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Near-infrared spectroscopy investigation on the hydration degree of a cement paste

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Abstract Near-infrared spectroscopy is a fast and easy-to-perform technique characterized by high sensitivity regarding water containing systems and for this reason it is a suitable tool for investigating structural modifications of hydrating cementing materials, even if the lack of knowledge in this field makes the interpretation of NIR vibrational bands very difficult. In this paper, the NIR spectrum of a hydrated ordinary Portland cement is extensively investigated and an interpretation of the different bands is proposed on the basis of both experimental evidence and reference to literature. The obtained results were applied to the investigation of cement hydration lasting up to 28 days, analyzing the variations detectable in the shape of the spectrum as the reaction went on. The degree of this variation, quantified through area calculations of the main significant bands, revealed a broad agreement with the degree of hydration of the paste measured by thermal methods. The findings of this research supply a solid foundation for future in-field application of NIR spectroscopy, for example, for investigations on cements with different hydration behavior, or to evaluate the effect of additives on cement pastes and, at a further level, for cement quality control.

Introduction

Cements are hydraulic binders, they react with water to form products having high adhesive and cohesive properties and high mechanical resistance: Portland cement is the most widely used material in the construction field.

Portland clinker is produced by burning, in a rotary kiln, a mixture of limestone and clay at 1500 °C: limestone is the precursor of CaO, while clay supplies aluminum and silica. During the burning process, a partial fusion of the components occurs and the result is the formation of four main mineral phases: tricalcium silicate (alite, Ca_3SiO_5); dicalcium silicate (belite, Ca_2SiO_4); tricalcium aluminate ($Ca_3Al_2O_6$); and tetracalcium aluminoferrite (ferrite, Ca_2AlFeO_5). Alite and belite are the most important phases in ordinary Portland clinker and generally they account for more than 70% [1]. By grinding Portland clinker together with a set regulating additive (traditionally 5% of calcium sulfate) in an industrial mill, Portland cement is obtained.

The principal physical, chemical and mechanical properties of cement derive from the interaction of its minerals with water. Hydration of silicate phases can be summarized as follows:

$$Ca_3SiO_5 + xH_2O \rightarrow Ca_mSi_nO_{(m+2n)} \cdot zH_2O + yCa(OH)_2 \tag{1}$$

$$Ca_2SiO_4 + xH_2O \rightarrow Ca_mSi_nO_{(m+2n)} \cdot zH_2O + wCa(OH)_2 \tag{2}$$

In both cases the main product of the reaction is a complex calcium–silicate–hydrate oxide, known as CSH, which precipitates as clusters of nanoscale colloidal particles formed by hydrated calcium silicate overlapped layers, where water molecules can be found in the interlayers [2]. Although this peculiar phase is widely

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responsible for the complex behavior of concrete, its structure has not yet been completely explained: the CaO/SiO_2 average ratio is generally accepted in the range 1.6–2.0, but the water amount and distribution are difficult to univocally describe, as different hydrating conditions (water amount, temperature, humidity) can strongly influence its structure and density. Many values for the H_2O/SiO_2 average ratio are indicated [1]: for the saturated samples $H_2O/SiO_2 = 4$; after liquid (non-bonded) water removal by equilibrating at 11% relative humidity, the H_2O/SiO_2 ratio is reduced to 2.1; after vacuum drying or after treating at 105 °C (removal of some physically bonded water within the colloidal CSH particles) the H_2O/SiO_2 ratio further decreases down to 1.4. A recent small-angle neutron scattering investigation [3], performed on non-treated samples, reported that the CSH formula is $(CaO)_{1.7}(SiO_2)(H_2O)_{1.8}$ and the density is 2.604 Mg m^{-3}, results that were also confirmed by a computational model [4].

Calcium hydroxide forms as a secondary product in silicate hydration: it is generally a well crystallized structure often interlaced with CSH.

Hydration of aluminate phases involves gypsum:

$$\begin{aligned}&Ca_3Al_2O_6 + 3CaSO_4 + 32H_2O\\&\quad\rightarrow \left[Ca_3Al(OH)_6\cdot 12H_2O\right]_2\cdot(SO_4)_3\cdot 2H_2O\end{aligned} \tag{3}$$

and

$$\begin{aligned}&Ca_2AlFeO_5 + 2CaSO_4 + 32H_2O\\&\quad\rightarrow \left[Ca_3(Al,Fe)(OH)_6\cdot 12H_2O\right]_2\cdot(SO_4)_3\cdot 2H_2O\end{aligned} \tag{4}$$

The main reaction product is ettringite, a calcium sulphoaluminate mineral characterized by high water content.

The hydration steps of an ordinary cement paste can be summarized as follows:

- pre-induction period: dissolution of soluble salts and hydrolysis of tricalcium aluminate and alite surfaces;
- induction period: formation of a low-permeability gelatinous coating on tricalcium aluminate and alite surfaces and slowing down in the hydration rate;
- acceleration period: breaking of the coating and increase in the hydration rate;
- controlled diffusion: hydration advance is extremely slow but mechanical properties still increase with the aging of the material.

Hydrated phases such as CSH are difficult to investigate mainly due to their low crystallinity: moreover they develop in the cement matrix, with environmental conditions difficult to recreate in laboratory tests. In many cases, the morphology and structure of these minerals can be influenced by the investigation technique itself, as in the case of high energetic techniques such as X-Ray Diffraction (XRD), Transmission Electron Microscopy (TEM), Scanning Electron Microscopy (SEM).

An interesting approach to the study of cement hydration is to focus attention on the water consumption rather than product formation. Near Infrared Spectroscopy has already been demonstrated to be a very sensitive tool for investigating the state of water in different systems and, in some cases, also in cementing systems [5–8].

This technique has multiple advantages: it is a low-energy technique, which avoids the risk of damaging the system being investigated; it is a non-destructive technique working with diffused reflectance and does not require any complex preparation of the specimens. Where cementing systems are concerned, its sensitivity regarding water allows the monitoring of variations induced by cement hydration, the energetic state of water and, subsequently, to evaluate the advancing degree of the hydration reaction.

At present, scientific literature supplies only a little information about this kind of application. The main studies concern hydration studies performed on single phases: Ridi et al. [6] have extensively investigated alite hydration, finding a good relationship between the evolution of the bands of NIR spectra of the hydrating system and a hydration degree evaluated thanks to calorimetric measurements and NMR data; ettringite and gypsum evolution have been followed in a calcium sulphoaluminate cementing system [7], CSH has been studied [8] with Near-, Mid- and Far-infrared spectroscopy and the effect of the calcium–silica ratio on spectroscopic behavior has been evaluated.

Nevertheless, a complex system like ordinary Portland hydrating cement can hardly be compared with the simplified situation supplied by isolated phases: the aim of this project has been to partially fill the gap present in the literature regarding NIR study on hydrating cements; moreover, the practical application of this method to the investigation of hydration cements could launch the basis of its future utilization to evaluate and compare the evolution of hydrating cementing systems, to estimate the effect of additives on hydration kinetics or to check the quality of products.

Since this technique is an innovative one, other techniques have been used as a comparison and as a confirmation of the effective validity of results.

Materials and methods

The cement was obtained by grinding clinker (95%) and gypsum (5%) in a laboratory mill: both materials were supplied by Buzzi Unicem S.p.A. The chemical composition and the mineralogical properties of the obtained cement are summarized in Table 1.

Table 1 Chemical and mineralogical characteristics of the investigated cement

Chemical composition (% in weight)		Mineralogical composition (% in weight)	
SiO_2	20.6	Ca_3SiO_5	49.7
Al_2O_3	6.2	Ca_2SiO_4	23.3
Fe_2O_3	2.6	$Ca_2(Al,Fe)O_5$	5.3
CaO	65.1	$Ca_3Al_2O_6$	11.8
SO_3	1.3	$CaSO_4 \cdot 2H_2O$	2.4
Other	4.2	Minor phases	7.5

Chemical analyses were performed by dispersive X-Ray fluorescence, using a Panalytical Axios spectrometer on pressed powder: the element content is expressed as a percentage in weight of the corresponding metal oxide.

The mineralogical investigation was performed by XRD analyses, using a Bruker AXS D4 Endeavor diffractometer working in Bragg–Brentano geometry, equipped with a ceramic X-ray tube KFF (CuKα radiation) and a "Linx Eye" dispersive detector. 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 phases were taken from the software database.

The NIR Spectrometer was a FT-MPA Bruker Optics: all measurements were performed with the reflection sphere sampling method. Specimens were prepared in apposite flat-bottomed glass vials: a weighed amount of cement was placed inside the vial, and then demineralized water was added with a pipette and mixed with a Vortex shaker. In order to guarantee high reproducibility in the preparation of the samples, mixing time and rate were kept constant for all the samples. Vials were then stored in a climatic room ($T = 20$ °C and relative humidity >95%) until they reached the desired age, then the vial was broken and the cylinder-shaped cement sample extracted. This sample was then cut in the middle and the NIR measurement was performed on the internal surface: all these precautions were taken in order to have a sample representative of the bulk of the specimen.

All spectra elaborations were performed by using the OPUS 6.5 (Bruker Optik GmbH) software: in the following results, spectra are mainly presented as they appeared when collected, except where differently indicated.

In order to easily evaluate the degree of hydration of a sample of cement paste at a specific aging time, aged samples were treated with acetone [9] in order to remove the residual free water and stop their hydration. These samples were then treated in an oven at 900 °C, a temperature which ensures that all the bonded water is removed from the sample. The difference in weight between the sample before and after the thermal treatment can be used as an indicator of the advance of hydration being the amount of bonded water directly related to the hydrated phases amount. The Hydration Degree (HD) parameter was calculated as:

$$\mathrm{HD}(t) = \frac{W_\mathrm{d}(t) - W_{900}(t)}{W_\mathrm{d}(t)} \times 100$$

where $W_\mathrm{d}(t)$ is the weight of the acetone dehydrated sample at aging time t and $W_{900}(t)$ is the weight of the same sample after thermal treatment.

Results and discussion

The NIR spectra of a hydrating cement, from 4 h up to 28 days, are shown in Fig. 1. All spectra are characterized

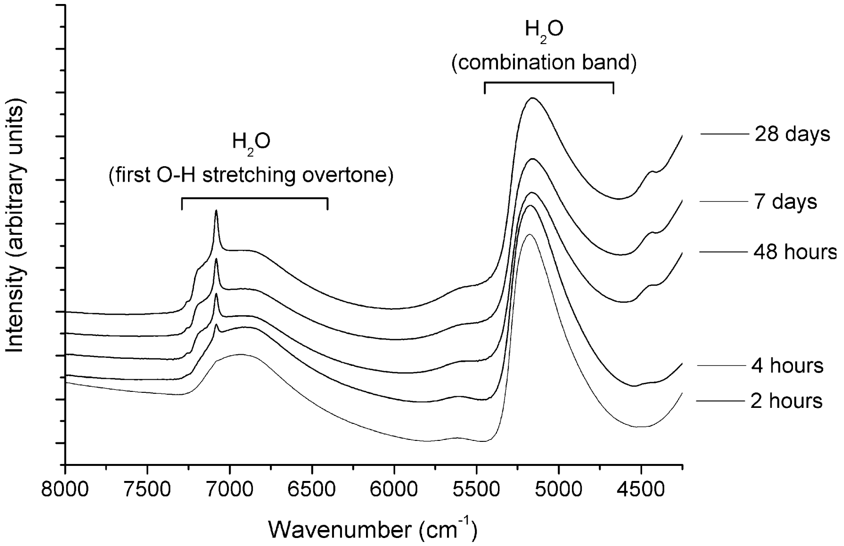

Fig. 1 Evolution of the NIR spectrum of a cement paste from to 2 h up to 28 days of hydration (spectra have been y-shifted in order to make the comparison easier)

by two wide intense bands around 7000 cm^{-1} and 5000 cm^{-1}, arising from the presence of a large amount of water in various coordination states. The first band is generally assigned to the first O–H stretching overtone ($2\nu_1$, $2\nu_3$ and $\nu_1 + \nu_3$), while the second one is an O–H combination band of water ($\nu_1 + \nu_3$) [6, 8, 10].

Even if these two main bands are present at each hydration step, the changes in the shape of the overall spectrum, in particular, the 7000 cm^{-1} band, are indicative of a progressive redistribution of the water molecules and suggest a gradual modification of their state as they become part of the different hydrated phases.

At the beginning of the hydration (2 h), the cement lies in the so-called *induction period* and no evident chemical interaction happens: the corresponding NIR spectrum shows the characteristic features of water [11], as the amount of free water is extremely high and its strong NIR signal covers all other bands possibly present.

Nevertheless, even after a few hours a sharp peak, overlapped at the 7000 cm^{-1} band, starts to appear: this peak, centered at 7083 cm^{-1}, is due to the formation of calcium hydroxide [6]. This is the main modification undergone by the NIR spectrum during the first hours of hydration.

After 2 days, some more evident changes in the shape of the NIR spectrum can be noted. First, the baseline slope changes, this behavior can be ascribed to a change in the microstructure of the system which, becoming denser and denser, has a higher surface reflectivity. Second, the band at 7000 cm^{-1} becomes wider, the $Ca(OH)_2$ peak intensity increases and a well-defined shoulder appears around 7200 cm^{-1}. The possible assignation of this band has been investigated and will be discussed in the following.

The spectrum as it appears after 2 days of hydration is substantially in its final form, as no significant modification can be observed, apart from an increase in the area of the bands and a slight further slope variation.

In order to interpret the complex band at 7000 cm^{-1} better, and to understand the reason for the 7200 cm^{-1} shoulder, a sample of hydrated cement aged for 8 h (spectrum a in Fig. 2) underwent to additional treatments aimed to selectively eliminate different types of water: at each step a NIR spectrum of the treated sample was obtained in order to collect information from the variation of its shape.

The first treatment was performed with the aim of removing the free water present in the system and obtaining in this way a snapshot of the structural water present in the sample after 8 h: the coarse ground sample was treated with acetone and dried in an oven at 40 °C [9]. The corresponding NIR spectrum (spectrum b in Fig. 2) shows, as expected, an overall reduction of the band intensities, due to the elimination of bulk water. Nevertheless, none of the bands have completely disappeared, witnessing that bulk water and structural water have similar spectroscopic behavior, even if free bulk water has much more intense bands. The wide band at 7000 cm^{-1} and the shoulder at 7200 cm^{-1} are both still visible, they are therefore related to structural water, meaning portlandite, ettringite, or CSH.

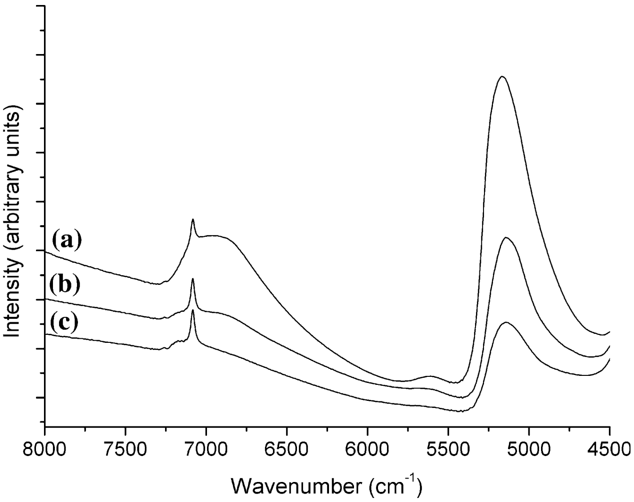

Fig. 2 NIR spectra of: (*a*) hydrated cement after 8 h; (*b*) the same as (*a*) after acetone dehydrating treatment; (*c*) the same as (*b*) after thermal treatment at 90 °C for 24 h

The NIR spectrum of portlandite is well known [6] and is characterized by a straight band at 7083 cm^{-1}.

The NIR spectrum of pure synthetic ettringite is also known [7], and is characterized by a main band at 6900 cm^{-1} and two side bands at 7100 and 6600 cm^{-1}: these three bands overlap extensively to form a wide band ranging from 7500 cm^{-1} to 6000 cm^{-1} and it is hard to definitely exclude the presence of a hidden band around 7200 cm^{-1}.

NIR spectrum of CSH having a different C/S ratio shows a weak band scarcely distinguishable between 7000 and 7300 cm^{-1} [8], whose position changes slightly depending on the calcium–silica ratio. Nevertheless, it has to be noted that in the Mid-infrared (MIR) spectrum of CSH ($CaO/SiO_2 = 1.7$) [8], a band round 3600 cm^{-1} is easily distinguishable, corresponding to the stretching vibration of Ca-bonded O–H groups: if it is considered that the first overtone of this mode should fall around 7200 cm^{-1}, it can be assumed that the unassigned shoulder visible in the spectrum of dehydrated cement is due to vibrational activity of water molecules included in the CSH structure.

A second treatment was performed by curing the ground dehydrated sample at 90 °C for 24 h: after this treatment the amount of ettringite in the sample was reduced from 13 to 3%, as demonstrated by a quantitative XRD analyses. The corresponding NIR spectrum (spectrum c in Fig. 2) shows a significant decrease of the 6900 cm^{-1} band, while the shoulder at 7200 cm^{-1} becomes even more evident: this behavior allows the exclusion of the assignation of the 7200 cm^{-1} to ettringite.

Summarizing, it can be confirmed that on the whole, the wide band ranging from 6500 to 7300 cm^{-1} is the result of a sum of many factors: the low frequency contributions are indistinguishable and are due to bulk water, free water, ettringite water and, in a small quantity, calcium silicate water; the sharp band at 7083 cm^{-1} is assigned to $Ca(OH)_2$; the high frequency component, visible as a shoulder at 7200 cm^{-1}, is due to CSH structural water which is the main hydrated component in ordinary Portland cement.

An approach to the evaluation of the progress of hydration through the evolution of the NIR spectrum has been done by calculating the “differential area” of the 7300–6500 cm^{-1} band. If it is assumed that after 2 h the water in the paste is still totally free, this spectrum can be considered as a reference blank spectrum: when subtracting it from all other spectra subsequently acquired, the differential spectra shown in Fig. 3 are obtained, revealing clearer evidence of the increase of the bands related to structural water at 7200 and 7083 cm^{-1}.

The overall area of the differential band in the area of interest is shown in Fig. 4 as a function of a square root of time; the comparison with HD values reveals a broad agreement, suggesting that the evolution of the structural water detected with the NIR spectrometer is really related to the progress of the hydration.

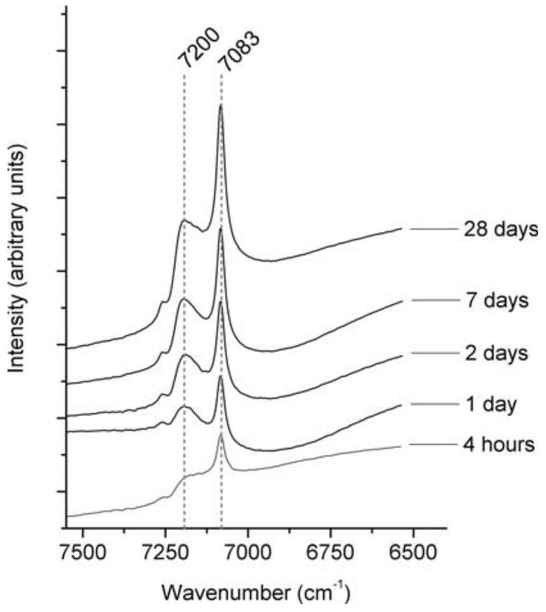

Fig. 3 Evolution of NIR differential spectra (magnification of the 7500–6500 cm^{-1} region—spectra have been *y*-shifted in order to make the comparison easier)

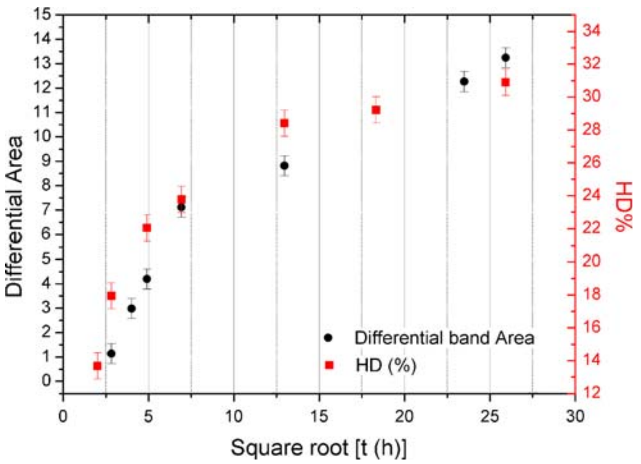

Fig. 4 Comparison between HD values of a hydrating cement paste and differential area of the 7300–6500 cm^{-1} NIR band acquired on the same materials

Conclusions

The knowledge about Near-Infrared vibrational frequencies of inorganic structures is currently still low due to the lack of reference literature and to difficulties in the interpretation of NIR bands, which are mostly wide and overlapping. Nevertheless, the high suitability of this technique regarding water containing structures is well established and its utilization in monitoring the evolution of hydrated phases in complex systems, both organic and inorganic, has been demonstrated.

This paper presents the results of a research project aimed at partially filling this lack of knowledge, proposing an interpretation of information available beneath the NIR spectrum of a hydrated Portland cement based both on reference literature and on experimental evidence. Hydrated Portland cement is a very complex structure and water, playing an important role in the formation of the hydrated structure, is one of the principal players responsible for the development of its mechanical resistance properties.

In the NIR spectrum of a hydrated cement, many factors can be identified: calcium hydroxide is easily detectable thanks to the sharp band at 7083 cm^{-1}; ettringite is characterized by a peculiar band at 7100 cm^{-1} related to the presence of Al-bonded O–H groups, and by wide bands at 6900 and 6600 cm^{-1}; CSH can be associated with the presence of a band (detectable as a shoulder) at 7200 cm^{-1}.

Furthermore, a successful example of a practical application is shown and described here: the utilization of the NIR spectrum for monitoring the evolution of the hydration of a cementing material. The increase of the amount of structural water inside a hydrating cement implies a variation in the shape of the NIR spectrum. At the beginning of hydration, the NIR spectrum is very similar to the spectrum of free water, but after only 4 h some bands due to hydrated phases start to appear; after 2 days the NIR spectrum has already assumed its definitive shape and following modifications imply the increase of the areas of hydrated structure without any further shape modification. By following this progress it is possible to obtain information about the degree of hydration of the material as demonstrated by the comparison between the differential areas of the 7300–6500 cm^{-1} band and the HD values.

The findings of this research project supply a solid base for the future in-field application of NIR spectroscopy, thanks also to the fact that it is a fast and easy-to-perform technique and does not require any sample manipulation: it could be used, for example, for comparing cements with different hydration behavior, or to evaluate the effect of setting regulators or other additives on cement pastes.

Moreover, its future use in the field of quality control can be envisaged, based on the fact that variations in the 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. The possibility of NIR spectroscopy utilization for the forecasting of the mechanical performance of cements is at the moment under investigation and promising results are being reached by cross-referencing NIR data of the 2-day hydrated sample with the compressive strength values through chemometric elaboration method.

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