

# The Application of Fluorescence Microscopy and Scanning Electron Microscopy in the Detection of Delayed Ettringite Formation in Concrete

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**Abstract:** The degradation of concrete structures caused by delayed ettringite formation (DEF) is a problem that nowadays affects many concrete structures worldwide. This pathology is due to the formation of an expansive compound – ettringite - inside the material. This is a hydrated calcium sulphoaluminate produced by the chemical reaction between sulphate ions, calcium hydroxide and alumina present in the Portland cement paste. This product, normally formed during the hydration of cement, presents an acicular morphology (needles) that can be observed by scanning electron microscopy (SEM). However, DEF can also be formed after the setting of the cement causing, in this case, a deleterious expansion of the concrete. This secondary ettringite can also be produced after an excessive heating of the concrete, caused by a high amount of cement or by the use of heat cure. SEM has been used to distinguish between expansive and non expansive ettringite based normally in morphology analysis, since the former is characterized by a compressed or compact nature where the needle shapes disappear or are welded together. Furthermore, the use of other techniques, like X-ray diffraction or micro-XRF, has been limited because the compressed or compact ettringite is badly crystallized or even amorphous and the elemental composition is similar and therefore it is difficult to detect. This article presents a methodology for the diagnosis of DEF using polished concrete thin sections and combining polarised and fluorescence light optical microscopy with SEM-EDS.

## Introduction

In the last years an increased number of concrete structures affected by expansive chemical reactions of internal origin [1] have been diagnosed, namely affected by the internal sulfatic reaction that is characterized by the formation of expansive ettringite ( $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 3\text{CaSO}_4\cdot 32\text{H}_2\text{O}$ ), which is associated with the formation of delayed ettringite formation (DEF).

DEF appears in concretes exposed to frequent humidity and subjected to relatively high heating temperatures ( $> 70^\circ\text{C}$ ) or having reached equivalent temperatures for other reasons (massive cast-in-place concrete, concrete casting during hot summer days, etc) [2, 3].

The ettringite is a resulting product of the Portland cement hydration and normally is homogeneously distributed in the hardened cement paste. This ettringite, denominated primary ettringite, does not generate expansion being different of the secondary ettringite that is formed after the concrete hardening due to external factors (external ingress of sulfates) or due to internal factors (internal sources of sulphates). A particular form of secondary ettringite, called delayed ettringite formation (DEF), is associated with concretes that have suffered heat-curing or have been

subject to high temperatures during the cure. DEF causes expansion followed by cracking of the cement paste and concrete at micro and macroscale.

The distinction between expansive and non expansive ettringite is normally performed by scanning electron microscopy (SEM) and is based in its morphology being the former characterized by its compressed or compact character where the notion of needles disappears or are welded together. Furthermore, the compressed or compact ettringite is badly crystallized or even amorphous and therefore is difficult to detect using others techniques like X-ray diffraction.

In this paper we present a methodology that enables the detection of the occurrence and the evaluation of the extent of DEF in concrete samples, using polished concrete thin sections and combining polarised light and fluorescence microscopy with SEM-EDS.

## Materials and methods

**Concrete mixes.** The work presented in this paper is part of an extensive study aimed at elucidating the role that mineral additions have in the inhibition mechanism of DEF in hardened concrete. Several concrete compositions were prepared using the same binder and aggregate types, same water/binder (w/b) ratio, with different mineral addition types, like fly ash (FA) metakaolin (MK), limestone filler (LF), ground granulated blast-furnace slag (GGBS) and silica fume (SF). The concrete mixes used are presented in Table 1. A control concrete (Control) was prepared in the same conditions but without additions.

In order to promote the occurrence of DEF, immediately after casting, the concretes were sealed and placed in a climatic chamber, with controlled temperature and humidity, to be heat-cured.

The heat-curing cycle used 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. 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 immersed in tap water for long-term storage at  $20 \pm 2^\circ\text{C}$ .

Table 1. Concrete mixtures used.

Aggregate type	w/b ratio	Composition (% mass of cement replacement)					
		Control	FA	MK	LF	GGBS	SF
siliceous	0.45	0	10	5	10	10	5
		-	15	10	15	15	10
		-	20	15	20	20	-
		-	30	20	30	40	-

**Expansion tests.** Length and mass measurements were taken periodically in accordance to the French concrete performance test for DEF [4].

**Optical microscopy.** Thin sections of each concrete mix were prepared in an IU-30 Logitech impregnation unit in vacuum with an epoxy resin. These were polished in a PM5 Logitech lapping/polishing machine with  $15\mu\text{m}$   $\text{Al}_2\text{O}_3$  abrasive and the final lapping was made with diamond pastes (6-3  $\mu\text{m}$ ). The observations were performed on an Olympus BX60 petrographic microscope in polarized light and fluorescent setups and images were recorded digitally.

**SEM/EDS observations.** SEM observations were performed on a scanning electron microscope (SEM) JEOL JSM-6400 coupled with an OXFORD energy dispersive spectrometer Si(Li) X-ray detector (EDX), on the same thin sections (using backscattered electrons – BEI images) after sputtering with gold-palladium in a Baltec sputter-coater.

## Results and discussion

**Expansion Measurements.** Figure 1 shows the expansion curves obtained for the different concrete mixes in test. From these results it can be seen that some mix compositions have expanded instead others did not present any expansion. The compositions that have presented the higher expansions are the LF mixes, the 10% GGBS and the 10% FA. This behaviour is related with the inhibition capacity in the DEF suppression of each addition type and its content.

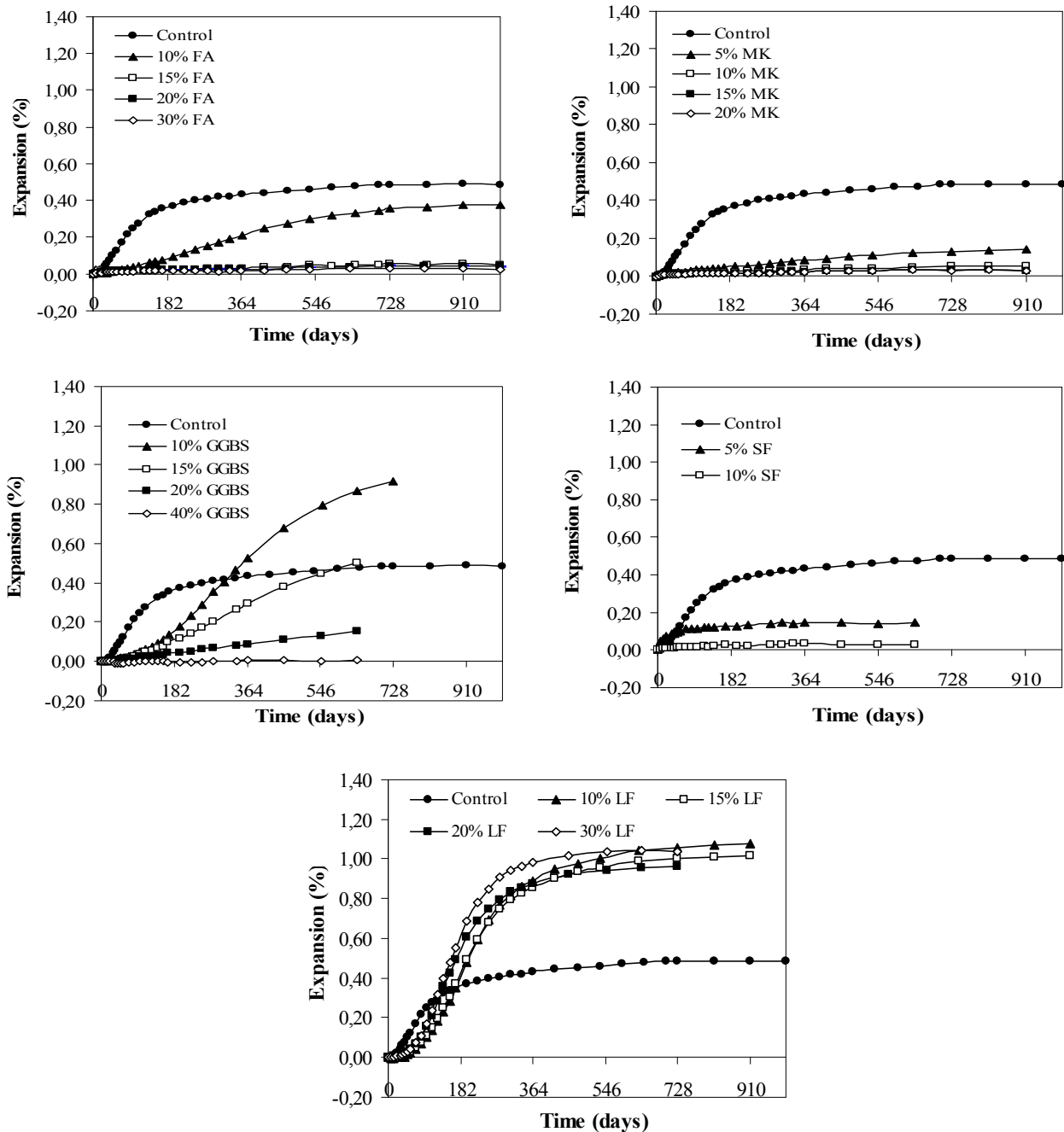
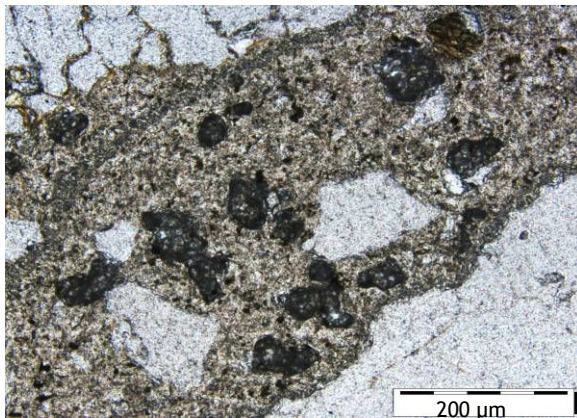


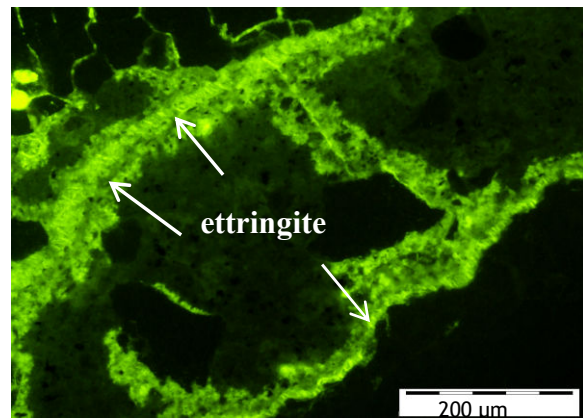
Fig. 1. Expansion curves of different heat-cured concrete compositions.

**Petrographic and SEM/EDS analysis of concrete samples.** Microscopy is the only technique capable to clearly identify the features associated with DEF in concrete, namely its morphology and the presence of ettringite bands around the aggregates, filling the voids and entrained air bubbles, or even disseminated in the cement paste in small crystals. When present in large quantity, the ettringite could be easily detected because it tends to form veins with considerable thickness. However, when the quantity of this product is reduced, its observation in the polarized light mode is

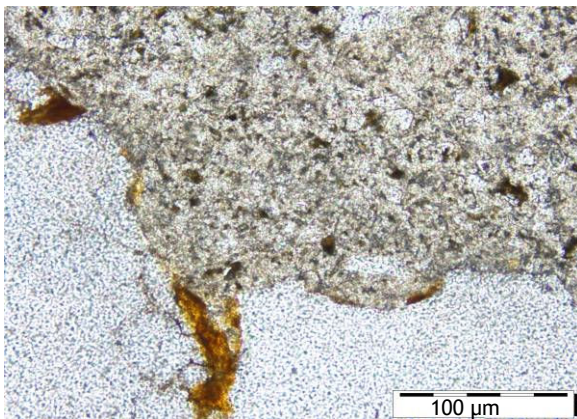
very difficult. In this situation, the observation of thin sections in fluorescence mode presents an interesting alternative in the identification of the DEF, namely for its detection in the cement paste matrix, (Figure 2).



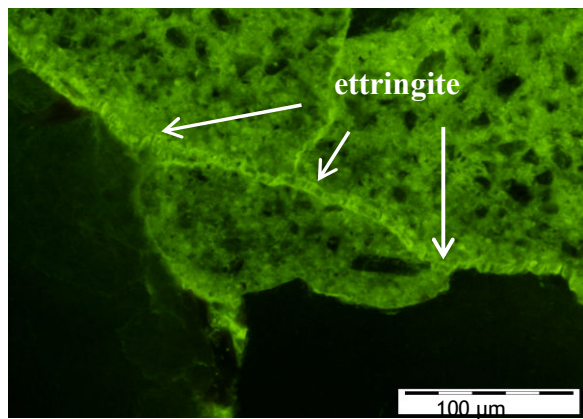
a) Control - 2 years of test, // nicols.



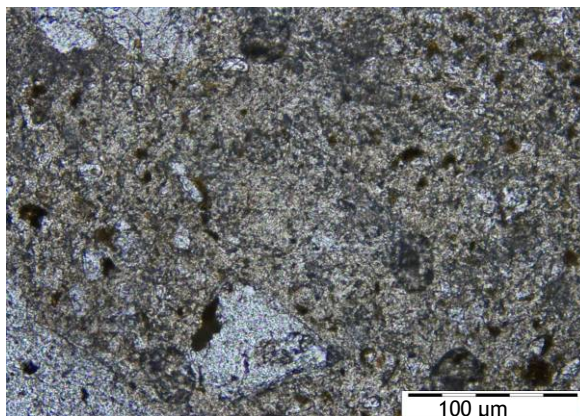
b) Control - 2 years of test, fluorescence.



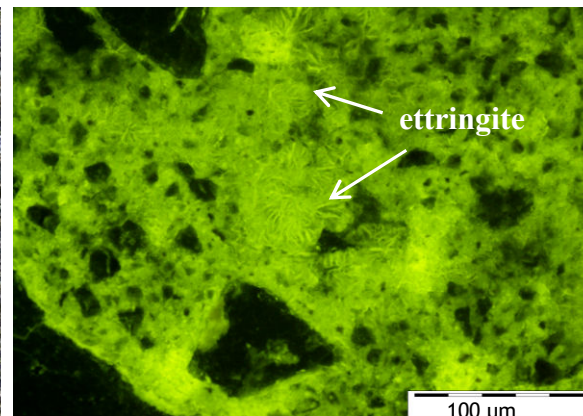
c) 20 LF - 1 year of test, // nicols.



d) 20 LF - 1 year of test, fluorescence.



e) 10 LF - 2 years of test, // nicols.



f) 10 LF - 2 years of test, fluorescence.

Fig. 2. Images of concrete thin sections in polarized and fluorescence modes at petrographic microscope showing the presence of DEF around aggregate particles and in the cement paste.

Figure 2 shows some images of different concrete mixes that have presented high expansion in the expansion tests obtained in the petrographic microscope in polarized and fluorescence light. These examples show the great improvement obtained with fluorescence light in the detection of DEF in concretes.

The observation of concrete samples in petrographic microscope could be complemented by its observation by SEM-EDS, which allows the confirmation of the ettringite chemical composition and its morphology (Figure 3).

The use of concrete thin sections in SEM allows s to obtain BSE images that could be associated to sulphur X-ray maps (Figure 4), that are, in the authors' opinion, a reliably diagnostic of DEF in a damaged concrete enabling a viable evaluation of its occurrence and extent.

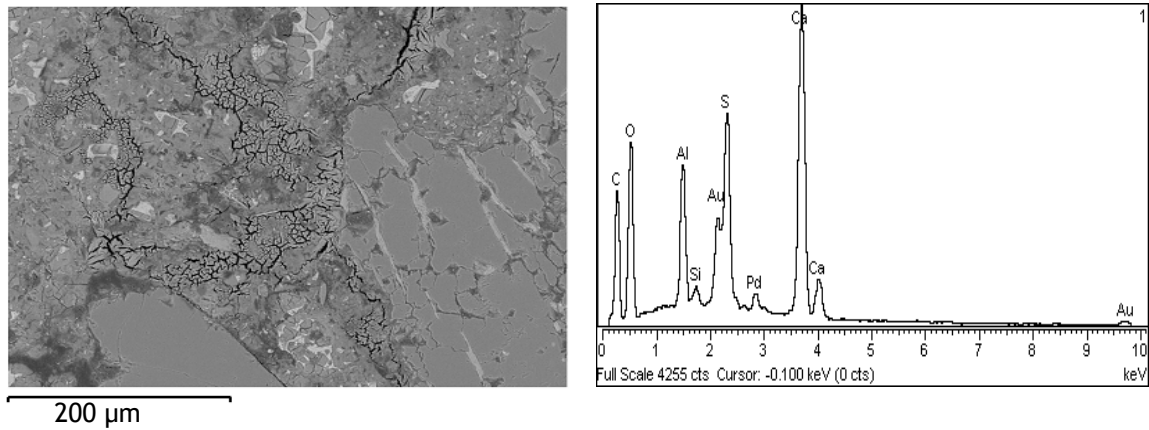


Fig. 3. SEM image of Control concrete showing massive ettringite around an aggregate particle and its EDS spectra.

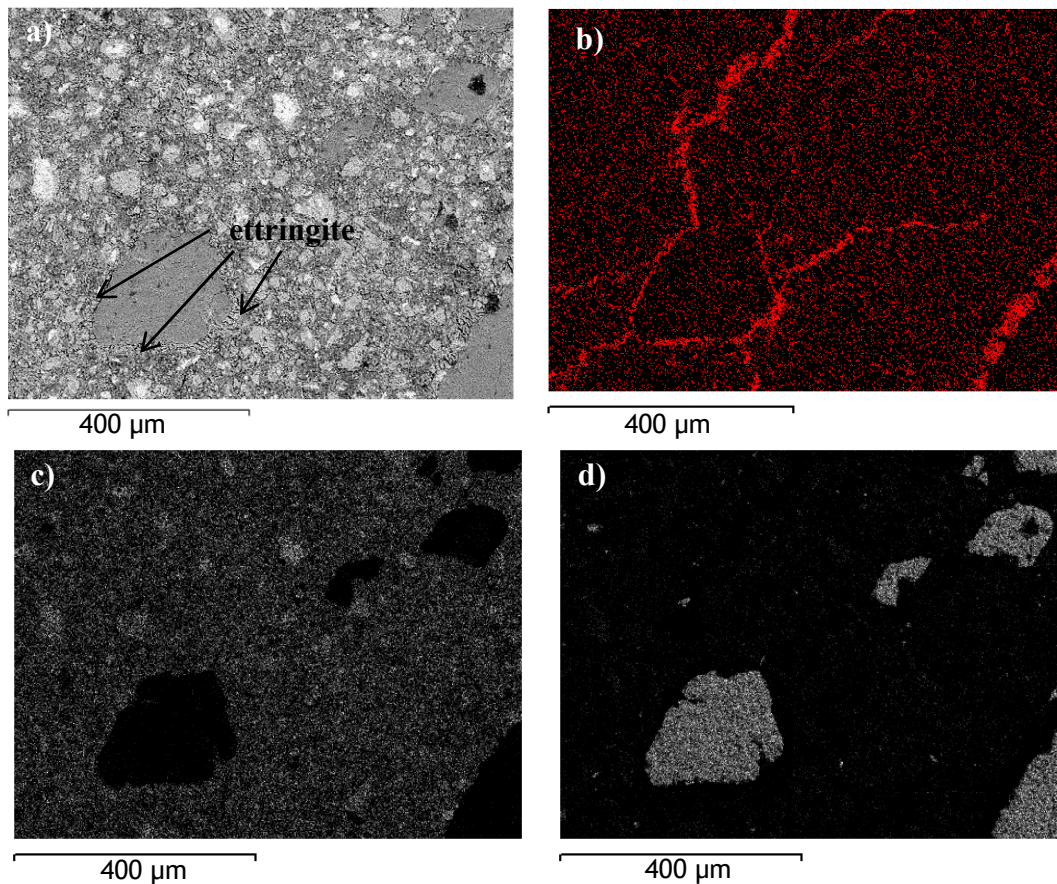


Fig. 4. a) BSE image of 10 LF concrete thin section with 2 years of test and the corresponding X-ray maps of sulphur (b), calcium (c) and silicon (d).

The visualization and quantification of the presence of DEF in hardened concrete by polarized light microscopy is difficult even if present in large quantity inside the cement paste. The difficulty in the

detection of this compound in polarized light could be related mainly with the fact that this is present in small thicknesses and in these conditions, the optical properties of ettringite are too close to the cement paste.

To overlap this difficulty we propose the use of fluorescence microscopy since the ettringite is highlighted, being more easily detected around the aggregates or in the cement paste. However, in some cases reliably diagnostic features may not be so evident and, even when they are present the contribution of DEF may be difficult to separate from other expansive mechanisms, like ASR. SEM/EDS analysis with sulfur X-ray maps would be required to a complete and exhaustive evaluation of its occurrence and extent in a damaged concrete and to eliminate any contribution from other distress mechanisms.

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