Influence of Mineral Additions in the Inhibition of Delayed Ettringite Formation in Cement based Materials – A Microstructural Characterization

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Abstract. The degradation of concrete structures caused by delayed ettringite formation (DEF) is a problem that affects many concrete structures worldwide [1]. This pathology is due to the formation of expansive ettringite inside the material and is very difficult to deal with, because presently there is no efficient method to repair concrete structures affected by DEF. Hence, there is an urgent need to find preventive methods that may enable the inhibition of DEF in new constructions.

This paper presents the findings of a long-term study [2,3] on the expansion rate and microstructure of heat-cured concretes with different amounts of mineral additions, like fly ash, metakaolin, ground granulated blast-furnace slag, silica fume and limestone filler. For this purpose different concrete compositions were produced using the same binder, water/binder (w/b) ratios and aggregate type. The concretes were prepared and subjected to a heat-curing cycle and subsequently to two drying-humidification cycles. After these cycles the concrete specimens were immersed in water for long-term storage at 20 ± 2ºC. Length changes of specimens were measured at regular intervals. The microstructures of old heat curing specimens were investigated by optical microscopy and SEM-EDS analysis. The results of the blended-concrete compositions were compared with control compositions, and the conclusions were extracted.

Introduction

Several dams and concrete bridge structures with unusual levels of deterioration and distress have been detected in Portugal over the last few years [4,5] which in some cases affect concrete structures that are only a few years old. The nature of the distress is mainly characterized by displacements and manifests itself as "map cracking" [6]. The diagnoses of this cracking have identified two degradation mechanisms, Alkali-Silica Reaction (ASR) and Delayed Ettringite Formation (DEF), which in some cases occur simultaneously. These mechanisms are normally referred as internal expansive reactions because the causes are related to the concrete internal constituents (alkalis and sulfates, respectively).

The ettringite ($3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O$) is a reaction product formed from the reaction of C_3A and C_4AF with gypsum during the hydration of Portland cement [7]. However, after concrete hardening, secondary or DEF may form, which usually has an expansive behavior. According to investigations by optical microscopy and scanning electron microscopy (SEM), many ettringite

bands can be observed in concretes or mortars that have suffered from expansion induced by DEF. DEF appears often in concretes exposed to frequent humidity and subjected to a relatively high thermal treatment (> 65º C) or having reached equivalent temperatures for other reasons (massive cast-in-place concrete, concrete preparation during summer, etc) [8]. The prevention of DEF is normally carried out having in mind the elimination of at least one of the factors that promote them, namely, by the control of: the maximum temperature of the concrete; the alkali content of the concrete and of aluminates and sulphates of the binder; the humidity (the maintenance of the concrete in a relatively dry state); and the calcium hydroxide content of the concrete [3]. Another form of preventing DEF is the use of mineral additions in replacement of part of the cement [2]. The additions may be classified into two types: type I, "almost inert" additions (ex. limestone filler – LF) and type II, pozzolanic (ex. fly ash – FA, metakaolin – MK and silica fume – SF) or latent hydraulic additions (e.g. ground granulated blast-furnace slag – GGBS). The type II additions have the ability to react with $Ca(OH)_2$ forming hydrated compounds similar to those of cement hydration, like CSH (calcium silicate hydrate), and control the alkalinity of the medium thus inhibiting the formation of expansive products.

The work presented in this paper is part of an extensive study aimed at elucidating the role that the mineral additions have in the mechanism of inhibition of DEF in concrete. Several concrete compositions were studied using the same w/b ratio, binder and aggregate types for different type and content of mineral additions, in order to verify their influence in the DEF suppression.

Experimental

Concrete cylinders (220mm length and 110mm diameter) were cast using a portland cement CEM I 42.5R with different mineral additions and a non reactive alluvial quartzite as coarse and fine aggregate. Control specimens were also prepared in the same conditions without additions. The chemical compositions of the materials used in the concrete formulations are presented in Table 1, and in Table 2 the different concrete mixes prepared.

In order to promote the occurrence of DEF immediately after casting the cylindrical casts were sealed and placed in a climatic chamber with controlled temperature and humidity, and the concretes were heat-cured. The heat-curing cycle used (Figure 1) was based on a temperature core rise obtained during setting of a massive cast-in-place concrete with 14 m length, 3.5 m width and 1.5 m high. The concrete reached a maximum temperature of 80ºC after 15 hours and was maintained at temperatures above 70ºC during 3 days. This cycle was computed by the TEXO program part of the CESAR-LCPC finite element design code. Following the heat-curing cycle, the concrete specimens were demoulded and subsequently subjected to two drying-humidification cycles.
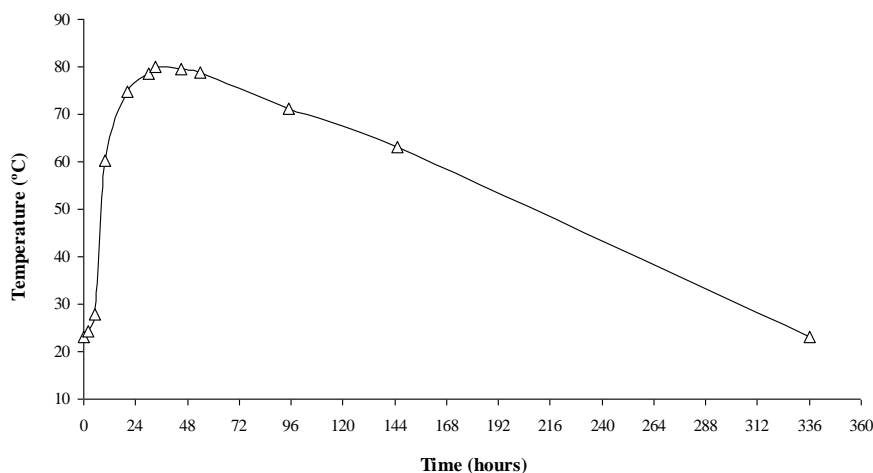

Fig. 1. Concrete heat-curing cycle used to promote the occurrence of DEF.

Each cycle lasted for 14 days and consisted of two phases: a first drying phase for 7 days in a chamber at 38ºC and RH <30% and after the immersion phase for 7 days in water at 20ºC. After these cycles the specimens were immersed in tap water for long-term storage at 20 ± 2ºC. Length and mass measurements were taken periodically in accordance to the French concrete performance test for delayed ettringite formation accelerated concrete performance LPC test method [9].

The microstructures of old heat curing specimens were investigated by petrographic and SEM-EDS analysis. The expansion rates and microstructures observed were compared with control specimens.

Table 1. Chemical analyses and physical properties of the materials used.

	Cement	FA	MK	GGBS	SF	LF
Chemical analyses (%)						
Silicon dioxide (SiO_2)	19.74	53.22	54.66	38.09	96.9	0.09
Aluminium oxide (Al_2O_3)	4.14	23.20	37.98	9.38	0.52	0.04
Ferric oxide (Fe_2O_3)	2.69	5.85	1.22	0.89	0.14	0.06
Calcium oxide (CaO)	63.54	5.36	0.01	36.24	0.58	55.66
Magnesium oxide (MgO)	2.42	1.63	0.46	7.40	0.00	0.10
Sulphur trioxide (SO_3)	3.11	1.00	0.01	0.27	0.13	0.02
Potassium oxide (K_2O)	0.64	1.42	3.09	0.52	0.42	0.04
Sodium oxide (Na_2O)	0.08	0.44	0.00	0.25	0.04	0.02
Equivalent alkali ($Na_2O + 0.658 K_2O$)	0.50	1.37	2.03	0.59	0.32	0.05
Loss on Ignition	3.13	5.16	0.94	2.66	5.56	43.23
Physical tests						
Density [kg/m^3]	3400	2340	2600	2840	2190	2720
Fineness						
$\quad$ $D_{50\%}$ [µm]	15	13	-	22	21	7
$\quad$ Specific Surface Blaine [m^2/kg]	384.7	-	-	453.0		628.0
$\quad$ Specific Surface BET [m^2/kg]	-	-	-	3570	24540	1250
Flexural Strength [MPa]						
$\quad$ 28-day	8.1	7.9	8.8	7.6	-	7.1
$\quad$ 90-day	8.7	8.9	9.4	8.4	-	7.8
Compressive Strength [MPa]						
$\quad$ 28-day	58.4	50.9	68.9	51.2	-	44.6
$\quad$ 90-day	64.9	65.4	77.3	61.3	-	47.0
Pozzolanic Activity Index [%]						
$\quad$ 28-day	-	87	118	88	-	76
$\quad$ 90-day	-	112	132	105	-	80
Bogue Potential Compound Composition						
Calcium sulphate ($CaSO_4$)	5.3	-	-	-	-	-
Tricalcium silicate (C_3S)	62.7	-	-	-	-	-
Dicalcium silicate (C_2S)	9.3	-	-	-	-	-
Tricalcium aluminate (C_3A)	6.4	-	-	-	-	-
Tetracalcium aluminoferrite (C_4AF)	8.2	-	-	-	-	-

Table 2. Concrete compositions used.

Type of aggregate	w/b ratio	% of addition (in mass)	Composition				
		0	Control (Tmáx=80ºc)				
			Fly Ash	Metakaolin	Limestone Filler	Ground Granulated Blast-furnace Slag	Silica Fume
		5	-	5 MK	-	-	5 SF
quartzitic	0.45	10	10 FA	10 MK	10 LF	10 GGBS	10 SF
		15	15 FA	15 MK	15 LF	15 GGBS	-
		20	20 FA	20 MK	20 LF	20 GGBS	-
		30	30 FA	-	30 LF	-	-
		40	-	-	-	40 GGBS	-

Results and discussion

Expansion Testing. Figure 2 illustrates the expansion curves obtained for the different heat-cured concrete compositions. The results clearly show that, in general, the mineral additions have a strong effect in the inhibition of the expansion due to DEF (Fig. 2a, b, c and d), with the exception of LF, for which there is an increase in expansion (Fig. 2e). In this case, the addition did not inhibited DEF increasing the expansion values to approximately double of the control composition. It seems that GGBS is, for the same addition content, the less efficient type II mineral addition studied in the inhibition of expansion due to DEF. This can be explained by the lower reactivity of GGBS comparing to FA, MK and SF (Table 1).
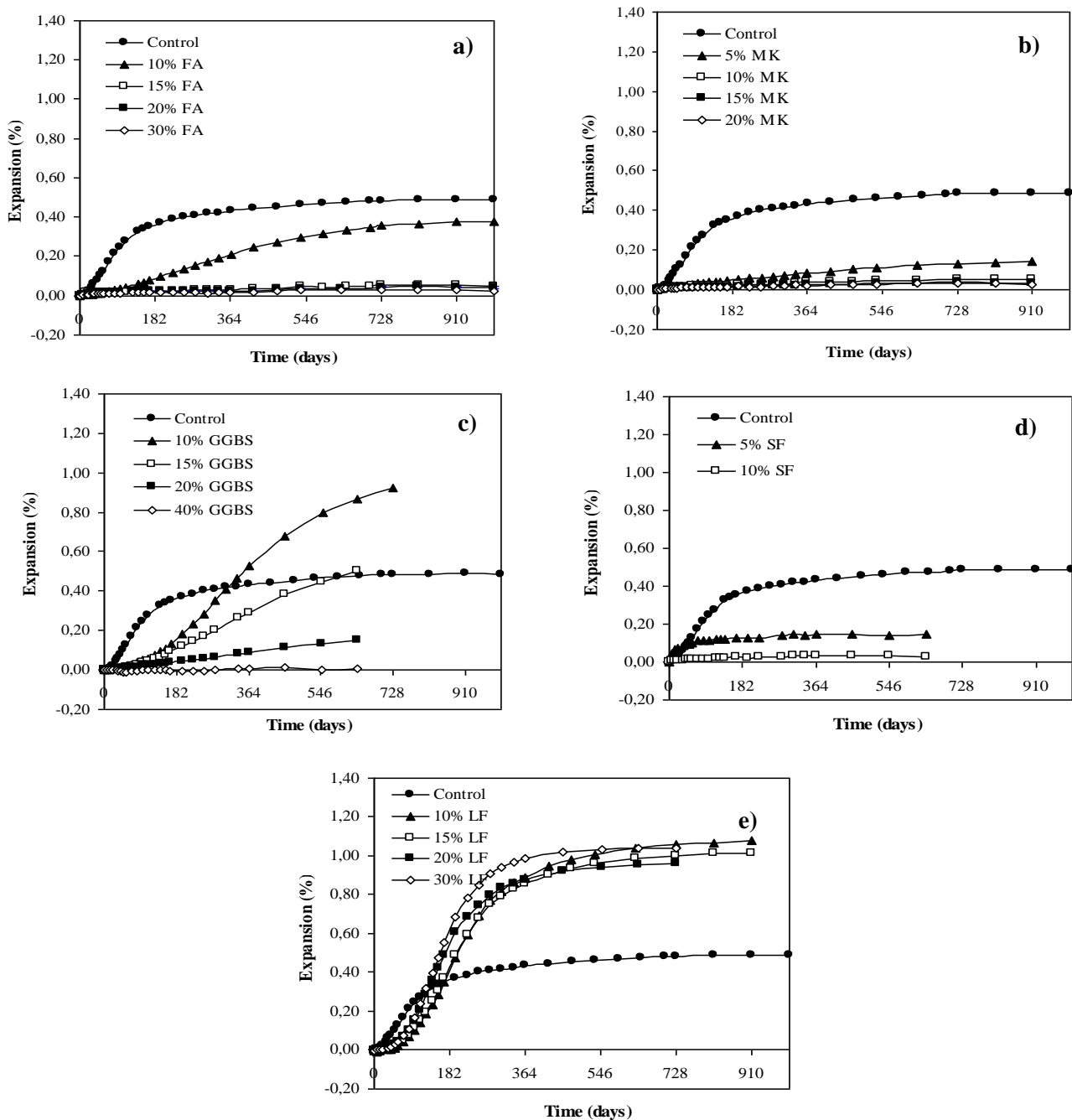
Fig. 2. Expansion curves of different heat-cured concrete compositions.

Petrographic Examination of Concrete Samples. In the compositions that have presented the higher expansion values the observations made at petrographic microscope show the occurrence of ettringite veins around aggregate particles and in some voids (Figure 3). Nevertheless, the distinction between the expansive and non-expansive massive ettringite forms was difficult to detect with this technique. No ettringite was observed in the non-expansive compositions.

Moreover, the petrographic observations have shown microstructural differences mainly related with the pore space available in each concrete composition. The limestone filler compositions have, in comparison with the others mixes and for the same level of cement replacement, the less porous pastes (Figure 4).
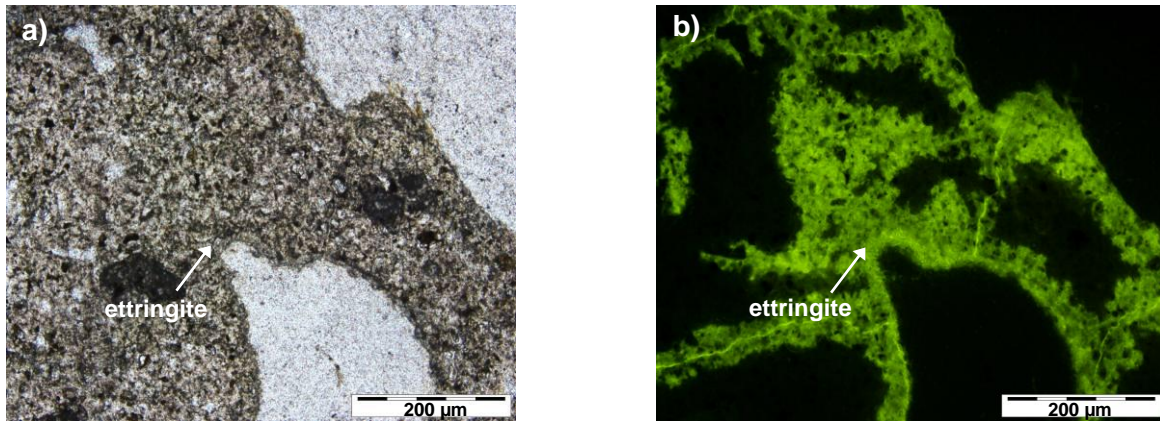
Fig. 3. Petrographic microscope images of a concrete sample after 365 days in (a) parallel nicols and (b) fluorescence light showing massive ettringite bands around aggregate particles.
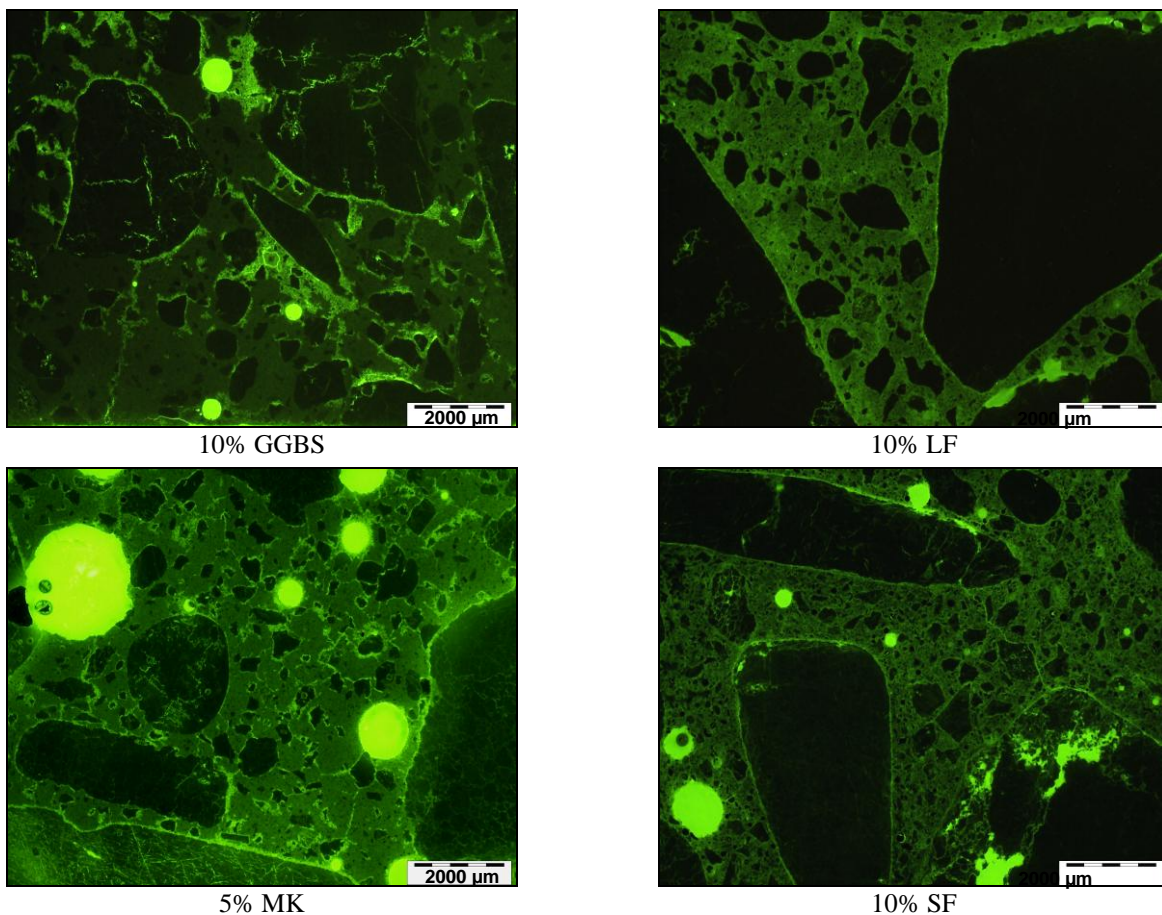

10% GGBS

10% LF

5% MK

10% SF

Fig. 4. Images of a concrete samples after 365 days in fluorescence light at petrographic microscope where is evident the less porous microstructure of the limestone filler composition.

SEM Examination and EDS Analysis of Concrete Samples. High amounts of massive expansive ettringite were observed by SEM-EDS in the concrete compositions with highest values of expansion (Figure 5), growing at the aggregate-paste interfaces and in some cases in the cement paste matrix. No expansive ettringite was detected in compositions in which there hasn't been expansion.
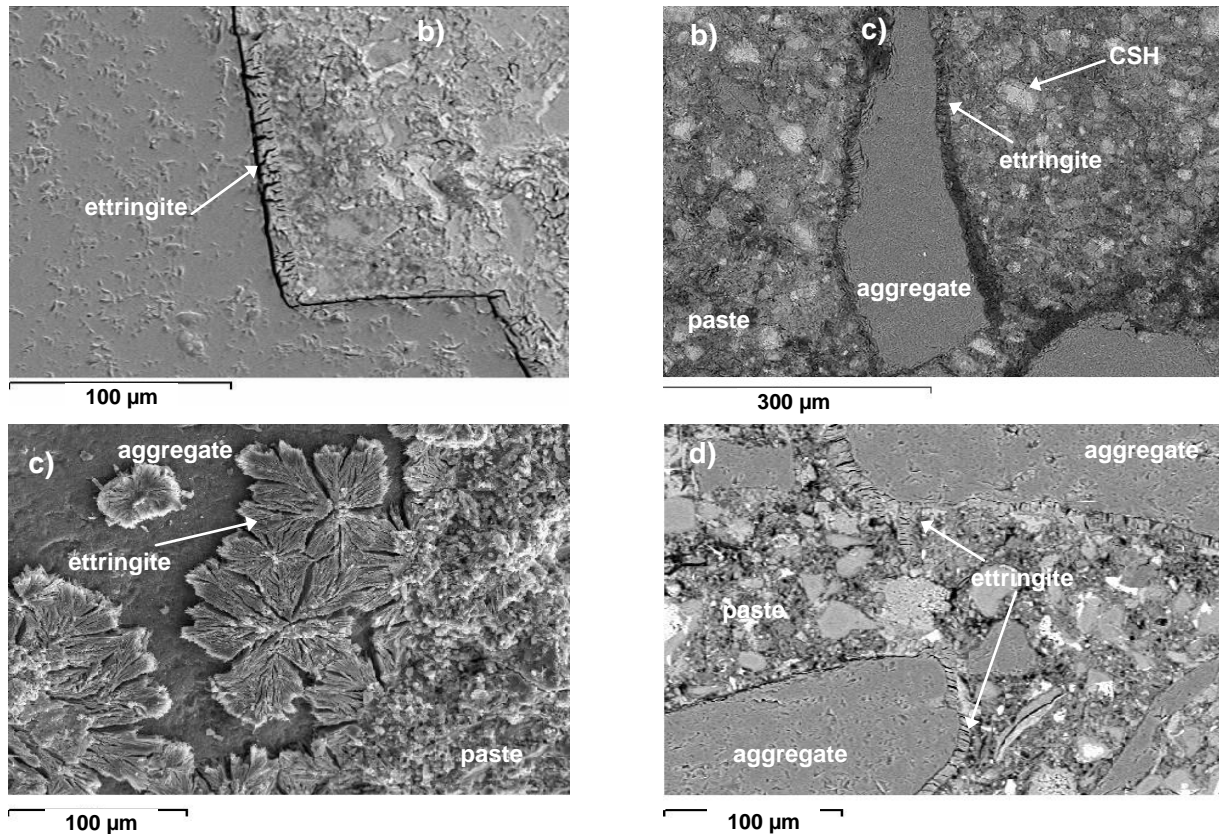

Fig. 5. SEM-images showing the presence of deleterious ettringite in aggregate-paste interfaces in heat-cured concrete compositions: (a) control, (b) 10% of GGBS and (c, d) 10% of LF.

As noted by some authors [10], the expansion associated with the formation of a given amount of ettringite is influenced by the microstructure of the material in which it is deposited. Therefore the results for LF additions can be explained considering the microstructural behaviour of such compositions (Figure 4). The incorporation of LF seems to make the paste more dense, which is in agreement with its role as a nucleation core for the hydration of the C_3S and C_2S, accelerating the hydration reactions and even activating reactions that are not or less prominent present in a traditional concrete without LF. A second hypothesis can be put forward if one considers that LF is not totally inert (Figure 6), being an active partner in the hydration reactions of aluminate phases of cement [11,12]. All of these effects could increase the expansion produced in the LF compositions and are not mutually exclusive. The existing data are inadequate to establish their relative importance and further work is required.

For the other concrete compositions, from a certain amount of addition the inhibition effect of the expansion is clearly visible. The percentages at which each addition begins to be more effective in inhibiting the expansive reaction are: 15% for FA, 10% for MK, 40% for GGBS and 10% for SF. These different values seem to be mainly related with the consumption of calcium hydroxide by each material, as can be confirmed by the results (Figure 7) obtained by thermogravimetry (TGA). For the age of one year, the compositions with higher content of mineral addition show less $Ca(OH)_2$ contents, which is related to the dilution effect and with the greater ability of each mineral addition type in consuming $Ca(OH)_2$ through the pozzolanic reaction.
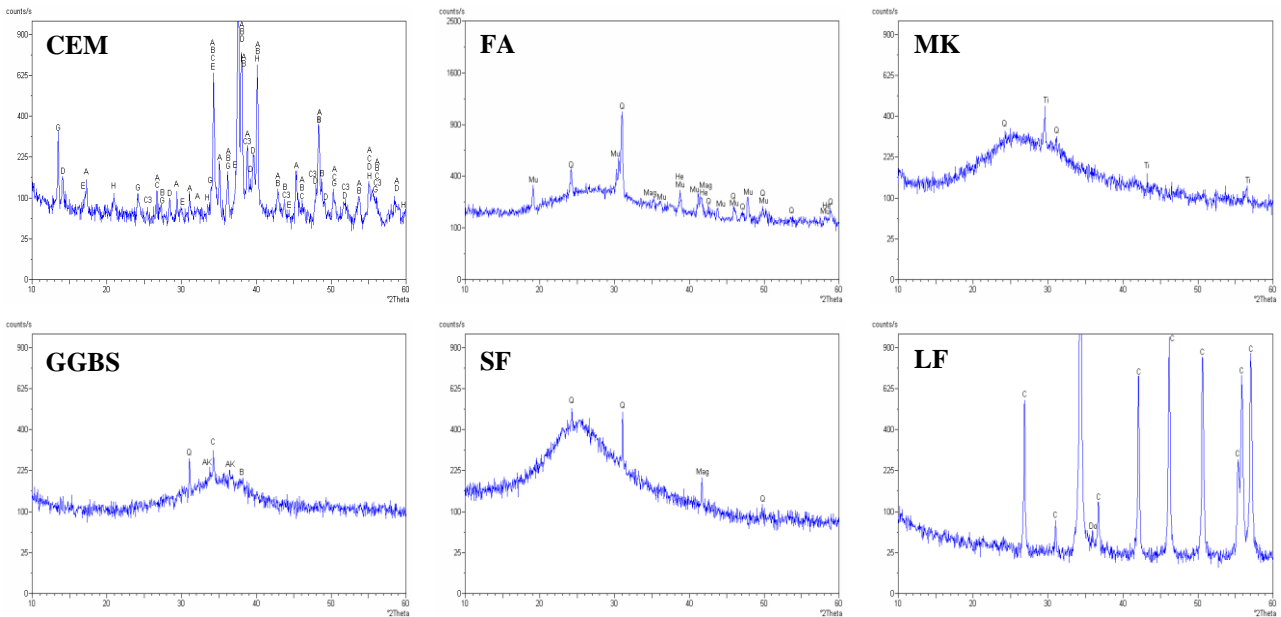
Legend: A - C_3S; B - C_3S; C - C_3A; D - C_4AF; H – Calcium hydroxide; C – Calcite; G – Gypsum; E – Bassanite; Do – Dolomite; Mu – Mulite; He – Hemtite; Mag – Magnetite; Q – Quartz; Ti – Anatase; Ak – Akermanite.

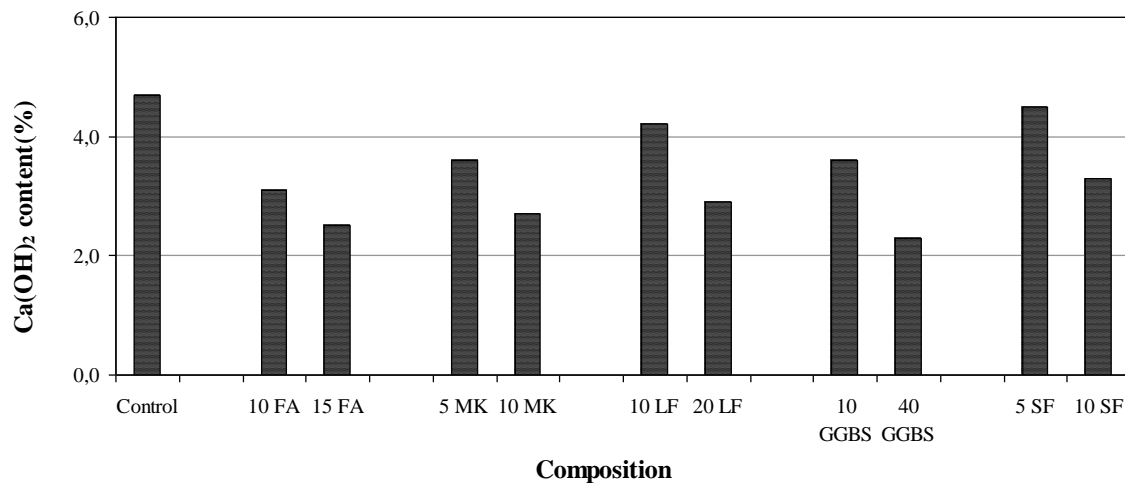Fig. 6. X-Ray difractograms of the cement and different mineral additions.

Fig. 7. $Ca(OH)_2$ content by TGA of different concrete compositions for the age of 365 days.

Conclusions

The results obtained at present (about 1000 days in accelerated exposition) suggest that the efficiency of mineral additions in the inhibition of DEF depends on the type of mineral addition, and only those of type II nature are effective. Moreover, its efficiency also depends on the content of material added and its capacity in the reduction of $Ca(OH)_2$ content.

In this study, it appears that the replacement rate (% mass) from which the reduction in expansion by DEF is efficient is 15% for FA, 10% for MK, 40% for GGBS and 10% for SF. The mechanism of DEF suppression, and how they act at this level, seems to be related essentially with its efficiency in the portlandite consumption.

Acknowledgments

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