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Analysis of the system $3CaO \cdot Al_2O_3–CaSO_4 \cdot 2H_2O–CaCO_3–H_2O$ by FT-IR spectroscopy☆

M.A. Trezza*, A.E. Lavat

Facultad de Ingeniería, Universidad Nacional del Centro, Av. del Valle 5737, B7400JWI Olavarría, Argentina

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Abstract

The main interaction of $CaCO_3$ with the cement involves the phase C_3A ($3CaO \cdot Al_2O_3$) resulting in the formation of hydrated carboaluminate, a similar compound to that obtained in the $3CaO \cdot Al_2O_3–CaSO_4 \cdot 2H_2O$ system. In this work gypsum partially substituted by $CaCO_3$ was studied during hydration and the phases formed as consequence of the competition between $CaCO_3$ and $CaSO_4 \cdot 2H_2O$ for the C_3A at early ages were characterized. Calcium mono- and tricarboaluminato formation (phases Afm and Aft, carbonate) during early C_3A hydration are discussed as well as the influence that limestone presence causes in the system. Infrared spectroscopy (FT-IR) technique confirmed the existence and formation of the phases reported during the early hydration step. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

The reaction of calcium carbonate with tricalcium aluminate is of interest because of the complex carboaluminates that may be formed. These compounds may also be obtained by reaction of a hydrating cement paste with carbon dioxide from the air or of carbonate aggregate in concrete [1,2].

The effect of limestone incorporation on the portland cement has been the subject of several studies [3–6]. All these reports suggest that the main interaction of $CaCO_3$ with the cement takes place through the phase C_3A ($3CaO \cdot Al_2O_3$) during the hydration, involving the formation of hydrated carboaluminate [7], a similar compound to that obtained in the $3CaO \cdot Al_2O_3–CaSO_4 \cdot 2H_2O$ [8,9] system.

Two forms of carboaluminate have been reported which correspond to the high and low sulfate variants of calcium sulfoaluminate hydrates. The calcium monocarboaluminate $C_3A \cdot CaCO_3 \cdot 11H_2O$ and tricarboaluminate $C_3A \cdot 3CaCO_3 \cdot 32H_2O$ were observed to form during early hydration [1,2].

In this work a partial substitution of gypsum by $CaCO_3$ is carried out with the aim to study the system during the hydration and characterize the phases formed as consequence of the competition between $CaCO_3$ and $CaSO_4 \cdot 2H_2O$ for the C_3A at early ages.

Previous reports [6,8] have studied the modifications of the system by means of differential thermal analysis, X-ray diffraction analysis (XRD) along with setting time and compression resistance module determinations. In order to get a deeper insight into the physicochemical behavior of this system we have incorporated FT-IR technique to confirm the existence and formation of the phases reported during the early hydration step. Infrared spectroscopic studies based in Fourier transform (FT-IR) dealing with the competition reaction between limestone and gypsum in the early period of hydration have never been reported yet. The accuracy of this technique allows the straightforward characterization of all compounds present in the system in real time.

Calcium mono- and tricarboaluminato formation (phases Afm and Aft, carbonate) during early C_3A hydration are discussed as well as the influence that limestone presence causes in the system.

☆ The conventional nomenclature in the chemistry of cement be used: $C=CaO$, $A=Al_2O_3$, $S=SO_4^{2-}$, $C=CO_3^{2-}$, $H=H_2O$.

* Corresponding author. Tel.: +54-2284-451055; fax: +54-2284-451055.

E-mail address: mtrezza@fio.unicen.edu.ar (M.A. Trezza).

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2. Experimental

The C_3A was prepared by solid state reaction at high temperature (1200°C) starting from a mixture of $CaCO_3$ (p.a.) and Al_2O_3 (p.a.) in stoichiometric ratio. Their purity was controlled by XRD and confirmed by FT-IR [11].

The samples used in this study were prepared and designated as shown in Table 1.

The samples hydrated at a $w/c = 0.4$ were characterized by X-ray power diffraction using a Philips PW 3710 diffractometer with a copper anode. The infrared spectra were recorded with a NICOLET FT-IR Magna 500 spectrophotometer using KBr pellets technique. The ages selected for the study were between 15 min and 24 h.

3. Discussion of results

The identification of the phases formed during the hydration has been carried out appropriately by FT-IR spectroscopic technique.

The complete assignment of the spectra could be performed by comparison with available data of the pure hydrated components, which allow to establish their typical absorption bands.

The main solids present in every hydrated sample after 15 min and 24 h of hydration could be clearly recognized and are shown in Table 2.

As may be inferred from this information the composition of each sample is almost identical despite the elapsed time. The only significant difference between both hydration ages is the presence of Afm$-SO_4^{2-}$ after 24 h instead of Aft phases originally formed at the beginning of the reaction as a consequence of decreasing SO_4^{2-} free concentration.

Nevertheless, results obtained after 24 h of hydration have been selected to carry out the discussion mainly because these IR spectra show better-resolved bands surely due to the presence of well-crystallized products. The exact positions of the frequencies in all investigated materials, at this stage of hydration, are presented in Table 3.

The FT-IR spectra of sample M1 allowed identification of the hexagonal hydrates CAH_{10}, C_2AH_8 and C_4AH_{13} [10] as consequence of C_3A hydration not regulated by retarding agents. These hydrates are not stable and later convert to C_3AH_6.

The IR spectra of CAH_{10}, C_2AH_8 and C_4AH_{13} showed similarities with each other as might be expected from their common hexagonal plate-type structures [7,11,12], but were significantly different from the spectrum of the cubic hydrate C_3AH_6. This is in accordance with the structural formulation $Ca_3[Al(OH)_6]_2$, so consequently the frequency $\nu 2$ corresponding to H_2O deformational mode located at 1600 cm^{-1} might disappear [13]. This is the main difference between cubic hydrates and the hexagonal ones. Nevertheless, their presence cannot be assured by this technique alone because all the hydration products can coexist under these conditions. The detection of hexagonal hydrates is possible in the region 3000–3600 cm^{-1} through some very wide bands, usually overlapped if more than one hexagonal aluminate coexist [14]. However, and based on the literature, the hydrate found in this experimental conditions coincides with C_4AH_{13} [11].

Table 1
The mixture ratios of samples

	Mixing ratio (wt.%)		
	C_3A	$CaSO_4{\cdot}2H_2O$	$CaCO_3$
M1	100	–	–
M2	80	20	–
M3	80	–	20
M4	80	10	10

Table 2
Main solids present at two hydration times, detected by FT-IR

	Main solid present in			
Time	M1	M2	M3	M4
15 min	Hexagonal hydrates	Ettringite	Monocarbo-aluminate	Hexagonal hydrates + ettringite
24 h	Hexagonal hydrates	Ettringite	Monocarbo-aluminate	Hexagonal hydrates + monosulfo-aluminate

The presence of a carbonate group indicates that the sample has absorbed CO_2 molecules from the air during the hydration; this situation is typical for samples hydrated under atmosphere conditions [4] and observed because of the high sensibility of the FT-IR technique to detect the carbonate group.

Ettringite, phase Aft-sulfate $-C_6AS_3H_{32}-$ is the main hydration product detected by FT-IR in Sample M2.

This hydration product is stable if there are enough sulfate ions provided by the medium as M2 to 24 h of hydration.

A singlet due to the vibration $\nu 3$-SO_4^{2-} located at 1120 cm^{-1} (vs) supported the evidence for the presence of ettringite. This is a very characteristic peak of ettringite in this spectroscopic region, instead of the typical doublet associated with the Afm phase and gypsum. An additional spectroscopic feature is related to the presence of $\nu 2$-H_2O as a doublet in 1640 (m) and 1675 cm^{-1} (s) assigned to deformation water mode in ettringite [15,16].

On the other hand, the difference in the IR activity of the internal modes of vibration in isolated SO_4^{2-} reflects the higher symmetry of this anion in the crystal environment of Aft-sulfate.

In Sample M3 to 24 h of hydration, the presence of monocarboaluminate of calcium (phase Afm-carbonate) as the main product has been identified. Bensted [17] have reported the complete assignment of this compound and it surely corresponds to the product obtained as consequence of M3 at this stage of hydration.

In the absence of gypsum C_3A reacts with $CaCO_3$ to form calcium tricarboaluminate (hexagonal prism)

Table 3
IR frequencies for the investigated samples and assignment

M1 (C_4AH_{13})		M2 ($C_6AS_3H_{32}$)		M3 ($C_3A \cdot CaCO_3 \cdot 11H_2O$)		M4 ($C_4AH_{13} + C_6AS_3H_{32}$)	
3675	OH^- free[a]			3676	OH^- free[b]	3676	OH^- free[a]
3645	OH^- associated $Ca(OH)_2$	3654	OH^- associated $Ca(OH)_2$	3642	OH^- associated $Ca(OH)_2$	3641	OH^- associated $Ca(OH)_2$
3623	OH^- free[a]	3421	$\nu 1 + \nu 3$-H_2O[c]	3624	OH^- associated[b]	3625	OH^- associated
3545	OH^- associated[a]			3555	$\nu 3$, H_2O[b]	3545	$\nu 1 + \nu 3$-H_2O[d]
3520	OH^- associated[a]			3525	OH^- associated[a]	3500	
3370	$\nu 1 + \nu 3$-H_2O[a]			3371	$\nu 1$, H_2O[b]	3371	$\nu 1 + \nu 3$-H_2O[a]
				3009			
1646	$\nu 2$, H_2O[a]	1686	$\nu 2$, H_2O[c]	1647	$\nu 2$, H_2O[b]	1643	$\nu 2$, H_2O
		1645					
1419	$\nu 3$, CO_3^{2-}[b]	1450	$\nu 3$, CO_3^{2-}	1426	$\nu 3$, CO_3^{2-}[b]	1416	$\nu 3$, CO_3^{2-}
1363		14??		1365		1367	
1070	Vibration AlO_6[a]	1112	$\nu 3$, SO_4^{2-}[c]	1066	$\nu 1$, CO_3^{2-}[b]	1190	$\nu 3$, SO_4^{2-}[d]
						1108	
954	Vibration AlO_6[a]			957	Vibration AlO_6[b]	950	Vibration AlO_6[a]
877	$\nu 2$, CO_3^{2-}	876	$\nu 2$, CO_3^{2-}	873	$\nu 2$, CO_3^{2-}	875	$\nu 2$, CO_3^{2-}
		855	Deformation Al-O-H[c]	812	Vibration AlO_6[b]		
793	Vibration AlO_6[a]					769	Vibration AlO_6[a]
716	$\nu 4$, CO_3^{2-}			716	$\nu 4$, CO_3^{2-}	712	$\nu 4$, CO_3^{2-}
		670	$\nu 4$, SO_4^{2-}[c]			667	$\nu 4$, SO_4^{2-}[d]
668	Vibration AlO_6[a]			674	Vibration AlO_6[b]		
587	Vibration AlO_6[a]						
531	Vibration AlO_6[a]	535	Vibration AlO_6[c]	539	Vibration AlO_6[b]	534	Vibration AlO_6[a]
423	Vibration AlO_6[a]			427	Vibration AlO_6[b]		
		420	$\nu 2$, SO_4^{2-}[c]			421	$\nu 2$, SO_4^{2-}[d]

[a] Associated to hexagonal hydrates.

[b] Associated to monocarboaluminato of calcium.

[c] Associated to ettringite.

[d] Associated to calcium monosulfoaluminate.

$C_3A \cdot 3CaCO_3 \cdot 30H_2O$ (Aft-carbonate phase) and the hexagonal plate phase, monocarboaluminate $C_3A \cdot CaCO_3 \cdot 11H_2O$ or Afm-carbonate phase [3,4]. Other Afm carboaluminate phase modifications are also possible. The formation of lower carbonate-content phases as hemicarboaluminate ($C_3A \cdot 1/2\ CaCO_3 \cdot 1/2\ Ca\ (OH)_2 \cdot 12H_2O$) and lower carbonate-content phases [4,18] have also been reported.

The carbonate Afm phase is a more stable product due to its greater insolubility [4] at ambient temperature and this is probably the reason for which the monocarboaluminate of calcium is observed as main hydration product at early age [3] in the spectra recorded of Sample M3 to 24 h.

The spectra of Afm compound can be assigned on the basis of the carbonate ion, CO_3^{2-}, being a planar tetra-atomic species with trigonal-D3h symmetry. The strong IR frequencies at 1365 and 1426 cm^{-1} are typical bands, assigned to $\nu 3$-CO_3^{2-}, split. A sharp band at 873 cm^{-1} ascribed to $\nu 2$-CO_3^{2-} and a very sharp one in 716 cm^{-1} of $\nu 4$-CO_3^{2-} [19].

A weak band at 1066 cm^{-1} can be assigned to $\nu 1$-CO_3^{2-} (which should be IR inactive under D3h-symmetry) indicating that the symmetry of the group CO_3^{2-} in the monocarboaluminate is not purely D3h, becoming this mode another characteristic peak of the hydrate.

The wide bands centered at 3009 and 3371 cm^{-1} can be assigned to the symmetrical stretching $\nu 2$-H_2O. The width of the band at 3009 cm^{-1} is a measure of the extension of hydrogen bonds.

This compound also presents free and associated OH^- ions, since it is commonly written as $C_3A \cdot CaCO_3 \cdot 11H_2O$ but is better described as $Ca_4[Al(OH)_6]_2CO_3 \cdot 5H_2O$.

The Sample M4 with 10% of $CaCO_3$ and 10% of gypsum allows identification after 24 h of hydration the bands belonging to monosulfate modes, through the split frequencies $\nu 3$-SO_4^{2-} (1108 and 1190 cm^{-1}), together with the change in the water deformation mode, $\nu 2$-H_2O band 1600 cm^{-1} and stretching region over 3000 cm^{-1}, differentiating it completely of the ettringite.

The hexagonal hydrates and the monocarboaluminate were detected in the spectra. The latter one being identified by the split $\nu 3$-CO_3^{2-} (1416 and 1367 cm^{-1}) together with $\nu 2$-CO_3^{2-} (875 cm^{-1}) and $\nu 4$-CO_3^{2-} (712 cm^{-1}) are detected. Unfortunately, in this sample at this stage of hydration $\nu 1$-CO_3^{2-}, which should be IR-active, is not observed to complete the assignment. This could be due to overlapping with sulfate bands close in energy.

This study shows that FT-IR spectroscopy is a very useful and straightforward technique to identify the phases coexisting during the hydration of cement in the presence of gypsum and limestone, corroborating the results reported by other authors using other conventional methods in the chemistry of cement.

Samples with intermediate substitutions to those shown were also analyzed, they are designated A (5% $CaSO_4{\cdot}2H_2O$–15% $CaCO_3$) and B (15% $CaSO_4{\cdot}2H_2O$–5% $CaCO_3$) in order to check the possibility of identifying the phases when they are formed simultaneously.

In Sample B the monosulfoaluminate seems to be the main hydration product together with the hexagonal aluminate. However, in Sample A the modes corresponding to the calcium monocarboaluminate can be identified, coexisting with the monosulfoaluminate. Their presence gives rise to the sharp peak around of 1400 cm^{-1}, split, and of $\nu 1$-CO_3^{2-} (sh) active in IR such as that may be observed in Samples A and M3.

4. Conclusions

- The identification of the phases Afm-sulfato, Aft-sulfate and Afm-carbonate in this system can be carried out unequivocally by IR spectroscopy at early stage of reaction, even during the first minutes of hydration.
- When more than one of the phases of Afm coexist it is possible to recognize all phases present such as in the Sample A coexisting Afm-sulfate and Afm-carbonate with certainty.
- This technique does not allow assuring the presence of the cubic hydrate C_3AH_6, final product of the hydration of the C_3A at early ages, because of the presence of hexagonal hydrates that coexist with it, presenting bands in the same region. It constitutes a disadvantage of the technique.

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