

# Infrared Spectroscopy in the Analysis of Building and Construction Materials

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*In memorial of Prof. Tomás Vázquez*

## 1. Introduction

In the characterization of building and construction materials, the most frequently analytical tool performed have been X-ray diffraction but also, thermal analysis and microscopic techniques. Nowadays, infrared and other spectroscopic techniques have become as a useful, non-destructive and easy technique to study the phase composition of initial but also the evolved materials due to their exposure to the climatic conditions. Moreover, by using this tool is possible the detection of crystalline but also the amorphous phases very frequently developed on certain cementitious materials, mainly at early ages. The infrared spectroscopy is used both to gather information about the structure of compounds and as analytical tool to assess in qualitative and quantitative analysis of mixtures.

The infrared spectra are quick and easy to achieve and refers to the spectrum region between the visible and microwave regions. In theory, infrared radiation is absorbed by molecules and converted into energy of molecular vibration; when the radiant energy matches the energy of a specific molecular vibration, absorption occurs. The frequencies at which a molecule absorbs radiation give information on the groups present in the molecule. As an approximation, the energy of a molecule can be separated into three additive components associated with the motion of the electrons in the molecule, the vibration of the constituent atoms, and the rotation of the molecule as a whole. The absorption in the infrared region arises predominantly from excitation of molecular vibrations. Then, if a molecule is placed in an electromagnetic field, a transfer of energy from the field to the molecule will occur when Bohr's frequency condition is satisfied.

$$\Delta E = h\nu$$

Where  $\Delta E$  is the difference in energy between two quantized states,  $h$  is the Planck's constant and  $\nu$  is the frequency of the light. Then the molecule "absorbs"  $\Delta E$  when it is excited from  $E_1$  to  $E_2$  and "emits"  $\Delta E$  when it reverts from  $E_2$  to  $E_1$ . The infrared absorption spectra originate in photons in the infrared region that are absorbed by transitions between two vibrational levels of the molecule in the electronic ground state.

The application of infrared spectroscopy to the inorganic compounds started as a more frequent technique during the 60's with Lawson. This author made a first attempt to compile the work done in the relatively new field-Inorganic Infrared Spectroscopy since 1952 where 1171 references were reported. Farmer, in 1964, studied the silicates and Nakamoto in relation to the coordinated compounds prepared a helpful atlas of these compounds. Afremow (1966) presented for an important research of inorganic pigments and extenders in the mid-infrared region from 1500  $\text{cm}^{-1}$  to 200  $\text{cm}^{-1}$ . The study of surface chemistry and the nature of surface functional groups was also advanced by Basila (1968).

In the first decade of infrared research on the study of Portland cements, Vázquez (1969), was a lead the way in the study by infrared spectroscopy the main present compounds in the Portland cement but also later, made some research about the carbonation processes of calcium aluminate cements. Also, the hydration of Portland cement and its constituents was developed by Bensted (1974).

After that initial period, several reports have been done in the study on cementitious materials by infrared. More recent studies in relation with the calcium aluminates cements were reported by Vázquez (1993). Later on, different papers have present some characterization of materials and evolution over several exposition conditions using the infrared spectroscopy as a complementary technique join to mainly XRD and SEM analytical tools.

Without doubt, the infrared spectroscopy has not been really used in the qualitative and quantitative analysis of these materials; the main uses have rather been in identification of compounds and few structural studies. The main objective of this chapter will be to present a revision of infrared spectra useful in the study of the building and construction materials, mainly cements, from the point of view of characterization.

## 2. Characterization of cementitious systems by infrared spectroscopy

As a general rule, as it is easier to bend a bond than to stretch or compress it, in the spectra the stretching frequencies are higher than the corresponding bending frequencies; bonds to hydrogen have higher stretching frequencies than those to heavier atoms; and double bonds have higher stretching frequencies than single bonds (Figure 1).

### 2.1 Portland cement

The ordinary Portland cement is made by firing raw materials - limestone, clay minerals, sand and iron minerals- at around 1500°C in a rotary kiln. At this temperature a series of chemical reaction take place and the clinker synthesized. Clinker is cooled, mixed with setting regulators (e.g. gypsum) grounded to a fine powder to obtain the cement. The common phases present in the cement clinkers are: alite ( $3\text{CaO} \cdot \text{SiO}_2$ ,  $\text{C}_3\text{S}^1$ ), belite ( $2\text{CaO} \cdot \text{SiO}_2$ ,  $\text{C}_2\text{S}^1$ ), tricalcium aluminate ( $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ ,  $\text{C}_3\text{A}^1$ ), and tetracalcium aluminate ferrite ( $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$ ,  $\text{C}_4\text{AF}^1$ ). One typical composition of cement consists of:  $\text{C}_3\text{S} = 55\text{-}60\%$  (wt);  $\text{C}_2\text{S} = 15\text{-}20\%$  (wt);  $\text{C}_3\text{A} = 5\text{-}10\%$  (wt);  $\text{C}_4\text{AF} = 5\text{-}8\%$  (wt) and  $\text{C}\bar{\text{S}}\text{H}_2 = 2.6\%$  (wt). In this chapter, synthetic silicates and aluminates phases have been used to identify infrared vibrations bands previous to study the more complicated commercial cement.

<sup>1</sup> Cement chemistry nomenclature is used:  $C = \text{CaO}$ ;  $S = \text{SiO}_2$ ;  $A = \text{Al}_2\text{O}_3$ ;  $F = \text{Fe}_2\text{O}_3$ ;  $H = \text{H}_2\text{O}$ ;  $\bar{S} = \text{SO}_3$

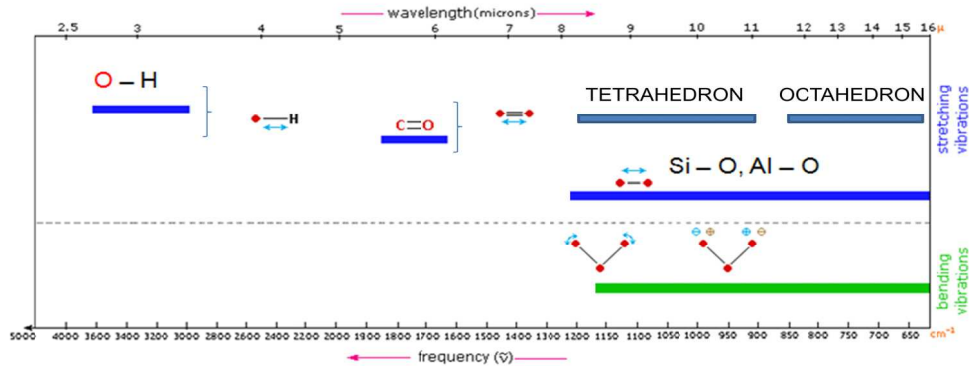


Fig. 1. General rules in the interpretation of building cementing material IR spectra.

As a resume, the vibrations can be divided in stretching and bending: vibrations can involve either a change in bond length (stretching) or bond angle (bending); some bonds can stretch in-phase (symmetrical stretching) or out-of-phase (asymmetric stretching). The main structure elements in building the crystal lattice of silicates are tetrahedral  $\text{SiO}_4$  groups, with may be either isolated as in the orthosilicates or connected with one another by common O atoms as in building an  $\text{Si}_2\text{O}_7$  group from two connected tetraheda [Matossi]. Connection of  $\text{SiO}_4$  groups so as to form a ring of tetrahedral occurs in the crystal of alite ( $\text{C}_3\text{S}$ ) or belite ( $\text{C}_2\text{S}$ ). The infrared spectra of all silicates [Matossi] contain two reflection maxima near 1000 and 500  $\text{cm}^{-1}$ , which have been interpreted as a two active frequencies of a tetrahedral point group. In addition to these, there may occur other maxima corresponding to other particular features of the crystal lattice.

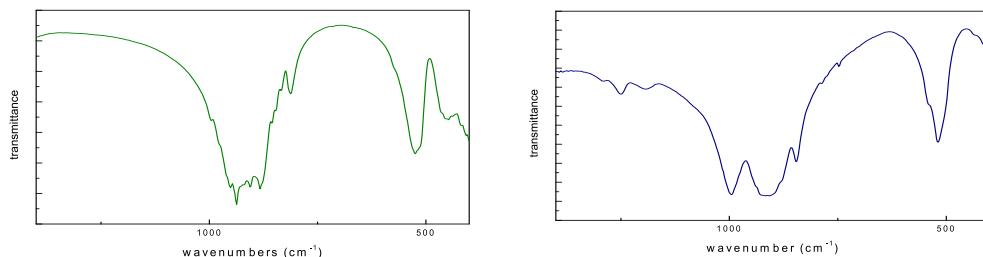
The spectrum of the main constituent of OPC,  $\text{C}_3\text{S}$ , shows two regions dominated by the internal modes of  $\text{SiO}_4^{4-}$  tetrahedral units, with two broad absorption bands centred between 890 and 955  $\text{cm}^{-1}$ , solved in to maxima near to 870 and 940  $\text{cm}^{-1}$  due to the symmetric and antisymmetric stretching of Si-O bonds within tetrahedral  $\text{SiO}_4$  groups,  $\nu_1$  and  $\nu_3$ , respectively. Another absorption band of medium intensity appears close to 525  $\text{cm}^{-1}$  and a lower intense band sited near to 450  $\text{cm}^{-1}$  due to the symmetric and antisymmetric bending of the O-Si-O bonds,  $\nu_2$  and  $\nu_4$ , respectively (see details of maxims in Table 1 and Figure 2). The other calcium silicate phase spectra,  $\text{C}_2\text{S}$ , exhibits strong bands in the area 1000-800  $\text{cm}^{-1}$  with maximums at 990 and 840  $\text{cm}^{-1}$  due the stretching Si-O bond of the silicon tetrahedron and the bending vibration absorption band appear at lower frequencies, 520  $\text{cm}^{-1}$  and a shoulder at 538  $\text{cm}^{-1}$ .

The  $\text{C}_3\text{A}$ -cubic tricalcium aluminate polymorph spectra (Figure 3), shows a well-defined spectra with two dominant absorption areas with very broad bands. The first ones appear in the area between 950-650  $\text{cm}^{-1}$  and the second ones appearing between 500-380  $\text{cm}^{-1}$ , respectively. The main observed maxima appear near to 900, 865, 820, 780, 720 and 705  $\text{cm}^{-1}$  of  $\text{AlO}_4$ -tetrahedral groups, and close to 520, 510, 460 and 414  $\text{cm}^{-1}$  due to  $\text{AlO}_6$ -octahedral groups. The Ca-O bands appear at lower frequencies.

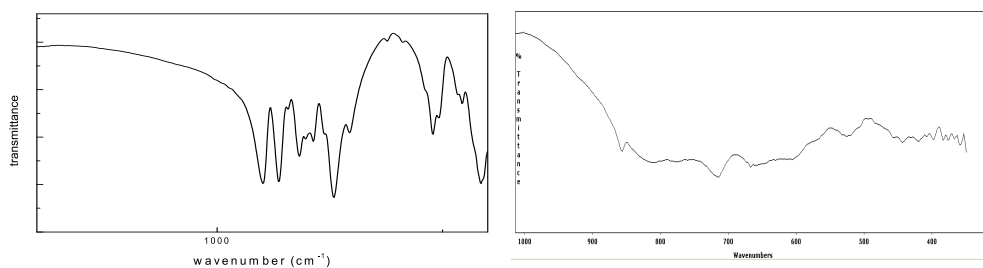
The grey colour of Portland cements is due to the presence of the names ferrite phases; in absence of elements other than calcium, aluminium, iron and oxygen, calcium

phase	Fundamental vibrations (cm <sup>-1</sup> )	
$C_3S$	935	521
$\beta - C_2S$	991, 879, 847	509
$C_3A$	900, 865, 820, 780, 720, 705	520, 510, 460, 414
$C_4AF$	700 - 500	

Table 1. Characteristic absorbance bands for cement Portland phases

Fig. 2. Infrared spectra of pure  $C_3S$  (left) and  $C_2S$  (right).

aluminoferrite forms a solid solution series of formula  $Ca_2(Al_xFe_{1-x})_2O_5$  for all values of  $x$  in the range 0-0.7, compositions with  $x > 0.7$  do not exist at ordinary pressures. The spectrum of  $C_4AF$  presents as significant absorption bands the sited between 800-830  $cm^{-1}$  with maxima close to 720  $cm^{-1}$  due to  $\nu_1$  [(Fe,Al)O<sub>4</sub><sup>5-</sup>]; moreover, a broad and less intense band with several maximums between 620 and 670  $cm^{-1}$  is also present (Figure 3).

Fig. 3. Infrared spectra of  $C_3A$  (left) and  $C_4AF$  (right).

In a real cement the main phases are alite ( $C_3S$ -base solid solutions i.e. MgO, Na<sub>2</sub>O) and belite ( $C_2S$ -base solid solutions i.e.- Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>). The presence of these impurities prompts a change in the crystalline structure of the silicate phases that may cause modifications in the Infrared spectra compared to the pure phases. Figure 4 present the infrared spectra of the ordinary Portland cement. In this spectrum, it is possible to identify different vibrations bands from the calcium silicates, calcium aluminates, and gypsum, the last one added as setting regulator.

The gypsum can lose part of the structure water and the sulfates can be present as bassanite and/or anhydrite. In the IR spectras, the strongest peak is presented at 1102, 1111, and 1094

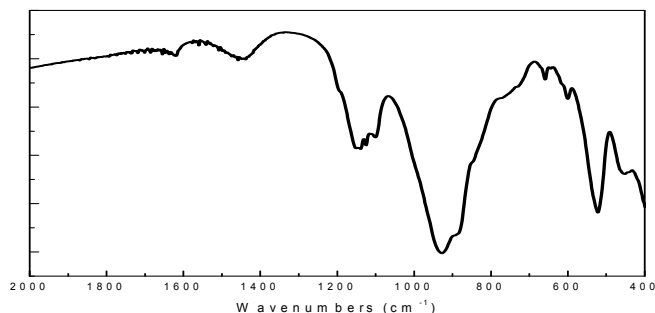


Fig. 4. IR Spectrum of ordinary Portland cement.

$\text{cm}^{-1}$ , for the gypsum, bassanite, and anhydrite, respectively. They are  $\nu_3$  antisymmetric stretch vibration modes of  $\text{SO}_4$  tetrahedra. The gypsum, bassanite, and anhydrite present two absorption bands ( $669, 604 \text{ cm}^{-1}$ ), three ( $660, 629, 600 \text{ cm}^{-1}$ ) and three ( $677, 615, 600 \text{ cm}^{-1}$ ), anti-symmetric bending vibrations, respectively. The peaks at  $595 \text{ cm}^{-1}$  in gypsum and  $594 \text{ cm}^{-1}$  in bassanite split into two peaks ( $610$  and  $591 \text{ cm}^{-1}$ ) in anhydrite, which indicates a lowering of symmetry in anhydrite. The shift of frequency from  $677 \text{ cm}^{-1}$  in anhydrite to  $660 \text{ cm}^{-1}$  in bassanite indicates that the sulfate ions in bassanite are linked with water molecules by hydrogen bonding, because in general the hydrogen bonding will lower the frequency of the absorption band. In addition, there is a very weak peak at  $1140 \text{ cm}^{-1}$  in gypsum,  $1150 \text{ cm}^{-1}$  in bassanite, and  $1150 \text{ cm}^{-1}$  in anhydrite, which should be the  $\nu_1$  symmetric stretch vibration modes of  $\text{SO}_4$  tetrahedral. The Table 2 present the characteristics absorption bands of sulfate compounds. For gypsum and bassanite presence it will be also possible to analyze  $4000\text{-}3000 \text{ cm}^{-1}$  region were  $\nu_1$  O-H absorptions can be observed ( $3553$  and  $3399 \text{ cm}^{-1}$  for gypsum and  $3611$  and  $3557 \text{ cm}^{-1}$  for bassanite).

Sulfates	FUNDAMENTALS			OVERTONES	OH-STRECHT	OH-BEND
	$\nu_1$	$\nu_3$	$\nu_4$			
gypsum	1140	1117	669, 604	2500 - 1900	3553, 3399	1686, 1618
Bassanite	1150	1117, 1098	660, 629, 600	2500 - 1900	3611, 3557	1618
anhydrite	1150	1120	677, 615, 600	2500 - 1900	---	---

Table 2. Absorption bands of sulfate compounds ( $\text{cm}^{-1}$ )

## 2.2 Calcium aluminate cement

The calcium aluminate cement (*CAC*) was developed as a solution to the sulphates attack in OPC, and was patented in France in 1908. The *CAC*s are cements consisting predominantly of hydraulic calcium aluminates: mainly monocalcium aluminate, *CA*, but also contains minor amounts of  $\text{C}_{12}\text{A}_7$ ,  $\text{CA}_2$  and  $\text{C}_4\text{AF}$ .

According to Tarte, in the interpretation of IR spectra of inorganic aluminates, the characteristic frequency ranges are "condensed"  $\text{AlO}_4$  tetrahedral in the  $900\text{-}700 \text{ cm}^{-1}$ , "isolated"  $\text{AlO}_4$  tetrahedral  $800\text{-}650 \text{ cm}^{-1}$ , "condensed"  $\text{AlO}_6$  octahedral in the  $680\text{-}500 \text{ cm}^{-1}$ ,

“isolated”  $\text{AlO}_6$  octahedral  $530\text{--}400\text{ cm}^{-1}$ . In the spectra of the main present phase of CAC, the CA, the most relevant signals are presented in the two region  $850\text{--}750\text{ cm}^{-1}$  and  $750\text{--}500\text{ cm}^{-1}$  due to the mentioned groups, with maxima near to  $840, 805, 780$  and  $720\text{ cm}^{-1}$  of  $\text{AlO}_4$  tetrahedral and close to  $680, 640, 570, 540, 450$  and  $420\text{ cm}^{-1}$  of  $\text{AlO}_6$  groups (Figure 5).

The infrared spectrum of  $\text{C}_{12}\text{A}_7$  contains absorption bands mainly in two regions: a very broad absorption region between  $680\text{--}900\text{ cm}^{-1}$  of tetrahedral groups and another area in the  $650\text{--}400\text{ cm}^{-1}$  range with very sharp and intense bands due to octahedral groups. The maxima appear close to  $850, 780, 610, 575, 460$  and  $410\text{ cm}^{-1}$  (Figure 5).

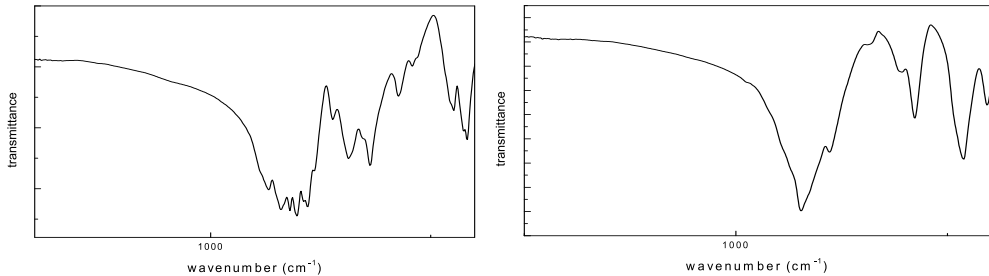


Fig. 5. Infrared spectra of CA (left) and  $\text{C}_{12}\text{A}_7$  (right).

The minor phases present in the CAC are the  $\text{CA}_2$  aluminate with the two absorption in the areas  $950\text{--}700\text{ cm}^{-1}$  and  $690\text{--}410\text{ cm}^{-1}$  with maxima at  $945, 920, 860, 840, 810$  and  $745\text{ cm}^{-1}$  of  $\text{AlO}_4$  groups and near to  $680, 660, 640, 575, 540, 440$  and  $422\text{ cm}^{-1}$  of  $\text{AlO}_6$  groups. The  $\text{C}_2\text{AS}$  mineral presents the  $\text{AlO}_4$  vibration area between  $920$  and  $720\text{ cm}^{-1}$  while the  $\text{AlO}_6$  groups give absorption bands between  $720\text{--}400\text{ cm}^{-1}$ . At higher frequencies, in this spectra appear the signals due to the Si-O vibrations,  $1020$  and  $973\text{ cm}^{-1}$ . The IR spectra of  $\text{CA}_2$  and  $\text{C}_2\text{AS}$  are presented in Figure 6.

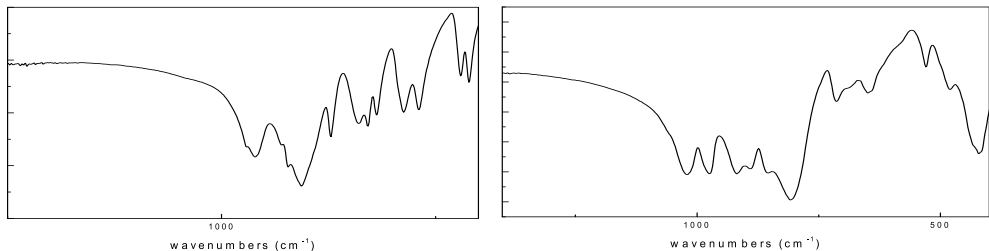


Fig. 6. Infrared spectra of  $\text{CA}_2$  (left) and  $\text{C}_2\text{AS}$  (right).

Then, the most relevant signals on the FTIR spectrum for CAC are the absorption bands in the region between  $850$  and  $650\text{ cm}^{-1}$  – the bands at around  $840, 805$  and  $780\text{ cm}^{-1}$  – attributed to  $\text{AlO}_4$  groups; the bands between  $750$  and  $400\text{ cm}^{-1}$  – with bands at about  $720, 685, 640$  and  $570\text{ cm}^{-1}$ , ascribed to  $\text{AlO}_6$  groups; and the bands at under  $400\text{ cm}^{-1}$  owing to Ca-O bonds [15, 16]. The Figure 7 shows the IR spectra of the commercial cement. The Table 3 presents the characteristics absorption bands of CAC mineral compounds.

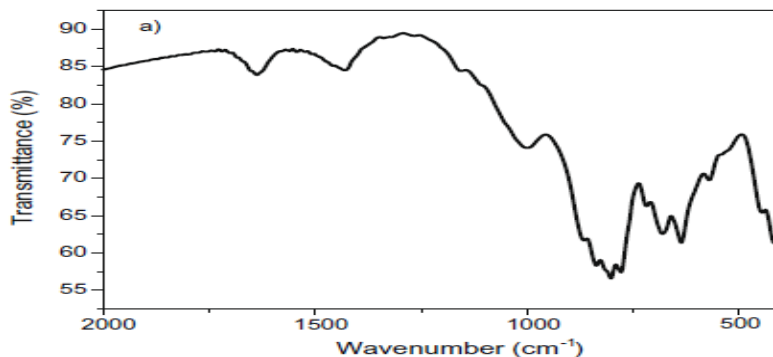


Fig. 7. IR spectra of commercial calcium aluminate cement.

phase	Fundamental vibrations (cm <sup>-1</sup> )	
CA	840, 805, 780, 720	680, 640, 570, 540, 450, 420
C <sub>12</sub> A <sub>7</sub>	850, 780,	610, 575, 460, 410
CA <sub>2</sub>	945, 920, 860, 840, 810, 745, 680,	660, 640, 575, 540, 440, 422
C <sub>2</sub> AS	920, 720, 710, 1020, 973	650, 530, 480, 420

Table 3. Characteristic absorbance bands for calcium aluminate cement phases.

### 2.3 Calcium sulfoaluminate cement

From the sustainability point of view new cement production has been developed in the past decades. One of these new cements is calcium sulfoaluminate (CSA) that was first developed in China in 1980's. Industrial production requires essentially gypsum, bauxite and limestone as raw materials, which are burnt at 1,300°C in a conventional rotary kiln. These starting materials lead to a final clinker based on the quinary system CaO-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>-Fe<sub>2</sub>O<sub>3</sub>-SO<sub>3</sub> and formed by three main minerals: tetracalcium trialuminate sulphate or yeelimite (C<sub>4</sub>A<sub>3</sub>S̄); dicalcium silicate or belite (C<sub>2</sub>S) and calcium sulphate or anhydrite (C̄S). Minor phases such as C<sub>3</sub>A, C<sub>4</sub>AF, C<sub>12</sub>A<sub>7</sub> and (C<sub>2</sub>AS) can also be present. The infrared spectra of main mineral phase of calcium sulfoaluminate cement can be described as follow: yeelimite has two absorption bands due to vibrational modes of sulphate [SO<sub>4</sub>]<sup>2-</sup> groups at 1110 cm<sup>-1</sup>, a very intense absorption band due to silicate groups near to 800 cm<sup>-1</sup>, the third band at 620 cm<sup>-1</sup> is due to vibrational modes of [AlO<sub>4</sub>]<sup>5-</sup> tetrahedra; ii) belite, anhydrite, C<sub>12</sub>A<sub>7</sub> and C<sub>2</sub>AS spectras have been described previously. Then, the infrared spectrum of the CSA cement presents the most intense bands located at 1110 and 800 cm<sup>-1</sup>, in the region where stretching vibrations of [SO<sub>4</sub>]<sup>2-</sup> groups lie. A broadened signal appears between 900 and 800 cm<sup>-1</sup>, centered at 857 cm<sup>-1</sup>. This feature is strongly asymmetrical: this is probably the result of the convolution of the two bands of C<sub>2</sub>S, that appear unresolved or as a consequence of lower crystal perfection caused by the presence of foreign ions in the lattice or because of the small particle size of minerals of CSA clinker. But it is also possible to highlight the presence of the three anhydrite bands at 677, 615, and 600 cm<sup>-1</sup>, respectively. The Figure 8 displays the IR spectra of yeelimite.

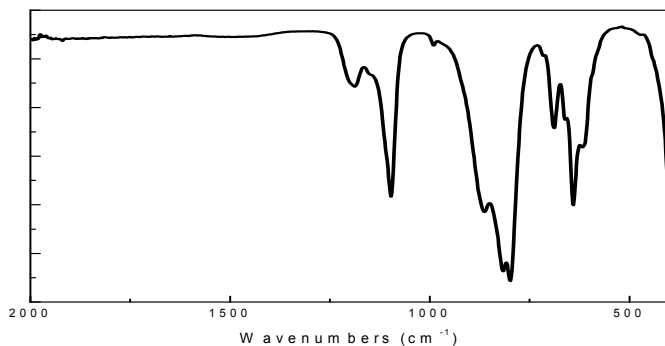


Fig. 8. Infrared spectra of yeelimite.

### 3. Infrared analysis of hydrated cementitious materials

The hydration of Portland cement give rise both, amorphous phase calcium silicate hydrated (C-S-H gel) and two crystalline phases, ettringite ( $\text{Ca}_6\text{Al}_2(\text{OH})_{12}(\text{SO}_4)_3 \cdot 26\text{H}_2\text{O}$ ) and portlandite. The C-S-H gel is the primary binding phase in Portland cement but poorly crystalline. The Figure 9 presents the infrared spectra of a hydrated commercial Portland cement.

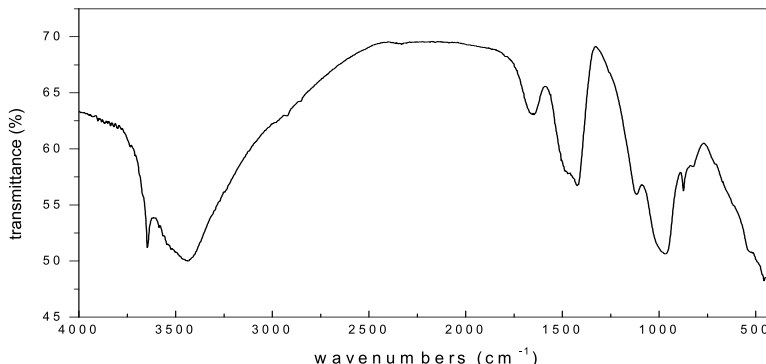


Fig. 9. IR spectra of hydrated Portland cement.

The ettringite ( $\text{C}_6\text{A}\bar{3}\text{H}_{32}$ ) is the first developed phase due to the reaction of aluminates with sulfates of Portland cement. According to the structure model by Taylor [76], the crystals are based on columns of cations of the composition  $\{\text{Ca}_3[\text{Al}(\text{OH})_6] \cdot 12 \text{H}_2\text{O}\}^{3+}$ . In there, the  $\text{Al}(\text{OH})_6^{3-}$ -octahedral are bound up with the edgesharing  $\text{CaO}_8$ -polyhedra, that means each aluminum-ion, bound into the crystal, is connected to  $\text{Ca}^{2+}$ -ions, with which they share OH-ions. The intervening channels contain the  $\text{SO}_4^{2-}$ -tetrahedral and the remaining  $\text{H}_2\text{O}$  molecules (fig. 2). The  $\text{H}_2\text{O}$  molecules are partly bound very loose into the ettringite structure. According to Bensted, the infrared spectra of ettringite  $\text{C}_3\text{A} \cdot 3\text{C}\bar{3} \cdot \text{H}_{32}$  or



$\text{Ca}_6[\text{Al}(\text{OH})_6]_2(\text{SO}_4)_3 \cdot 26\text{H}_2\text{O}$  presents a very strong anti-symmetrical stretching frequency of the sulphate ion ( $\nu_3 \text{SO}_4$ ) centred towards  $1120 \text{ cm}^{-1}$ ; this band is indicative of relative isolation of this ion in the hexagonal prism structure. The water absorption bands appear in the region  $1600\text{-}1700 \text{ cm}^{-1}$  ( $1640$  and  $1675 \text{ cm}^{-1}$   $\nu_2 \text{H}_2\text{O}$ ) and above  $3000 \text{ cm}^{-1}$  ( $3420$  due to  $\nu_1 \text{H}_2\text{O}$  and  $3635 \text{ cm}^{-1}$  from  $\nu \text{OH}_{\text{free}}$ ). The presence of aluminate bands are near to  $550 \text{ cm}^{-1}$  ( $\nu \text{AlO}_6$ ) due to stretching Al-O groups, and  $855 \text{ cm}^{-1}$  (Al-O-H bending). The Figure 10 shows the structure and the infrared spectra of ettringite compound.

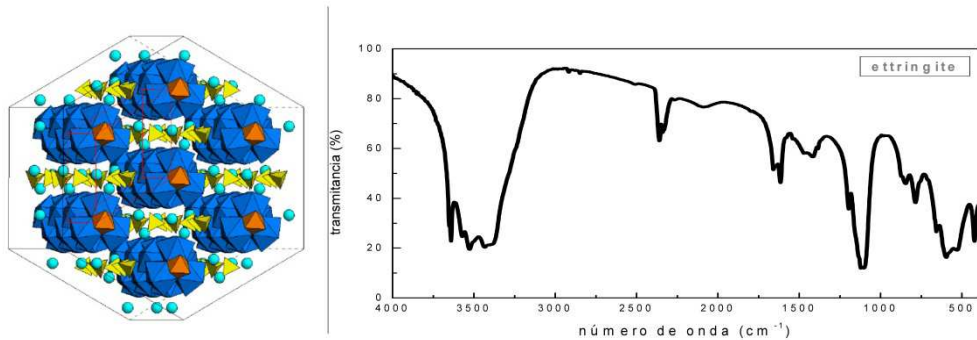


Fig. 10. Structure model of ettringite (according to Dr. J. Neubauer/University Erlangen/Germany) (left), infrared spectra of ettringite (right).

The other crystalline phase present in cement hydration, *portlandite*,  $\text{Ca}(\text{OH})_2$ , shows two prominent sharp peaks, the first one at  $3645 \text{ cm}^{-1}$  due to the presence of OH stretching and the second one at  $353 \text{ cm}^{-1}$  assigned to Ca-O lattice vibrations (Figure 11).

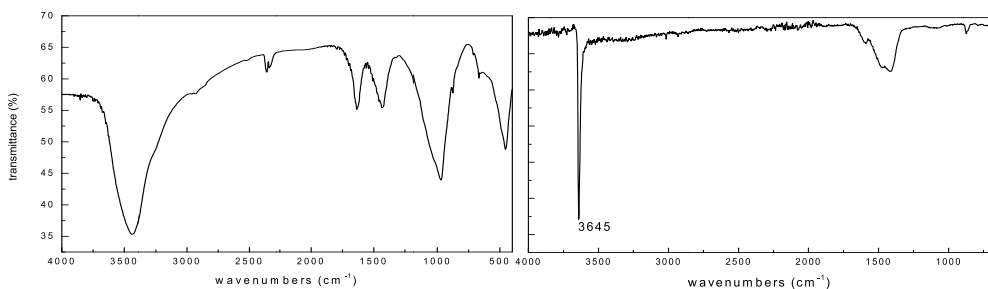


Fig. 11. Infrared spectra of gel C-S-H (left) and portlandite (right)

While crystalline materials give sharp well-defined bands and the glasses give broad, poorly defined bands, the C-S-H samples lie between these two extremes. The distribution function, which describes the line shape of the bands, is strongly dependent upon the

distribution of bond angles and bond lengths within common environments, and the broad half-width of the absorption bands of the C-S-H samples reflect their low symmetry and crystallinity. This distribution is assumed to be symmetry for glasses; hence, any asymmetry of the shape of the bands is due to a superimposition of several symmetrically shaped bands. The infrared spectra of synthetic C-S-H *gel* samples show a broad band in the 3800-3000  $\text{cm}^{-1}$  region attributed to OH stretching vibrations of water molecules with maxima close to 3420 and 3626  $\text{cm}^{-1}$ , 1428 and 666  $\text{cm}^{-1}$  (Figure 11). According to Martinez-Ramirez, depending on the C/S ratio of the C-S-H gel the frequency of the maximum can be different.

With respect to the CACs, the normal CAC hydration with water gives up to the development of hydrated calcium aluminates,  $\text{CAH}_{10}$  at low temperatures but  $\text{C}_2\text{AH}_8$  and  $\text{C}_3\text{AH}_6$  at intermediate and high temperatures joint to  $\text{AH}_3$  according to the following reactions:



High early strength, good chemical resistance and high temperature resistance of calcium aluminate cement (CAC) products had encouraged the use of CAC in certain applications. However, conversion of hexagonal phases,  $\text{CAH}_{10}$  and/or  $\text{C}_2\text{AH}_8$  to cubic  $\text{C}_3\text{AH}_6$  and  $\text{AH}_3$  in hydrated CAC cement under certain temperature conditions has been the major consequence in limiting its use to special applications. The presence of a minor amount of  $\text{C}_2\text{ASH}_8$  (strätlingite) in CAC at later ages may be responsible of some strength recovery after conversion process.

The IR spectra of  $\text{CAH}_{10}$  have a very broad and intense band due to hydroxyl vibration in the 3400-3550  $\text{cm}^{-1}$  region, with maxima near to 3500  $\text{cm}^{-1}$ . A very weak band at 1650  $\text{cm}^{-1}$  is associated to the H-O-H deformation vibration. The 1200-400  $\text{cm}^{-1}$  region is a very poor resolution area due to the complexity and associated vibrations sometimes indicating a low crystalline grade; but some absorption bands at 1,024, 774 (shoulder) 699 and a doublet close to 573-528  $\text{cm}^{-1}$ . The IR spectra of the  $\text{CAH}_{10}$  phase are depicted in Figure 12. The  $\beta\text{-C}_2\text{AH}_8$  hexagonal phase presents in the 3400-3700  $\text{cm}^{-1}$  region absorption bands at 3,465 and 3,625  $\text{cm}^{-1}$  due to OH vibrations of the molecular water. In the 1100-400  $\text{cm}^{-1}$  region there is a very complex vibration area with difficulties in the interpretation.

The  $\text{C}_3\text{AH}_6$  and the gibbsite are the stable phases in this system. The  $\text{C}_3\text{AH}_6$  structure can be described as  $[\text{Al}(\text{OH})_6]^{2-}$  octahedrals connected by  $\text{Ca}^{2+}$  cations. The IR spectra presents a very intense OH-free band at 3670  $\text{cm}^{-1}$ . This compound do not presents water molecular in the structure so, in the area between 3,400 and 3,600  $\text{cm}^{-1}$ , there is not the presence of the deformation H-O-H band. Others fundamental bands due to the stretching and bending vibrations of the Al-O in the octahedral  $\text{AlO}_6$  groups, appear at 802, 525 and 412  $\text{cm}^{-1}$  (Figure 12).

Different  $\text{AH}_3$  polymorphs can be identified by FTIR (Table 4). Although the differences in the strength of OH bond are reflected mainly by the numerous absorption maxima in the

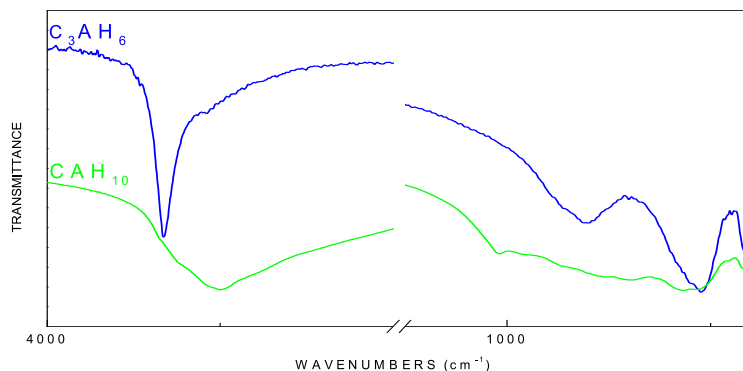


Fig. 12. Infrared spectra of main CAC hydrates,  $CAH_{10}$  and  $C_3AH_6$ .

area of 3000-3700  $cm^{-1}$  of the various polymorphs of the aluminium hydroxide (Fig. 13), the spectroscopy of the calcium aluminate cement does not specify clearly the difference between the three forms of the  $Al(OH)_3$ . However and as guidance that can help in the interpretation, the bayerite has a band in 3550  $cm^{-1}$ , a shoulder in 3430  $cm^{-1}$  and one other shoulder in 3660  $cm^{-1}$ ; these are not observed in the spectrum of gibbsite. Table 4 shows the bands of greater interest in the three polymorphisms, according to some authors (Fernández, Frederickson, Van der Marel).

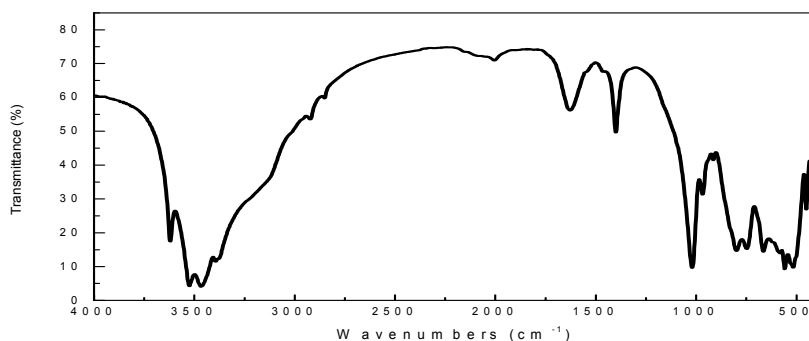


Fig. 13. Aluminium hydroxide, gibbsite, infrared spectra.

	Absorption bands ( $cm^{-1}$ )	references
Gibbsite	3620, 3524, 3468, 3395 1025, 969	Fernández
Bayerite	3360, 3620, 3540, 3420, 3401, 3454, 3533 1024, 975	Frederickson
Nordstrandite	3660, 3558, 3521, 3490, 3455, 3380, 3360 1060, 1030, 823, 770, 461	Van der Marel

Table 4. Characteristic frequencies of aluminium hydroxides.

#### 4. Carbonated compounds

The infrared spectroscopy is very sensitive to detect the presence of carbonates. The bands more features and more valid for its identification are those indicated in Table 5. The *Calcium carbonate* phases formed after portlandite carbonation, calcite, aragonite or/and vaterite; although vaterite is the least thermodynamically stable of the three crystalline calcium carbonate polymorphs. Indeed, vaterite has been observed following exposure of C-S-H gels to carbon dioxide (accelerated carbonation). The formation of vaterite may occur upon carbonation of pastes with high lime contents, and is favoured by the presence of imperfectly crystalline portlandite. The observed absorptions bands for calcium carbonate phases are due to the planar  $\text{CO}_3^{2-}$  ion. There are four vibrational modes in the free  $\text{CO}_3^{2-}$  ion: i) the symmetric stretching,  $\nu_1[\text{CO}_3]$ ; ii) the out-of-plane bend,  $\nu_2[\text{CO}_3]$ ; iii) the asymmetric stretch,  $\nu_3[\text{CO}_3]$ ; and iv) the split in-plane bending vibrations  $\nu_4[\text{CO}_3]$ ; and Ca-O lattice vibrations. Depending on the calcium carbonate polymorph the vibration of the bands appears at different wavenumber. Figure 14 shows the spectra of calcite, vaterite and aragonite.

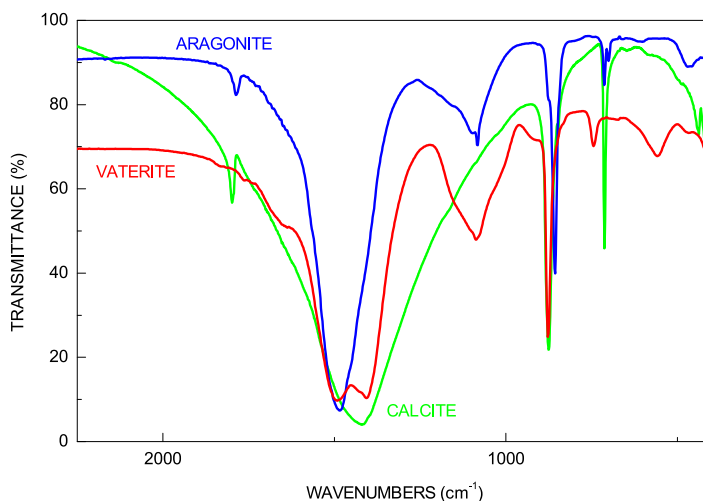


Fig. 14. Infrared spectra of calcite, vaterite and aragonite.

	calcite	vaterite	aragonite
$\nu_1$	1063	1085	
$\nu_3$	1420	1482	1492-1404
$\nu_4$	875, 848	856	877
$\nu_2$	712	713, 700	744

Table 5. Calcium carbonate polymorphs infrared bands

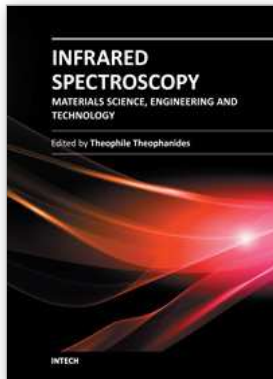
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