

Overview about the use of Fourier Transform Infrared spectroscopy to study cementitious materials

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Abstract

Fourier-Transform Infrared (FT-IR) spectroscopy shows several advantages that make it interesting to investigate cementitious materials: from clinker or hydrated phases to the bulk or the surface of hardened concrete. The FT-IR analyses in Transmission mode need only a few milligrams of material to provide its composition while other techniques (such as thermo-gravimetric analysis, X-ray diffraction, X-ray fluorescence) need a few grams. Moreover, FT-IR analyses are rapid and give results after a few minutes while other methods need at least a few hours to study one sample. The analyses done in Attenuated Total Reflection mode allow studying the surface of materials without any specific sampling methods (such as cleaning with solvent or storage under vacuum), which can alter the final composition. Clinker and anhydrous cement phases were already studied in 70s to establish the specific peaks of alite, belite and calcium aluminate. The study of major hydrates has been largely performed for the last two decades. FT-IR spectroscopy highlights easily the presence of portlandite ($\text{Ca}(\text{OH})_2$), which is detected by a thin unique peak. Moreover, the shift of the peaks assigned to Calcium Silicate Hydrate (C-S-H) can be detected using transmission mode, in order to study the polymerization of the silicates according to the conditions of cure and ageing. AFt and AFm phases (such as ettringite, sulfoaluminate or hemihydrate) can also be studied using FT-IR spectroscopy. Finally, this method is also able to detect organic demolding agents or CaCO_3 efflorescences at the surface of hardened concrete and can be used to study the interface between the hydrated paste and the polymers or coatings.

Keywords: FT-IR, clinker phases, hydrates, C-S-H, afwillite, cement paste, concrete.



1 Introduction

This work deals with the description of the advantages and limits of the FT-IR spectroscopy to analyze the cementitious materials. Contrary to organic solutions, polymers and coating, the Fourier-Transform Infrared (FT-IR) spectroscopy is not usually used to study cementitious materials. Indeed, researchers prefer to characterize these materials using other methods such as thermo-gravimetric analysis (TGA), X-ray diffraction (XRD), X-ray fluorescence (XRF)...etc [1]. However, FT-IR spectroscopy was already used in 70' to characterize the clinker phases and shows several advantages that make it useful to study a large range of cementitious materials.

In this paper, several applied results are described in parallel of a short bibliographic review. First, the main analytical modes available on a FT-IR spectrometer are rapidly described: (i) transmission mode (Tr); (ii) Attenuated Total Reflection mode (ATR); and (iii) diffuse reflectance spectroscopy (DRIFTS). The advantages and limits of FT-IR spectroscopy to study the cementitious materials are then specified. In a second part, a brief overview of the scientific literature is presented in parallel of selected FT-IR results for each topic (clinker phases, anhydrous cement, synthetic hydrates, hydrated cement paste, bulk of mortar and concrete surface).

2 Presentation of the FT-IR spectroscopy

2.1 Main modes of analyses

The FT-IR results shown in this work were obtained using a Nicolet iS10 spectrometer (Thermo Fisher Scientific Inc.). It was equipped with a deuterated triglycine sulfate (DTGS) detector and controlled by OMNIC software.

In Transmission mode (Tr), our sampled pellets were manufactured by mixing 250 mg of potassium bromide (KBr) with 3 mg of material (clinker or cement powder, or powder directly sampled into the bulk of hardened samples). 16 scans were recorded over the range 4,000–400 cm^{-1} with a spectral resolution of 4 cm^{-1} . The background spectrum was collected using a pure KBr pellet and the spectra of samples were corrected with a linear baseline.

In Attenuated Total Reflexion (ATR) mode, our hardened samples were directly analyzed over a thickness of a few μm and a sampling area of about 1 mm^2 . The crystal used was made of diamond. 16 scans were routinely recorded over the range 4000–650 cm^{-1} with a spectral resolution of 4 cm^{-1} . The background spectrum was collected at ambient atmosphere before analyzing each sample. The spectra of hardened samples were corrected with a linear baseline.

The diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) allowed measuring a range between 400 and 4000 cm^{-1} . The incident beam was reflected off the ground sample towards an overhead mirror upon which the diffusely scattered rays were collected and measured in the detector.

2.2 Advantages and limits compared to other methods

2.2.1 Main advantages

First, the analyses in Transmission mode need only a few milligrams of material to provide its composition while other techniques need a few grams. This specific light sampling is particularly relevant when only a small mass of hydrates can be synthesized. It is also easy to sample the cement paste into the bulk of mortar/concrete without any contamination from sand or aggregates.

Second, FT-IR results are directly obtained a few minutes after analyses without any complex treatment while other methods (TGA, XRD, XRF...etc) need at least a few hours to study one sample.

Third, the analyses in Attenuated Total Reflection (ATR) mode allow studying the surface of the cementitious materials without any specific sampling methods (such as cleaning with solvent or storage under vacuum, which can modify the composition of the material).

2.2.2 Main limits

FT-IR spectroscopy cannot be considered such as a quantifying method. Even if the intensity of certain specific IR bands, such as the one of portlandite, can vary as a function of their content in the sample (semi-quantification), it is not possible to make the relation between the intensity or the area of an IR band and a specific ratio.

Moreover, traces of chemical compounds can be under-estimated or erased due to the high intensity of certain IR bands, such as those of silica or calcium carbonate.

Finally, the presence of a large amount of capillary water into the hydrated sample can mask certain chemical compounds and disturb the interpretation of the spectra.

3 Selection of results obtained on cementitious materials

3.1 Analyses of anhydrous clinker phases

Clinker and anhydrous cement phases were already studied in the 70s in order to characterize the IR bands of alite, belite and calcium aluminate. Bensted and Varma [2], and Ghosh and Chatterjee [3, 4] published in 1974 certain of the first main papers about the FT-IR analyses applied in the cement industry. Ghosh and Handoo [5] wrote one of the first review papers in 1980. These first papers were mainly devoted to the analyses using transmission mode (only [4] used ATR mode).

Table 1 and Figure 1 show our own analyses done in Transmission mode concerning the specific peaks of synthetic clinker phases. Indeed, pure Ca_3SiO_5 and Ca_2SiO_4 phases were prepared by successive heating (at 1600°C) of a mixture of finely divided calcium carbonate (from Sigma-Aldrich, Germany) and silica (Aerosil 200 from Degussa, France) with appropriate stoichiometric proportions. All the spectra are conformed to those found in literature [2–5].



A double peak at 995-900 and 938-883 cm^{-1} , assigned to Si-O asymmetric stretching vibrations, characterizes mainly C2S and C3S phases, respectively. The detection of ferrite phase is difficult due to the absence of resolved and fixed peaks but aluminates phase (C3A) is easier to detect due to a large set of thin peaks assigned to Al-O bond.

Table 1: FT-IR bands of the synthetic clinker phases.

Clinker phases	Wave-number (cm^{-1}) with intensity of the band (s: strong; m: medium; l: low)					
	Si-O	Al-O	Si-O	Al-O	Si-O	
C3S - Ca_3SiO_5	938 s 883 s		812 l		522 s	430 s
B-C2S - Ca_2SiO_4	995 s, 900 s		844 s, 810 l		518 s	
C3A - $\text{Ca}_3\text{Al}_2\text{O}_6$		898 s	817 s	786 l, 739 s, 704 s, 588 l, 521 s	456 s	
<i>C4AF</i> - $\text{Ca}_4\text{Al}_2\text{Fe}_2\text{O}_{10}$			<i>Poorly resolved bands</i>			

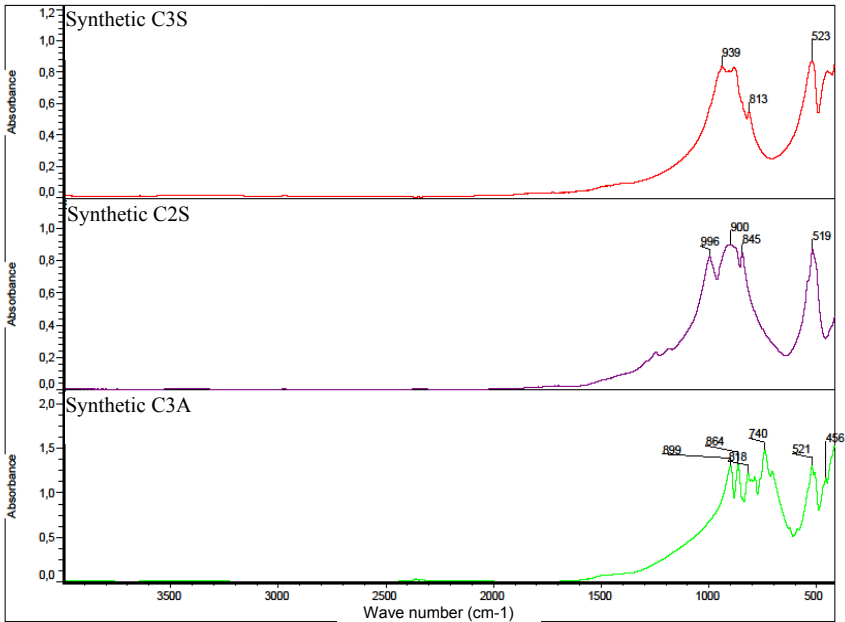


Figure 1: IR spectra of synthetic C3S, C2S and C3A.

3.2 Analyses of hydrated cement phases

3.2.1 Detection of the main hydrated phases

FT-IR spectroscopy highlights easily the presence of portlandite ($\text{Ca}(\text{OH})_2$), which is well detected by a resolute unique peak at 3640 cm^{-1} . This method is also used to study the shift of the bands assigned to Calcium Silicate Hydrate (C-S-H) according to the conditions of cure and ageing.

Table 2: FT-IR bands of the main hydrated phases.

Main hydrated phases	Wave-number (cm^{-1}) with intensity of the band (s=strong; m=medium; l=low)						
	O-H	O-H; H_2O capil.	Si-O (asym. stretching vib.)		Si-O	Si-O (out-of plane vib.)	Si-O (in-plane vib.)
Afwillite (crystalline micro-structure; Ca/Si ratio=1.5)		3352 l, 1660 l	985 m, 963 s	911 s	860 m, 781 m	617 m, 520 s, 490 s	450 s
C-S-H (colloidal gel like structure; Ca/Si ratio=1.5)		3356 l, 1640 l	1000 s, 950 s	950 s	814 m	667 l, 496 s	456 s
Portlandite – $\text{Ca}(\text{OH})_2$	3642 s						

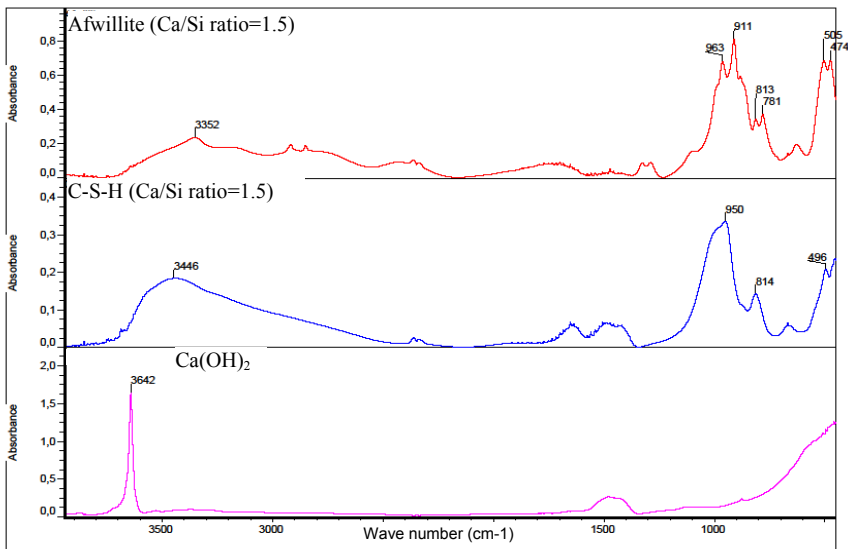


Figure 2: IR spectra of synthetic $\text{Ca}(\text{OH})_2$, C-S-H (Ca/Si=1.5) and afwillite.

Table 2 and Figure 2 provide our own analyses done in Transmission mode on synthetic hydrated phases. The $\text{Ca}(\text{OH})_2$ (portlandite) was provided directly

by a supplier (Sigma-Aldrich) while the calcium silicate hydrates (C-S-H, a colloidal gel like structure [6]) were prepared by mixing CaO (Sigma-Aldrich) and pure silica (Aerosil 200 from Degussa) with a calcium/silicon ratio of 1.5 and 0.9. A crystalline calcium silicate hydrate (afwillite) was also manufactured using a grinding process with ball milling and a calcium/silicon ratio of 1.5 [7]. The main IR bands of our powder samples made of C-S-H or afwillite are conformed to those detected in literature [8].

3.2.2 Shift due to the silica polymerization of C-S-H

The main characteristic peaks of C-S-H are located in the range between 1100 and 900 cm^{-1} . During ageing and de-calcification process, these IR bands shift according to the process of polymerization of the silica [9].

García-Lodeiro *et al.* [10, 11] and Bhat and Debnath [12] studied the hydration of C-S-H gel by FT-IR (in transmission mode). An interesting deconvolution of Si-O asymmetric stretching bands has been done [11].

Moreover, Ylmén *et al.* [13, 14] performed FT-IR analyses by DRIFTS to study different types of C-S-H according to the hydration time.

Hughes *et al.* [15] summarized the different assignment of IR bands (detected by DRIFTS) concerning the cement before and after hydration (clinker phases, sulfate-based and hydrated/carbonated products). The authors highlighted that the peak area of O-H of $\text{Ca}(\text{OH})_2$ was proportional to the peak area of $\text{Ca}(\text{OH})_2$ measured by TGA.

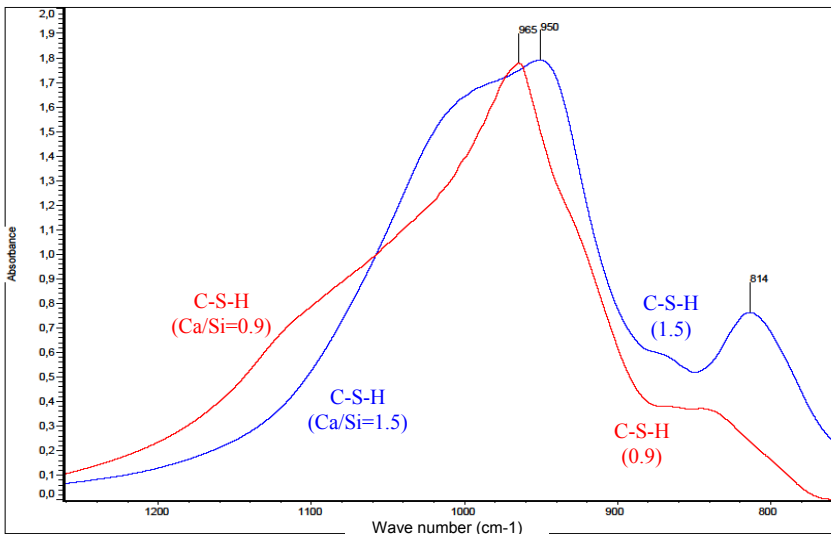


Figure 3: Main IR bands of C-S-H (1.5) and C-S-H (0.9).

Yu *et al.* [16] investigated the structure of different synthetic C-S-H. The FT-IR spectra of their C-S-H were compared to those of tobermorite in order to establish that the IR bands of C-S-H (between 980 and 1080 cm^{-1}) varied according to the calcium/silicon ratio. Indeed, the 1100–950 cm^{-1} region (assigned to Si-O stretching) shifted to lower wave-numbers due to the decreasing polymerization.

Figure 3 shows the IR bands of our synthetic C-S-H samples in the 1300–700 cm^{-1} range. The spectrum of C-S-H 1.5 (calcium/silicon ratio of 1.5), which is usually found in young hardened cement paste, is then compared to the one of aged C-S-H (calcium/silicon ratio of 0.9). A shift of the bands to higher wave numbers is then highlighted after ageing, due to the polymerization of silica during the de-calcification process.

3.2.3 Detection of the Aft/AFm phases

A part of the actual studies done using FT-IR spectroscopy is devoted to the investigation of Aft and AFm phases (such as ettringite, sulfoaluminate, hemicarboaluminate, monosulfoaluminate, C4AH13...etc), which can be responsible for an anticipated ageing of the hydrated cement paste. For example, precipitation of secondary ettringite can be responsible for the swelling, the fissuring and the decreasing of the mechanical resistance of concrete [17].

Certain works are focused on the evolution of the hydration when silica fumes and fly ash are added into the cement paste. Hidalgo Lopez *et al.* [18] showed by FT-IR in transmission mode certain phases formed in the hydrated pastes, such as Stratlingite (C2ASH8), hydrogarnet (C3AH6), gibbsite ($\text{Al}(\text{OH})_3$) and hydrated tetracalcium aluminate (C4AcH11).

We performed FT-IR analyses in transmission mode on different synthetic Aft/AFm phases (created using specific mixes made of pure AlSO_4 , CaO, $\text{Ca}(\text{OH})_2$, CaCO_3 , C3A and/or gypsum and processed at distinct temperatures). Table 3 provides the assignment of IR bands of the spectra of ettringite, mono-carbo-aluminate, hemi-carbo-aluminate, mono-sulfo-aluminate, C4AH13, C3AH6 (hydrogarnet) and C2ASH8 (stratlingite). The contaminations due to the process of synthesis were deduced by using XRD analyses and were removed (e.g. ettringite in sulfo-aluminate or portlandite in hemi-carbo-aluminate). All these phases show complex spectra (as shown in Figure 4) due to the presence of aluminate, sulfate and carbonate units. We notice that both the IR spectra of hemi- and mono-carbo-aluminates are equivalent.

3.3 Analyses of the bulk and surface of hardened pastes

FT-IR spectroscopy is mainly known for its efficiency to characterize polymer or organic compounds [19]. This specific ability can be useful to: (i) investigate the bulk of lightweight mortar containing aggregates made of polymer waste; (ii) detect residues of demolding agents (e.g. based on vegetable base oil) [20]; (iii) highlight the presence of CaCO_3 efflorescences [21]; (iv) study the interface between concrete and protective coating [21].

Table 3: FT-IR bands of Aft/AFm phases (contamination due to the creation process deduced).

AFt/AFm phases	Wave-number (cm ⁻¹) with intensity of the band (s=strong; m=medium; l=low)									
	O-H			O-H; H ₂ O capil.	C-O; [CO ₃] ²⁻	S-O; [SO ₄] ²⁻	Si-O	Al-O		
Ettringite Ca ₆ Al ₂ (SO ₄) ₃ (OH) ₁₂ / 26H ₂ O		3637s		3431m, 1680- 1640m		1115s, 617m		857l		537m
Mono-Carbo- aluminate Ca ₄ Al ₂ (CO ₃)(OH) ₁₂ / 5H ₂ O	3676m	3624m	3543m	3363m, 3005m, 1650l	1363s			953m	669l	535s
Hemi-Carbo- aluminate Ca ₄ Al ₂ (CO ₃) _{0.5} (OH) ₁₃ / 5.5H ₂ O	3676m	3642m, 3624m	3544m	3367- 3007m, 1645l	1364s			954m	671l	537s
Mono-sulfo- aluminate Ca ₄ Al ₂ (SO ₄)(OH) ₁₂ / 6H ₂ O	3672m		3549m	3423s, 1650m	1380l	1150m			579m	525s
C4AH13 ; Ca ₄ Al ₂ (OH) ₁₄ / 6H ₂ O	3673m		3541m	3400m, 1641l	1383l				667l	522s
C3AH6 (Hydrogarnet) ; Ca ₃ Al ₂ (OH) ₁₂	3660s							810l		537s
C2ASH8 (Stratlingite) ; Ca ₂ Al ₂ SiO ₂ (OH) ₁₀ / 2.25H ₂ O	3669l			3442m, 1652l			1050s, 452s	951s		524s

Indeed, FT-IR spectroscopy in transmission mode was used to study the bulk of lightweight mortar containing polyamide waste powder. The polymer waste powder was then recycled as aggregates to substitute 50% of the sand (in volume ratio) contained in the mortar. Table 4 describes the IR spectra obtained 28 days after demolding. Specific bands assigned to polyamide are perfectly detected (data in *italic*). Several samplings performed into the bulk show a homogeneous dispersion of the polymer powder into the mortar mix. Assignment of the other bands did not show any specific disturbance of hydration: portlandite was detected at 3640 cm⁻¹ (O-H stretching vibration); C-S-H were characterized by the major bands at 1030-970 cm⁻¹ (Si-O asymmetric stretching vibration); the S-O stretching vibration of [SO₄]²⁻ was also detected at 1150-1100 cm⁻¹.

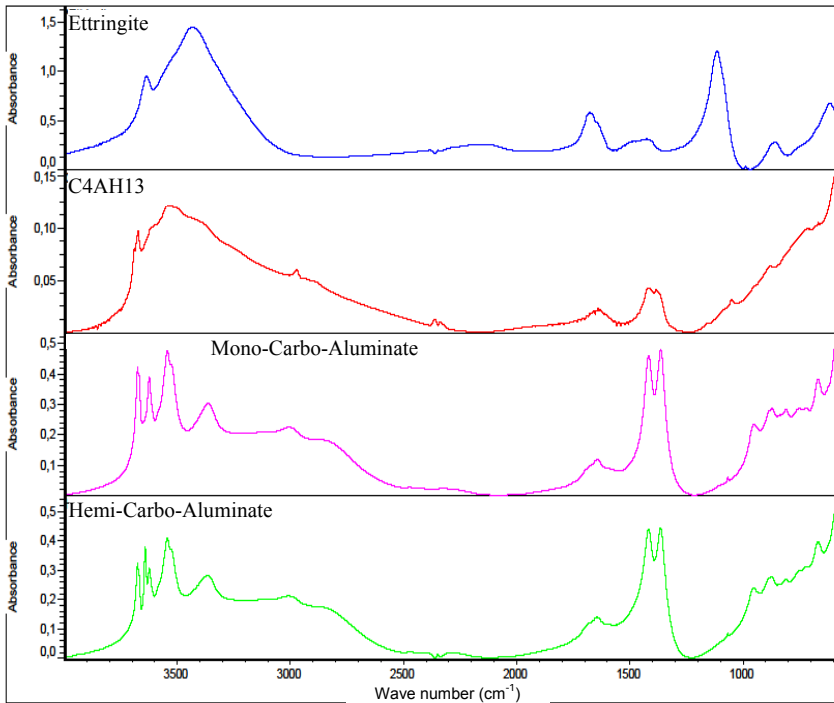


Figure 4: IR spectra of the different Aft/AFm phases studied.

Table 4: FT-IR bands of the bulk of mortar containing polymer recycled waste.

Bulk of mortar containing polyamide waste powder	Wave-number (cm ⁻¹) with intensity of the band (s=strong; m=medium; l=low)								
	O-H	O-H; H ₂ O capil.	N-H	CH ₂ / CH ₃	C-O ; [CO ₃] ²⁻	C=O	C-N	S-O ; [SO ₄] ²⁻	Si-O (asym. stretching vib.)
	3640m	3400 m, 1650 l	3300s, 3100m, 1460m	2920s, 2850s	2510l, 1410s, 872m, 710s	1640s	1560s	1100s	1030s - 970s

A concrete sample, protected by a polyurethane based resin, was also studied by FT-IR. The coating was sprayed on the concrete surface 28 days after demolding. The ATR mode was used to investigate the interface between concrete surface and coating. Table 5 provides the assignment of the main IR bands detected from the concrete. Portlandite (at 3640 cm⁻¹) and C-S-H (1020-970 cm⁻¹) were well detected. A double peak at 935–900 cm⁻¹ was assigned to the presence of anhydrous alite. The FT-IR spectroscopy highlighted the

presence of CaCO_3 (3 distinct bands at 1410, 870 and 710 cm^{-1}). The detection of CaCO_3 was assigned to the carbonation process or to the limestone filler used into the concrete mix. On the other hand, specific peaks of PU-based coating were well detected (data in italic in Table 5). No specific band attributed to the isocyanates group (at 2270 cm^{-1}) was detected, confirming a complete crosslinking of the resin.

Table 5: FT-IR bands of the interface between concrete and PU resin.

Interface between concrete and a PU based resin	Wave-number (cm^{-1}) with intensity of the band (s=strong; m=medium; l=low)									
	O-H	OH; H_2O capil.	N-H	CH_2 / CH_3	C-O; $[\text{CO}_3]^{2-}$	C=O	S-O; $[\text{SO}_4]^{2-}$	Si-O (asym. stretching) vib.	Si-O	Si-O
	3640m	3400m, 1650l	3335s, 1450m	2950s, 2850s	2510 l, 1410 s, 872 m, 710 s	1690s	1110s	1020s, 970s	935l, 900l	797m, 777m

4 Conclusions

FT-IR spectroscopy is a useful and convenient method to study the cementitious materials. This technique of characterization benefits certain advantages such as a small amount of sampling material, a short time of interpretation and a simplified sampling process compared to other usual methods of characterization. Moreover, specific modes of analysis such as ATR can directly investigate the surface of the hardened cementitious samples. However, FT-IR spectroscopy does not give any quantifying interpretation and is limited to detect the traces of certain compounds. Concerning the different applications, clinker phases and anhydrous cement can be well characterized by FT-IR in order to highlight the presence of C3S, C2S and C3A. Synthetic hydrated powders are easily investigated to detect the presence of major hydrates such as portlandite and C-S-H. The shift of the position of the major bands of C-S-H is studied to obtain specific data about the polymerization of silica and the decalcification process that occur during the ageing of the hydrated cement paste. New developments are under progress to study the presence of phases such as secondary ettringite, hemicarbonate, monosulfoaluminate, sulfoaluminate, C4AH13, etc. Finally, FT-IR spectroscopy is also interesting to characterize the mortar or concrete samples, containing or covered by polymer compounds, such as organic coatings.

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