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

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ABSTRACT

NIR Infrared spectroscopy is a fast and easy-to-perform technique characterized by a high sensitivity towards 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 deeply investigated and an interpretation of the different bands is proposed on the basis of both experimental evidences and literature reference.

The obtained results have been then applied to the investigation of the cement hydration advancing up to 28 days, analyzing the variations detectable in the shape of the spectrum as the reaction goes on. The entity of this variation, quantified through area calculations of main significant bands, revealed a good agreement with the hydration degree of the paste measured by thermal method.

The findings of this research supply a solid base 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.

Keywords: NIR Spectroscopy, Cement hydration, CSH, Hydration degree.

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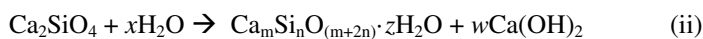
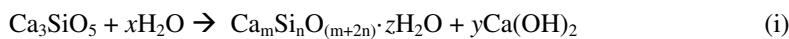
INTRODUCTION

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 diffused material in construction field.

Portland clinker is produced by burning in a rotary kiln a mixture of limestone and clay at 1500°C: limestone is precursor of CaO, while clay supplies aluminum and silica. During the burning process, a partial fusion of the component happens and the result is the formation of four main mineral phases: tricalcium silicate (alite, Ca₃SiO₅), dicalcium silicate (belite, Ca₂SiO₄), tricalcium aluminate (Ca₃Al₂O₆) and tetracalcium aluminoferrite (ferrite, Ca₂AlFeO₅). Alite and belite are the most important phases in the ordinary Portland clinker and generally they accounts for more than 70% [1]. By grinding Portland clinker together with a set regulating additive (traditionally 5% of calcium sulphate) in an industrial mill, Portland cement is obtained.

Main physical, chemical and mechanical properties of cement derive from the interaction of its minerals with water.

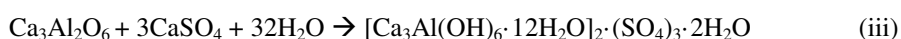
Hydration of silicate phases can be summarized as follows:



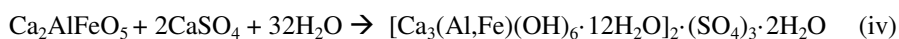
In both cases the main reaction product is a complex calcium-silicate-hydrate oxide, known as CSH, which precipitates as clusters of nanoscale colloidal particles formed by hydrated calcium silicate overlapped layers, where water molecules take place in the interlayers [2]. Although this peculiar phase is widely responsible for the complex behavior of concrete, its structure has not been completely explained yet: CaO/SiO₂ average ratio is generally accepted in the range 1.6-2.0, but 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 H₂O/SiO₂ average ratio are indicated [1]: for saturated samples H₂O/SiO₂ = 4; after liquid (non-bonded) water removal by equilibrating at 11% relative humidity, H₂O/SiO₂ 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) H₂O/SiO₂ further decreases down to 1.4. A recent small-angle neutron scattering investigation [3], performed on non treated samples, reports for CSH the formula (CaO)_{1.7}(SiO₂)(H₂O)_{1.8} and a density of 2.604 Mg·m⁻³, results that also found a confirmation in a computational model [4].

Calcium hydroxide forms as secondary product in silicate hydration: it is generally a well crystallized structure often intergrown with CSH. (Io evidenzierai questa parte, magari scrivendola in rosso, in modo che al referee sia chiaro che è stato aggiunto del materiale)

Hydration of aluminate phases involves gypsum:



and



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 increasing of the hydration rate;
- controlled diffusion: hydration advancing is extremely slow but mechanical properties still increase with the aging of the material.

Hydrated phases such as CSH are difficult to investigate due mainly to their low crystallinity: moreover they develop in the cement matrix, with environmental conditions difficult to recreate in laboratory tests. In many cases, 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 the attention towards the water consumption rather than product formation. Near Infrared Spectroscopy has already demonstrated to be a very sensitive tool for investigate the state of water in different systems and, in some cases, also in cementing system [5-8].

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

At present, scientific literature supplies only few information about this kind of application. Main works concern hydration studies performed on single phases: Ridi et al [6] have deeply investigated alite hydration, finding a good relation between the evolution of the bands of NIR spectra of hydrating system and a hydration degree valuated 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 calcium-silica ratio on spectroscopic behavior has been evaluated.

Nevertheless, a complex system like ordinary Portland hydrating cement, can hardly be compared with simplified situation supplied by isolated phases: the aim of this work 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 can throw the basis for 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.

Being this technique 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. Mineralogical properties of the obtained cement are summarized in Tab. 1.

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

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 (Cu K α 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.

NIR Spectrometer is a FT-MPA Bruker Optics: all measurements have been performed with the reflection sphere sampling method. Specimens have been prepared in apposite flat-bottomed glass vials: a weighted amount of cement has been placed inside the vial, and then demineralized water has been 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 have been kept constant for all the samples. Vials were then stored in a climatic room ($T = 20^{\circ}\text{C}$ 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 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 have been performed by using the OPUS 6.5 (Bruker Optik GmbH) software: in the following, spectra are mainly presented as they appeared when collected, except where differently indicated.

In order to easily evaluate the hydration degree 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 a oven at 900°C , temperature which ensure that all the bonded water leaves the sample. The difference in weight between the sample before and after the thermal treatment can be used as an indicator of the advancing of hydration, being the amount of bonded water directly related to the amount hydrated phases amount. The Hydration Degree (HD) parameter has been calculated as:

$$\text{HD}(t) = \frac{W_d(t) - W_{900}(t)}{W_d(t)} \times 100$$

Where $W_d(t)$ is the weight of the acetone dehydrated samples at aging time t and $W_{900}(t)$ is the weight of the same sample after thermal treatment.

RESULTS AND DISCUSSION

NIR spectra of a hydrating cement, from 4 hours up to 28 days, is shown in Fig. 1. All spectra are characterized by two wide and intense bands around 7000 cm^{-1} and 5000 cm^{-1} , arising from the presence of a large amount of water in various coordination state. 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 shape changes of the overall spectrum, and, in particular, of the 7000 cm^{-1} band, are indicative of a progressive redistribution of the water molecules and suggest a gradual modification of their state as far as they become part of the different hydrated phases.

At the beginning of the hydration (2 hours), 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, eventually present.

Nevertheless, already after few hours a sharp peak, overlapped to 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 two days some more evident changes in the shape of the NIR spectrum can be noticed. Firstly, the baseline slope changes, behavior that can be ascribed to a change in the microstructure of the system which, becoming denser and denser, has a higher surface reflectivity. Secondly, the band at 7000 cm^{-1} becomes wider, the $\text{Ca}(\text{OH})_2$ peak intensity

increase 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 two days of hydration is substantially in its final form, as no significant modification can be observed, apart an increase in the area of the bands and a slight further slope variation.

In order to better interpret the complex band at 7000 cm^{-1} and to understand the belonging of the 7200 cm^{-1} shoulder to a specific hydrated phase, a sample of 8 hours aged hydrated cement (spectrum a in Fig. 2) has been undergone to some treatments aimed to selectively eliminate different types of water: at each step the NIR spectrum of the treated sample has been acquired in order to collect information from the variation of its shape.

The first treatment has been performed with the aim to remove the free water present in the system and obtaining in this way a sort of picture of the structural water present in the sample after 8 hours: the coarse grinded sample has been treated with acetone and dried in a 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 has 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.

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 are strongly overlapped 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 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, in the MIR spectrum of CSH ($\text{CaO/SiO}_2 = 1.7$) [8], a band round 3600 cm^{-1} is easily distinguishable, corresponding to the stretching vibration of Ca-bonded O-H groups: if we consider that the first overtone of this mode should fall around 7200 , we can suppose 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 grinded dehydrated sample at 90°C for 24 hours: after this treatment the amount of ettringite inside 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 strong decrease of the 6900 cm^{-1} band, while the shoulder at 7200 cm^{-1} becomes even more evident: this behavior allows to exclude the assignation of the 7200 cm^{-1} to ettringite.

Summarizing, we can affirm that on the whole, the wide band ranging from 6500 to 7300 cm^{-1} is the result of a sum of many contributions: the low frequency contributions are indistinguishable and are due to bulk water, free water, ettringite water and, in minor amount, calcium silicate water; the sharp band at 7083 cm^{-1} is assigned to $\text{Ca}(\text{OH})_2$; 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 the ordinary Portland cement.

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

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

CONCLUSIONS

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

This paper presents the results of a research aimed to partially fill this lack of knowledge, proposing an interpretation of information available beneath the NIR spectrum of a hydrated Portland cement based both on literature reference and on experimental evidences. Hydrated Portland cement is a really complex structure and water, playing an important role in the formation of hydrated structure, is one of the main character responsible for the development of its mechanical resistance properties.

In the NIR spectrum of a hydrated cement many contributions can be identified: calcium hydroxide is well 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 to the presence of a band (detectable as a shoulder) at 7200 cm^{-1} .

Furthermore, a successful example of a practical application is here shown and described: 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 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 already after 4 hours some bands due to hydrated phases start to appear; after two 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 hydration degree of the material as demonstrated by the comparison between the differential areas of the $7300\text{-}6500\text{ cm}^{-1}$ band and the HD values.

The findings of this research supply a solid base for a future in-field application of NIR spectroscopy, also thanks to the fact that it is a fast and easy-to-perform technique and that it doesn't 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 supposed, 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 utilization of NIR spectroscopy for the forecast of mechanical performances of cements is at the moment under investigation and actually promising results are gained by crossing NIR data of the 2-days hydrated sample with compressive strength values through chemometric elaboration method.

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TABLE CAPTIONS

Tab.1 Chemical and mineralogical characteristics of the investigated cement.

FIGURE CAPTIONS

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

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

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.

TABLES

Tab.1

Chemical composition (% in weight)		Mineralogical composition (% in weight)	
SiO ₂	20.6	Ca ₃ SiO ₅	49.7
Al ₂ O ₃	6.2	Ca ₂ SiO ₄	23.3
Fe ₂ O ₃	2.6	Ca ₂ AlFeO ₅	5.3
CaO	65.1	Ca ₃ Al ₂ O ₆	11.8
SO ₃	1.3	CaSO ₄ ·2H ₂ O	2.4
Other	4.2	Minor phases	7.5

FIGURES

Fig. 1

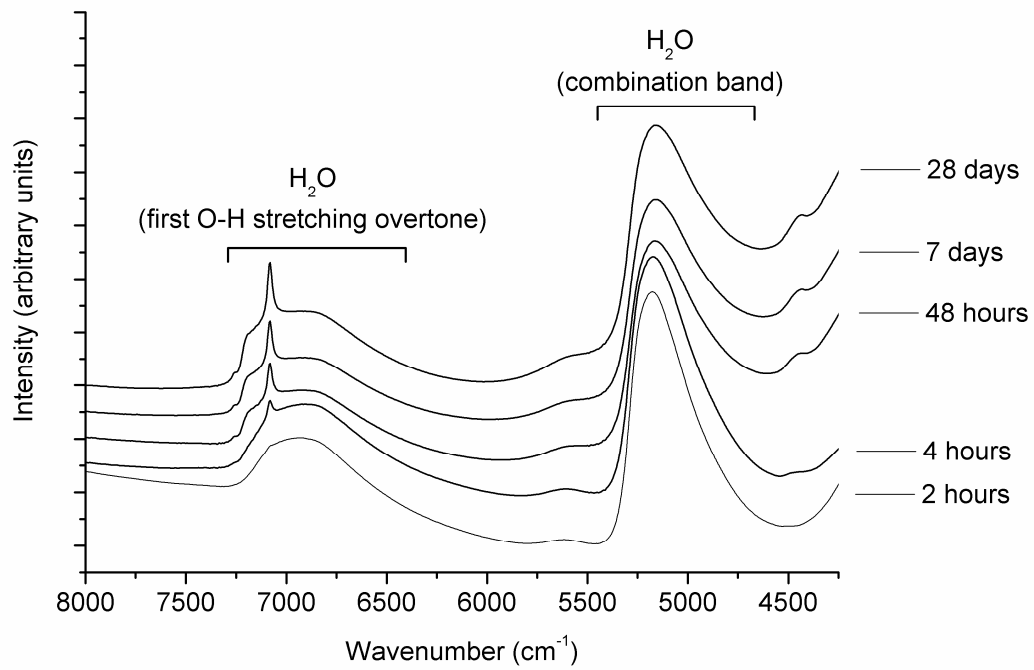


Fig. 2

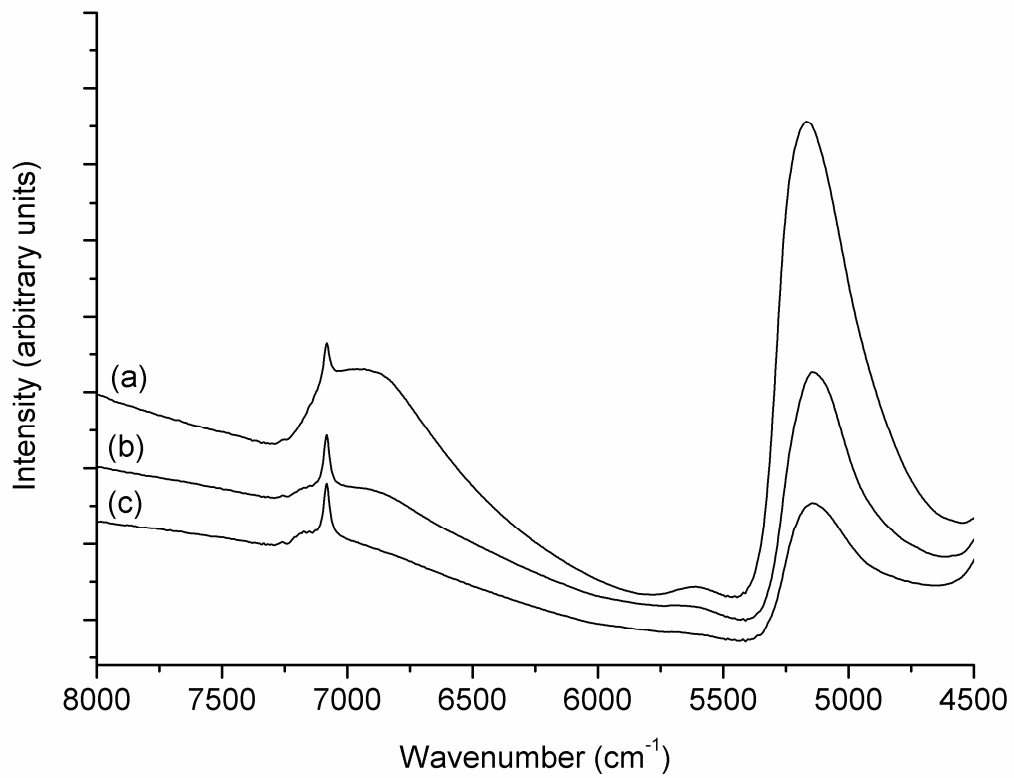


Fig. 3

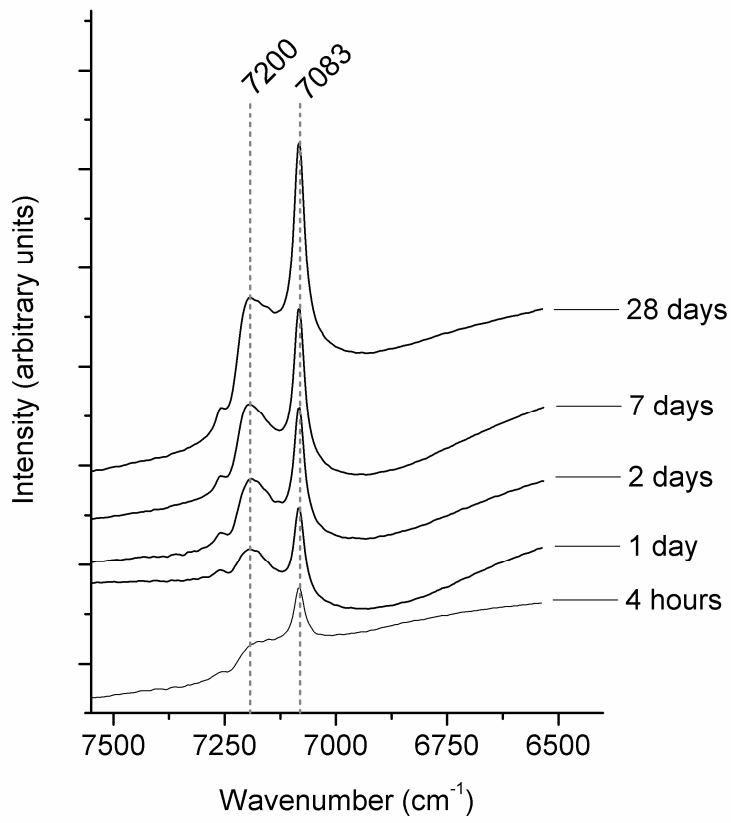


Fig. 4

