresponding increase in intensity of its band nor a shape modification.

Between 4 and 8 h, a significant modification in the NIR spectrum is observed: after 4 h the amount of ettringite increases significantly and in the NIR spectrum an enhancement of the baseline is observed (due to modification in the aggregation state of the matter) together with an increase in the area of the two bands around 7000 and 5250 cm^{-1}, attesting to the increased total water amount in the sample. As a matter of fact, mineralogical investigation shows that the ettringite amount increases more than three times: ettringite is the main hydrated phase that forms and this explains the strong modification of the NIR spectrum at this step.

After 24 h from hydration, the NIR spectrum continues to change consistently, the background still enhances and all bands become more defined: in particular the 7000 cm^{-1} band becomes clearly a double peak, the band at 5588 cm^{-1}, characteristic of ettringite, appears clearer and the 5100 cm^{-1} band becomes more intense. The overall shape of the spectrum is now extremely similar to the spectrum of pure ettringite (Fig. 1).

Between 24 and 48 h, the reaction slows down: the NIR spectrum only shows an increase in the bands already present after 24 h and no more substantial modifications are observed after 48 h up to 28 days, consistently with XRD analyses and with previous literature [15], attesting that after 2 days the hydration of CSA cement can be considered almost complete.

Conclusions

Little is known about vibrational behavior of inorganic structures in the NIR region: this is due to both the lack of reference spectra and to the fact that NIR bands are wide and often overlapped, two aspects that make their interpretation difficult. Nevertheless, the high sensitivity of this investigation technique toward water makes it a suitable tool for investigation on the amount and distribution of water in water-containing samples. Moreover, this feature also suggests its utilization for monitoring the evolution of hydrated phases in a complex system as, for example, cement: a structure whose hydration degree is indicative of the development of mechanical properties.

This study presents different fields of application, both theoretical and practical, of this powerful investigation technique. The main investigation target is ettringite, a suitable mineral for NIR analyses, thanks to its high water content in different coordination states. The NIR spectrum of ettringite shows bands in positions that are typical for water-containing structures, nevertheless it is characterized by a distinctive and peculiar shape, discussed and interpreted with the help of mid-infrared spectroscopy.

Furthermore, two successful examples of monitoring of water content are shown and described.

The first one, related to thermal decomposition of ettringite, describes NIR spectrum modifications in the temperature range of 25–400 °C. The observation of NIR spectrum thermal evolution allows the satisfactory analyses of structural modification, suggesting a four-step decomposition: loss of non-structural water up to 90–100 °C; collapse of the structure to form alumino-monosulfate and variously hydrated calcium sulfate between 100 and 150 °C; decomposition of monosulfate to aluminum-hydrated phases and gradual dehydration of sulfatic phases from 150 to 300 °C; dehydration of aluminate phases from 300 to 400 °C.

The second application is a more practical one: the monitoring of the hydration of CSA cement. CSA cement is well suited to this study as its main hydrated phase is ettringite: modifications of NIR spectrum are strictly related to the development of hydrated phases and, subsequently, they can also be traced back to the development of mechanical properties.

This last application is very interesting; it suggests a possible future utilization for comparison among cements with different setting times, or, for example, in order to evaluate the effect of additives on cement paste setting times.

The real success of this technique lies in the fact that NIR spectroscopy is a fast and easy to perform non-destructive technique that is particularly suitable for in situ investigations.

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