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Studies on the carboaluminate formation in limestone filler-blended cements

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Abstract

Carboaluminates are hydration products of limestone-blended cements and they compete with monosulfoaluminate stability and ettringite transformation. In this paper a study about the hydration of pure C_3A phase with $CaCO_3$ in the presence or not of gypsum and in a calcium hydroxide solution is related to the hydration products of portland and limestone-blended cements. Results show the formation of monocarboaluminates in systems containing C_3A and $CaCO_3$ while the tricarboaluminate was not found. Calcium hydroxide intervenes in these systems to form a calcium hemicarboaluminate hydroxide. In limestone-blended cements, calcium monocarboaluminate is immediately detected after hydration begun and the transformation of monosulfoaluminate to monocarboaluminate occurs at 28 days while the conversion of ettringite to monosulfoaluminate is deferred. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Limestone filler addition to portland cement produces several effects on the mechanism and kinetics of cement hydration. Filler effect imparted by limestone filler causes a hydration acceleration of portland clinker grains (especially the C_3S [1]) at early ages, improves the particle packing of the cementitious system [2], provides new nucleation sites for calcium hydroxide [3], and produces the formation of calcium carboaluminates as results of the reaction between $CaCO_3$ from limestone and C_3A from portland clinker [4].

Researches carried out by Feldman et al. [5] reveal that the reaction between C_3A and $CaCO_3$ takes place by a solid state mechanism and the addition of $CaCO_3$ modifies the vigorous initial reaction of C_3A with the water due to the rapid formation of a barrier of hydrated calcium carboaluminate ($C_3A \cdot CaCO_3 \cdot x H_2O$) developed on the surface of C_3A grains. According to Fierens et al. [6], hydrated calcium carboaluminate can be formed from the hexagonal (C_4AH_{13}) and cubic (C_3AH_6) calcium aluminate hydrates.

Hydration reactions of C_3A in the presence of gypsum have been amply discussed [7,8]. Initially, ettringite crystallizes and then if the sulfate is consumed before the C_3A consumption, the ettringite conversion to monosulfoaluminate occurs. In portland cements, the limestone addition modifies these reactions. First, the ettringite formation is accelerated by the presence of $CaCO_3$ [4]. Secondly, the ettringite conversion to monosulfoaluminate will be delayed or stopped when a large amount of carbonate is present in the hydrated paste. This phenomenon occurs because some sulfate ions can be interchanged by carbonate ions during the C_3A hydration [9].

Carbonate additions also influence the C_3S hydration. Ramachandran and Zhang [10] report that C_3S hydration rate is accelerated when the amount and fineness of $CaCO_3$ increase. They found that C-S-H incorporates a significant amount of $CaCO_3$ into its structure. Additionally, Husson et al. [11] determined the formation of calcium silicocarbonate hydrates during the hydration of C_3S in the presence of large quantities of carbonate.

In the cement paste, Gegout et al. [12] found that limestone filler increases the hydration rate from 1 to 90 days. They corroborate that monocarboaluminate and

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ettringite coexist in the paste ($C_3A = 11.5\%$) after 7 days. Klemm and Adams [13] also detected monocarboaluminate after 7 days in cement paste ($C_3A = 6.4\%$) with 15% of limestone.

The long-term durability of cementitious material is dependent upon the physical and chemical parameters. It is recognized that the more important prerequisite is reducing the permeability of material to the ionic species. Considering the durability topics involving the C_3A-related compounds, attention should be given to the sulfate resistance and the chloride binding capacity that depend on the stability of C_3A hydrates forming before the attack. In sulfate attack, ettringite formed prior to the immersion in sulfate solution will be a stable phase while the monosulfoaluminate and the monocarboaluminate will be unstable phases. Complementarily, thaumasite formation has been associated with the ettringite formation at early ages of attack [14]. In chloride environment, the binding captivity also depends on C_3A-compound present prior to the exposure. When monocarboaluminate or monosulfoaluminate are present in the cement paste, the chloride ions from the environment react with them to form chloroaluminates [15]. However, the chloride cannot be binding when the ettringite is the hydration compound. For this reason, it is important to determine the compound formed in limestone-blended cements to infer the probable compound formation.

This paper presents a review on the pure systems and its application during the hydration of limestone-blended cements about the formation and detection of monocarboaluminate, monosulfoaluminate and ettringite. Studied pure systems include the hydration of C_3A with $CaCO_3$ or gypsum in a calcium hydroxide environment and the ternary system $C_3A-CaCO_3-$gypsum in the same environment. The hydration of limestone-blended cements involves several complexes and simultaneous reactions and their interacts. To simplify and to understand this complex system, it is assumed that the hydration of pure compounds of portland cements is a reasonable approximation. Consequently, results of pure systems are used to discuss the formation and the stability of monocarboaluminate and monosulfoaluminate in limestone-blended cements.

2. Experimental procedures

2.1. Pure systems

For studying pure systems, a tricalcium aluminate prepared in laboratory, gypsum and calcium carbonate of LR grade were used. To prepare the C_3A, a molar mixture corresponding to C_3A was prepared by using LR grade $CaCO_3$ and Al_2O_3. The reagents were finely ground because the C_3A formation is a solid state reaction. Then, the mixture was fired at 800°C for 20 h and at 1200°C for 10 h in an electric furnace. The formation of C_3A was checked by X-ray diffraction analysis.

Three pure compound mixtures were prepared: (a) 80% C_3A and 20% $CaSO_4 \cdot 2H_2O$; (b) 80% C_3A and 20% $CaCO_3$; and (c) 80% C_3A, 10% $CaCO_3$ and 10% $CaSO_4 \cdot 2H_2O$. These percentages are based on total weight of C_3A.

The dry mixtures were transferred to clean sealed recipients and calcium hydroxide saturated water was gradually added to attain a water/solid ratio of 1. At the times of 15, 30, 720 and 1440 min, samples were removed and the hydration stopped by immersion in acetone. Then the paste was dried at 40°C during 24 h and was ground to a particle size smaller than 45 μm for XRD analysis.

2.2. Cement pastes

The portland cement had a mineralogical composition of $C_3A = 5.6\%$, $C_3S = 51.2\%$, $C_2S = 25.9\%$, $C_4AF = 9.8\%$ and $SO_3 = 2.5\%$, and a specific surface (Blaine) of 285 m^2/kg. The parameters of particle size distribution curve were $n = 0.9$ and $x' = 26.6$ μm. Limestone filler contains 85% of $CaCO_3$ in calcite form without clay minerals. The main impurity was quartz ($SiO_2 = 11\%$) and it was ground at a Blaine fineness of 710 m^2/kg and the parameters of particle size distribution curve were $n = 0.61$ and $x' = 13.2$ μm. The limestone-blended cement was obtained by replacing 20% of weight of cement by limestone filler. Cements were mixed with distilled water (water/binder = 0.4) and stored 1 day at 100% relative humidity. Then the specimens were demolded and cured in a lime-saturated water until 1, 3, 7, 28 and 90 days. Thereafter, pastes were treated using the same procedure described for the pure systems.

2.3. XRD analysis

XRD measurements were performed on a diffractometer (Philips X'Pert) equipped with a graphite monochromator using CuKα radiation and operating at 40 kV and 20 mA. Step scanning was used with a scan speed of 2°/min and sampling interval of 0.02° 2θ. To determine the amount of gypsum, carbonate and CH present in pure paste a quantitative XRD analysis was made using the internal standard model supplied by the APD software package.

3. Results and discussion

Table 1 reports the results of the quantitative analysis of pure compound consumed during hydration in each system. For each pure system and cement pastes analyzed, the main changes were:

3.1. $C_3A-CaSO_4 \cdot 2H_2O-CH-H_2O$ system

Fig. 1a shows the XRD pattern confirming that both hydration products (ettringite and monosulfoaluminate)

Table 1
Percentage of consumption of calcium hydroxide, gypsum and calcium carbonate during the hydration of pure systems

System	$C_3A-CaSO_4{\cdot}2H_2O-CH-H$		$C_3A-CaCO_3-CH-H$		$C_3A-CaCO_3-CaSO_4{\cdot}2H_2O-CH-H$		
Time (min)	$CaSO_4{\cdot}2H_2O$ (%)	CH (%)	$CaCO_3$ (%)	CH (%)	$CaCO_3$ (%)	$CaSO_4{\cdot}2H_2O$ (%)	CH (%)
0	0	0	0	0	0	0	0
15	75	0	13	35	25	95	6
30	76	0	67	75	33	98	15
720	88	0	74	75	39	99	21
1440	95	0	77	75	50	100	30

coexist with gypsum at 15 min. These results agree with the data reported by Ramachandran and Zhang [4] in the absence of CH. After 30 min and later times, gypsum is consumed and the monosulfoaluminate is transformed to ettringite, which is a more stable product.

Quantitative analysis (Fig. 1b) shows that the CH content is approximately constant during all times studied, indicating that this compound does not directly intervene in C_3A hydration. After 15 min of hydration, three quarters of gypsum have been consumed to form ettringite and monosulfoaluminate. Monosulfoaluminate can be formed before ettringite when gypsum is not able to rapidly supply enough sulfate ions to a reactive C_3A [16]. When hydration progresses, sufficient sulfate ions cause the ettringite formation. The later conversion of ettringite does not occur due to the $C_3A/CaSO_4{\cdot}2H_2O$ ratio used. In addition, some hexagonal and cubic aluminate hydrates are also detected by XRD analysis.

3.2. $C_3A-CaCO_3-CH-H_2O$ system

Fig. 2a shows the XRD patterns for this system. At early hydration, the formation of calcium monocarboaluminate occurs by the reaction between C_3A and carbonate ions as reported by several authors [4,5] in the absence of CH. A calcium hemicarboaluminate hydroxide ($C_3A{\cdot}0.5CaCO_3{\cdot}0.5Ca(OH)_2{\cdot}11.5H_2O$) is also detected as a reaction product in three compounds [17,18]. The crystallization of these hydrates increases during the first 30 min. Consequently, a decrease of carbonate and calcium hydroxide peaks is easily detected. As reported by Jambor [19], the hydrated calcium tricarboaluminate (a similar compound to ettringite) cannot be detected as a reaction product of this system. The tricarboaluminate is a nonstable compound at 20°C [20]. According to Lea [8], it is stable when formed from monocarboaluminate and $C_4A{\cdot}1/2CO_2{\cdot}12H_2O$ in sulfate solutions.

Quantitative analysis (Fig. 2b and Table 1) shows that 75% of the initial CH is consumed to form the calcium hemicarboluminate hydroxide during the first 30 min of hydration. The carbonate consumption until 30 min is 67%. As hydration progresses, a large amount of monocarboaluminate is found and 77% of carbonate is combined at 24 h. Calcium hydroxide remains constant after the 30 min of hydration. X-ray reveals the total consumption of C_3A after 30 min and the formation of hydrogarnet.

3.3. $C_3A-CaCO_3-CaSO_4{\cdot}2H_2O-CH-H_2O$ system

In this system (Fig. 3a), the hydration products detected are ettringite, calcium monosulfoaluminate, calcium monocarboaluminate and calcium hemicarbonate hydroxide. These results agree with the compounds detected by Poellmann [17] and Vernet and Noworyta [9].

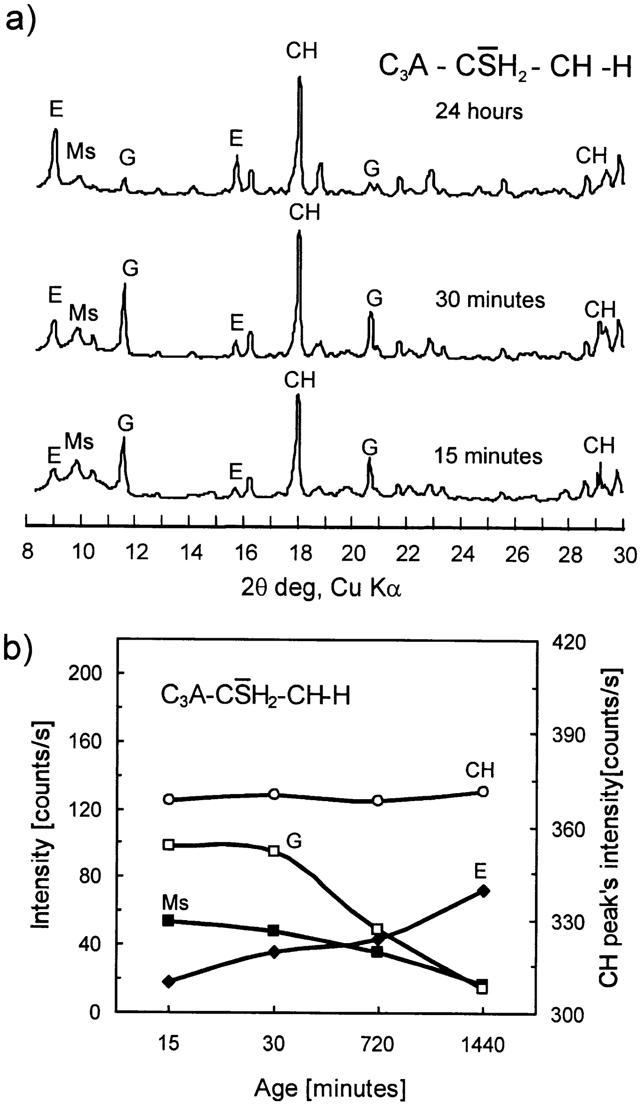

Fig. 1. Evolution of compounds in the $C_3A-CaSO_4{\cdot}2H_2O-CH-H_2O$ system. E = ettringite, G = gypsum, Ms = monosulfoaluminate and CH = calcium hydroxide.

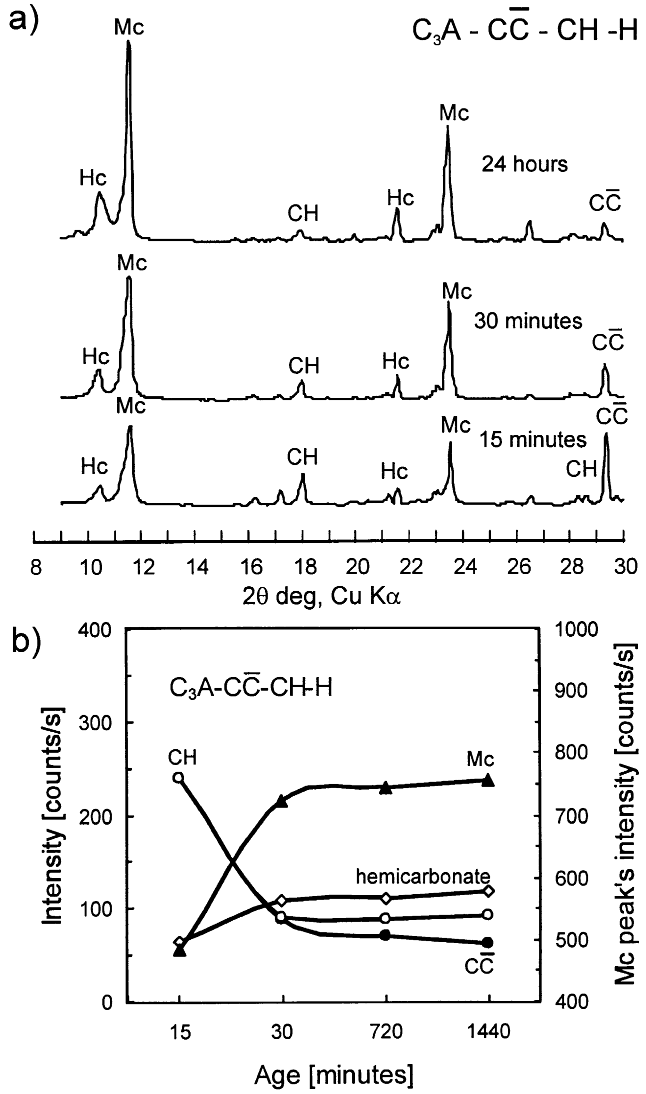

Fig. 2. Evolution of compounds in the $C_3A-CaCO_3-CH-H_2O$ system. Mc = monocarboaluminate, Hc = hemicarboaluminate, CH = calcium hydroxide and $C\bar{C}$ = calcium carbonate.

The ettringite formation is quite evident at 15 min (Fig. 3c), then it decreases and a small amount ($2\theta = 9.08°$, $d = 9.72$ nm) may be detected at 24 h. Conversion of ettringite to monosulfoaluminate is accelerated by the substitution $CaCO_3$ to gypsum [4] and the peaks of monosulfoaluminate increase 1.5 times from 30 min up to 24 h (Fig. 3b), whereas in the system C_3A–gypsum–CH the ettringite decreases during all hydration progress (Fig. 3c). A large amount of gypsum (95%) was consumed at 15 min.

Examination of XRD data shows that the presence of gypsum delays the reaction between C_3A, $CaCO_3$ and CH. The formation of calcium hemicarboaluminate hydroxide progresses slowly up to the final determination whereas it was virtually completed after 30 min in the $C_3A-CaCO_3-$CH system (Fig. 2b). On the other hand, the quantitative analysis shows that $CaCO_3$ consumption after 24 h was 50%

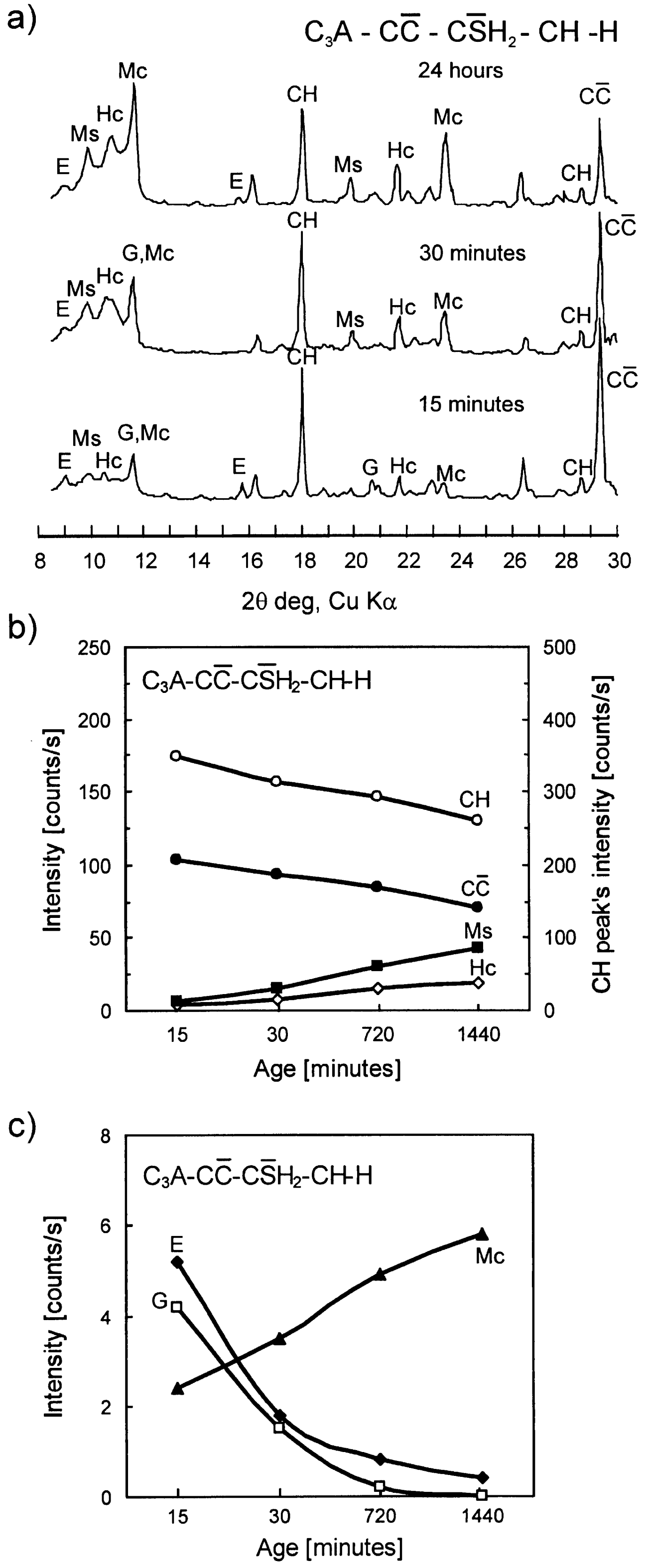

Fig. 3. Evolution of compounds in the $C_3A-CaSO_4{\cdot}2H_2O-CaCO_3-CH-H_2O$ system. E = ettringite, G = gypsum, Mc = monocarboaluminate, Ms = monosulfoaluminate, Hc = hemicarboaluminate, CH = calcium hydroxide and $C\bar{C}$ = calcium carbonate.

(Table 1) while this value was 77% in the C_3A–$CaCO_3$–CH system. Calcium monocarboaluminate is detected at 15 min and the amount of this compound increases until 24 h.

Results indicate that the reaction between C_3A and gypsum occurs during the first hydration minutes. Consequently, gypsum was almost consumed after 15 min, remaining most of $CaCO_3$ without combination at the final age studied compared to corresponding system containing only carbonates. This confirms the reaction between C_3A and gypsum is preferential with respect to the C_3A–$CaCO_3$ reaction [4,20].

3.4. Portland cement paste

Fig. 4a and b shows the XRD patterns corresponding to the plain cement paste and the evolution of peak intensity for ettringite and monosulfoaluminate, respectively. At 1 day, hydration products were ettringite and calcium hydroxide from silicate hydration reactions. In the XRD pattern at 3 days, the ettringite conversion to monosulfoaluminate was detected. This conversion implied a progressive increase of the monosulfoaluminate peak up to 90 days (Fig. 4b). For the portland cement used ($SO_3/C_3A = 1.5$), it was governed by the deficiency of sulfate ions related to the C_3A content [13].

3.5. Limestone-blended cement paste

XRD patterns of cement paste containing 20% of limestone filler are shown in Fig. 5a. It can be observed that ettringite and CH were found at 1 day of hydration. Ettringite remains stable up to 7 days, then conversion of ettringite to monosulfoaluminate is detected. At 28 days no clear peaks of ettringite are found.

Monocarboaluminate is detected at 3 days of hydration. Consequently, a reduction of approximately 15% in the peaks of $CaCO_3$ was determined. This compound was detected by Ingram et al. [21] at 14 days and by Klemm and Adams [13] beyond 7 days in cements containing 12.5% and 6.4% of C_3A, respectively. From 7 to 28 days of hydration, the monocarboaluminate and the carbonate peaks remain approximately constant. At this time a decrease of monosulfoaluminate peaks occurs. As a result of this reaction an increase of monocarboaluminate and ettringite was detected by a second conversion of C_3A hydrated phase in the cement paste at 90 days (Fig. 5b).

The initial conversion of ettringite to monosulfoaluminate occurs due to a lack of gypsum in the paste. At later ages a conversion of monosulfoaluminate to ettringite occurs due the presence of a new source of sulfate ions. In this case the sulfate ions are provided by the monosulfoaluminate decomposition in the paste containing limestone filler. Carbonate ions supplied by limestone filler produces the monosulfoaluminate–monocarboaluminate transformation because the last compound is more stable according to its solubility products ($K_{sp}(CaCO_3) = 8.7 \times 10^{-9}$, K_{sp}(monosulfoaluminate) = 1.7×10^{-28}, K_{sp}(monocarboaluminate) = 1.4×10^{-30}, K_{sp}(ettringite) = 1.1×10^{-40} [7]). For the level of filler replacement used, about three-quarters of carbonate supplied by limestone have not reacted at 90 days.

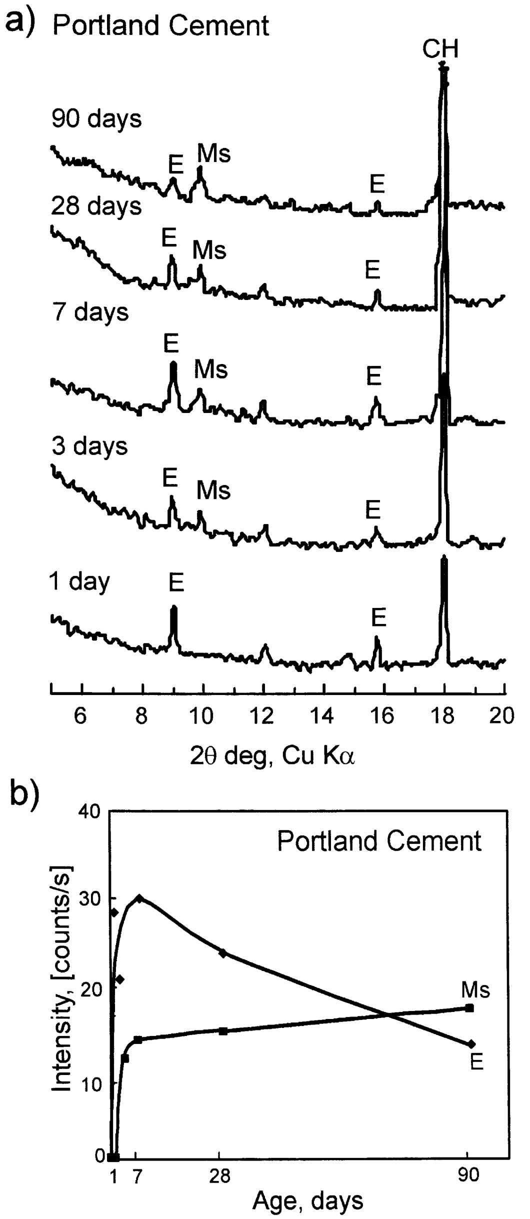

Fig. 4. Evolution of hydration products in portland cement paste. E = ettringite, Ms = monosulfoaluminate and CH = calcium hydroxide.

Regarding the previous compounds reported for pure systems, the characteristic peaks of calcium hemicarboaluminate hydroxide ($2\theta = 10.78°$, $d = 8.20$ nm) detected in pure systems and calcium silicocarbonate ($2\theta = 14.9°$; $d = 5.94$ nm) reported by Husson et al. [11] were not found by XRD analysis.

A summary of this experience shows that the hydration compounds found in the limestone-blended cements paste are similar to the system C_3A–$CaSO_4{\cdot}2H_2O$–$CaCO_3$–CH–H_2O, except for calcium hemicarboaluminate hydro-

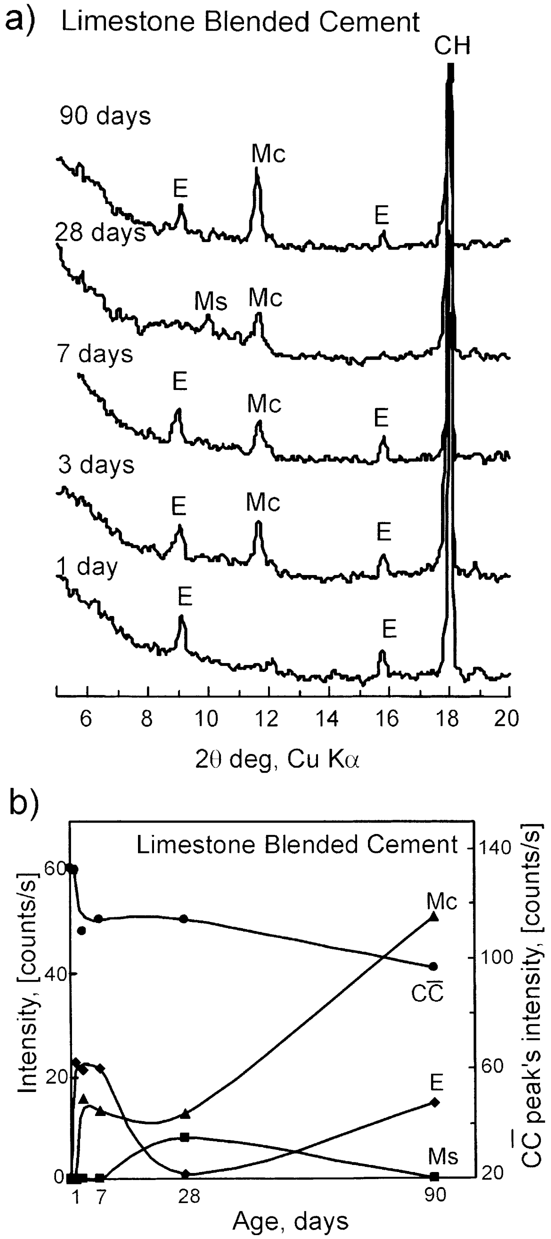

Fig. 5. Evolution of hydration products in limestone-blended cement. E = ettringite, Mc = monocarboaluminate, Ms = monosulfoaluminate, CH = calcium hydroxide and $C\bar{C}$ = calcium carbonate.

xide. In the plain cement paste, hydration reaction products are similar to hydrates from the C_3A–$CaSO_4 \cdot 2H_2O$–H_2O system because the CH does not interfere in the reaction.

4. Conclusions

The following conclusions can be drawn from this study:

- In pure systems, the reaction of carbonate ions and C_3A to form monocarboaluminates was easily detected while the tricarboaluminate was not found in any system. Thus is also proved that the calcium hydroxide intervenes in the system containing calcium carbonate and tricalcium aluminate.
- In limestone-blended cements, calcium monocarboaluminate was easily detected at 3 days and its amount increases after 28 days of hydration. The excess of carbonate ions in cement paste produced the transformation of monosulfoaluminate to monocarboaluminate. This promoted the reconversion of monosulfoaluminate to ettringite in limestone-blended cements due to the sulfate liberated during the carbonate substitution reaction. The conversion of ettringite to monosulfoaluminate is deferred by the presence of limestone filler in the cement. Finally, monocarboaluminate is the final hydration product of C_3A in limestone-blended cement, which is an unstable compound in sulfate and chloride environment.

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