



## Secondary ettringite formation in concrete subjected to different curing conditions

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### Abstract

The large amount of ettringite detected in concrete affected by different failure mechanisms (alkali-silica reaction [ASR], freezing and thawing [FT], and wetting and drying [WD]) in sulfate-free environments has been a matter of concern for many researchers over the past years. Two major lines to approach this issue have been defined. One of them considers ettringite as the main cause of damage and the other assumes that it appears after concrete distress. In order to contribute to the clarification of this phenomenon, research was conducted to cover the above issues. This paper reports on the conclusions arrived at up to date, from studies conducted on concrete affected by different damaging mechanisms: FT, WD, and precracking induced by loading and ASR. Changes in length and mechanical strength of test concrete are reported, as well as the evaluations made by optical microscopy (OM), scanning electron microscopy (SEM) and energy dispersive X-ray analysis (EDAX). Secondary ettringite formation (SEF) is closely linked to pore fluid transport in the mass of concrete. Although it was not possible to define clearly its participation in the damaging processes related to ASR or to FT, secondary ettringite crystallization in concretes subjected to WD cycles seems to be one of the most likely mechanisms to account for the volumetric instability observed in these concretes. © 2000 Elsevier Science Ltd. All rights reserved.

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### 1. Introduction

The deterioration of a large number of concrete structures in contact with sulfate-free environments and linked to secondary ettringite formation (SEF) is currently one of the major and highly controversial research issues worldwide [1].

The term “delayed ettringite formation” (DEF) was first used in the literature in the 1980s to explain the deterioration of steam-cured precast concrete structures, due to the development of a significant amount of secondary ettringite in cracks and matrix–aggregate interfaces, in spite of being sulfate ion-free external environments [2].

Research on this subject by Fu et al. [3] suggests that the explanation for this phenomenon lies in the quick sulfate adsorption by the calcium silicate hydrate (C-S-H), thereby preventing the usual formation of ettringite at early ages. Later, the release of these sulfates to the concrete pore fluid causes ettringite crystallization and expansion-induced

phenomena, with existing cracks [4] and diffusion processes inside the material [5] playing a key role throughout this process.

Subsequent studies conducted by Mielenz et al. [6], however, have shown that DEF can occur even in concrete cured under ambient conditions due to the particular mineralogy of cement. These studies have also shown that a large part of the ettringite detected is submicroscopic or of an amorphous nature and has an appearance similar to the gel formed due to ASR [7], which has given rise to a confusion with the failures caused by these phenomena [6,8–11].

In a recently published paper, Collepardi [12], applying a holistic approach, summarizes that the damage caused by SEF is based on a chain of three essential elements: (a) microcracking, (b) exposure to water or saturated air, and (c) late sulfate release.

This paper reports on the results from laboratory studies performed up to the age of 2 years on concrete specimens affected by different deterioration mechanisms: alkali-silica reaction (ASR), freezing and thawing (FT), wetting and drying (WD) and microcracking due to mechanical action (MM). Concrete strength (modulus of rupture, MR), longitudinal expansion, and observations of

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Table 1  
Physico-chemical characteristics of the portland cements used

	Type I	Type III
<i>Physical properties</i>		
Fineness, Blaine air permeability (m <sup>2</sup> /kg)	311	459
Autoclave expansion (%)	0.17	0.00
7-day compressive strength (MPa)	29.2	44.4
28-day compressive strength (MPa)	46.0	55.4
Vicat-initial set (min)	85	145
Vicat-final set (h)	2.8	3.3
<i>Chemical properties</i>		
Silicon dioxide, SiO <sub>2</sub> (%)	21.6	21.8
Calcium oxide, CaO (%)	58.0	62.9
Aluminum oxide, Al <sub>2</sub> O <sub>3</sub> (%)	6.2	4.0
Ferric oxide, Fe <sub>2</sub> O <sub>3</sub> (%)	3.7	4.6
Magnesium oxide, MgO (%)	3.6	0.5
Sulfur trioxide, SO <sub>3</sub> (%)	2.0	2.8
Alkalies (Na <sub>2</sub> O + 0.658 K <sub>2</sub> O) (%)	1.14	0.84

the material by optical microscopy (OM), scanning electron microscopy (SEM), and energy dispersive X-ray analysis (EDAX) are reported.

## 2. Experimental

As it is known [13,14], the cement type and particularly the ratio of sulfates to aluminates (SO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub>) are important for determining the potential for SEF. This led to the selection of two cements: (a) a portland cement of high early strength (Type III, according to ASTM C 150), with a SO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> ratio equal to 0.70; and (b) a normal portland cement (similar to ASTM C 150 Type I), with a SO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> ratio equal to 0.32, and a slag content of the order of 10% (an admixture permitted for this type of cement, up to 10% replacement, by Argentine standards).

In the former case, a Type III cement was chosen because it is quoted in the literature as one of the cements that is potentially more vulnerable to deterioration due to SEF. In the latter case, however, in spite of being a normal cement with a low SO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> ratio, there is background information that shows that concrete made with this cement and affected by ASR causes the formation of large amounts of secondary ettringite [15]. The characteristics of these cements are reported in Table 1.

Table 2  
Damage-inducing treatments applied to concrete specimens

Damage-inducing treatment	Description
Control (C)	Continuously cured in lime-water at 23°C.
Cracking induced by loading (CL)	Cured in lime-water at 23°C for 14 days. Loading to 80% of flexure strength was applied.
FT cycles	Cured in lime-water at 23°C for 14 days. 420 FT cycles were applied. A cycle consisted of 16 h freezing at -20°C and 8-h thawing in water at ambient temperature.
WD cycles	Cured in lime-water at 23°C for 14 days. 120 WD cycles were applied. A cycle consisted of 4 days wetting under lime-water at ambient temperature and 3 days drying in an oven at 38°C.
ASR	Continuously immersed in sealed plastic bags with 20 ml of water at 23°C in fog room.

A granitic rock from the area of Tandil (Buenos Aires) with a maximum size of 12,7 mm// was used as coarse aggregate. The fine aggregate was a siliceous sand from the River Plate, with a fineness modulus of 3.0. Both aggregates have innocuous characteristics with respect to the alkalies, as confirmed by previous studies.

For making concretes having the ASR, 10%, by weight, of the natural siliceous sand was replaced by crushed siliceous (opaline sandstone, of high alkali reactivity) [16].

Concrete was proportioned with a water/cement ratio of 0.44, an aggregate/cement ratio of 3.39, and a slump of 12.0 ± 1.0 cm.

With these mixtures three 4 × 4 × 16 cm specimens were molded, per test and age. In addition, other specimens were cast to perform supplementary studies (OM and SEM-EDAX). Specimens were stored in the humid room and kept in their molds for the first 24 h. They were then demolded and different treatments were applied, as shown in Table 2.

Length changes and MR with center-point loading up to 2 years were determined on concrete specimens prepared as described in Table 2. Evaluations were made at the microstructural level by OM and SEM-EDAX using an Olympus SZ40 trinocular stereoscopic microscope and a JEOL JSM 35 CP scanning electron microscope equipped with an EDAX DX 4 probe.

## 3. Results and discussions

### 3.1. Expansion and MR of concretes

Expansion and MR values of concretes subjected to different exposure conditions are shown in Table 3.

The results presented in Table 3 indicate that the greater the expansion, whether caused by FT and WD cycles, or ASR, the more noticeable the drop in flexure strength is as expected. It is evident that the observed decrease in strength of concretes made with Type I cement is larger due to their weaker microstructure (enhanced porosity), especially in the case of concretes subjected to FT. It is not easy to explain, however, the substantial expansion observed in concretes subjected to WD cycles.

### 3.2. OM evaluations

Table 3  
Expansion and modulus of rupture of the concretes subjected to damage-inducing treatments

Group	Cement	Expansion (%) at		Modulus of rupture at 24 months	
		12 months	24 months	MPa	Percent of control
C	Type I	0.030	0.050	10.2	100
CL		0.036	0.038	9.9	97
FT		0.229	0.745	1.6	15
WD		0.059	0.144	8.1	80
ASR		0.452	0.475	4.9	48
C	Type III	0.018	0.029	10.5	100
CL		0.022	0.006	11.0	104
FT		0.045	0.096	8.2	77
WD		0.001	0.026	9.6	91
ASR		0.434	0.449	6.0	57

Evaluations of concrete by the use of the stereoscopic microscope are summarized in Table 4.

### 3.2.1. Concretes made with Type I cement

C: At the age of 18 months, concrete was not damaged and had abundant portlandite (CH). At 24 months the characteristics were similar, although voids formed by entrapped air were filled with portlandite and, in some case, ettringite, forming very thin needle-shaped crystals.

CL: Concrete was microcracked. At 18 months, portlandite and ettringite occurred inside pores. Unlike the above case (control), ettringite crystals were short, thicker and clustered. At 24 months, ettringite development was greater. It had the same morphological characteristics as at 18 months; it was also crystallized at the aggregate–paste interface.

WD: At 18 months, rosette-like portlandite and ettringite occurred inside pores. At 24 months, rosette-like portlandite and ettringite were found in the larger voids, while smaller voids were filled with very thin needle-shaped ettringite.

FT: No ettringite was found at 18 months. At 24 months, concrete was severely deteriorated. Abundant calcium carbonate was observed in the paste, covering even the coarse aggregate clasts. No ettringite was detected. Abundant portlandite occurred inside voids.

ASR: Concrete was deeply cracked. At 18 months, there was abundant portlandite but no ettringite. Similar characteristics were found at 24 months, but large amounts of

clusters of thin and short ettringite needles could be seen. The surface of the coarse aggregates was covered with calcium carbonate and ettringite.

### 3.2.2. Concretes made with Type III cement

C: At 18 months, the specimen evidenced no damage, clasts were clean, only the presence of portlandite was observed. At 24 months, the characteristics were the same, although a small amount of ettringite was detected, filling entrapped air voids.

CL: The surface exhibited cracks, which were fine and sometimes healed. Portlandite and ettringite occurred inside voids. Crystals developed in the form of short and thick clusters. These characteristics were observed in specimens at 18 and 24 months.

WD: No ettringite was observed at 18 months. Portlandite was abundant. At 24 months, ettringite occurred in the form of very small clusters. They completely lined voids. In both cases the specimen evidenced no damage.

FT: At 18 months, the specimen was found to have suffered no damage. At 24 months, some damage had occurred although not as significant as in the specimen made with normal cement. No ettringite was observed in both cases.

ASR: At 18 months, no ettringite was detected, portlandite was abundant and reaction phenomena highly developed. At 24 months, the development of the ASR was significant. Clasts made with opaline sandstone were covered with a hard and white material. Calcium carbonate,

Table 4  
Minerals detected in concretes studied under the stereoscopic microscope

Group	Cement Type I		Cement Type III	
	18 months	24 months	18 months	24 months
C	CH	CH and AFt (scarse) in pores	CH	CH and AFt (scarse) in pores
CL	CH and AFt in pores, concrete microcracking	AFt in pores and MATZ	CH and AFt in pores, healing of microcracks	CH and AFt in pores
WD	CH and AFt in pores	CH and AFt in pores	CH	AFt (scarse)
FT	No AFt	CC and CH, No AFt	No AFt	No AFt
ASR	Gels and CH, No AFt	Gels, CH, CC, abundant AFt in pores and MATZ	No AFt	CH, CC and AFt

Note: CH: calcium hydroxide, CC: Calcium carbonate, AFt: ettringite, MATZ: matrix–aggregate transition zone.

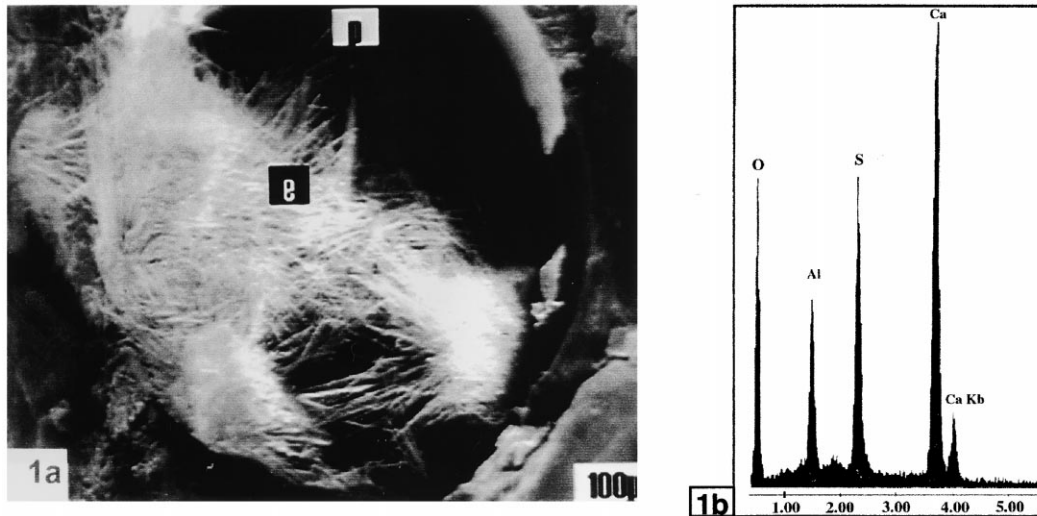


Fig. 1. (a) SEM micrograph. Specimen C. Portlandite-related ettringite. (b) EDAX, ettringite shown in (a).

portlandite, and ettringite were abundant, both in voids and on the surface of the coarse aggregates. Ettringite developed in voids forming short and thick crystals.

XRD analyses were performed on the mortar fraction of the concrete, after removing the coarse aggregate as much as possible, pulverizing the material (particle sizes smaller than 150  $\mu\text{m}$ ). By this methodology, however, no ettringite could be identified in any of the specimens due to the small content of this material and the operating impossibility to separate the fine (quartz) aggregate. Crack filling materials were mainly composed of calcite and portlandite.

### 3.3. Evaluations carried out by SEM–EDAX

The observations made by SEM are summarized in the following paragraphs.

C: No ettringite could be identified at 18 months. At 24 months, very thin and long needle-like ettringite was observed in some pores (Fig. 1a). The EDAX spectrum of ettringite, where the S, Al, Ca, and O peaks characteristic of this mineral can be observed, is shown in Fig. 1b. The high increase in calcium is due to the presence of  $\text{Ca}(\text{OH})_2$ .

CL: All specimens exhibited abundant ettringite, which developed both in voids and in the interface between the aggregate and paste. A SEM photomicrograph of the CL group (concrete made with Type III cement), at the age of 24 months, where ettringite development can be observed (e), is shown in Fig. 2. S, Al, O, and Ca were detected in the EDAX spectrum.

FT: Scarce ettringite was generally found. There is massive deposition in fracture areas and on the surface of aggregates (Fig. 3).

WD: Large amount of ettringite was observed both inside pores forming large clusters (crystalline ettringite) (Figs. 4

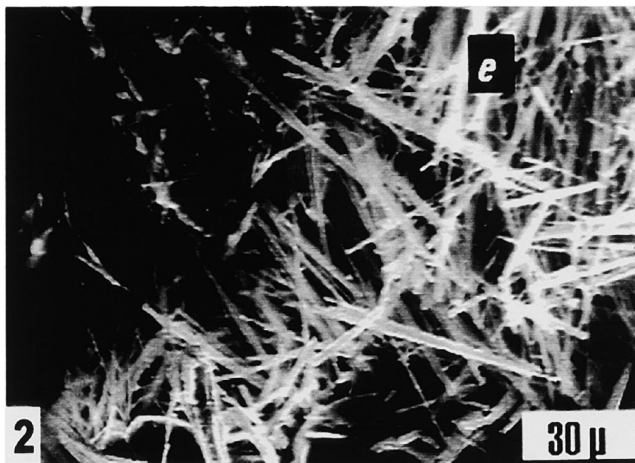


Fig. 2. SEM micrograph. Specimen CL made with Type III cement, ettringite (e).

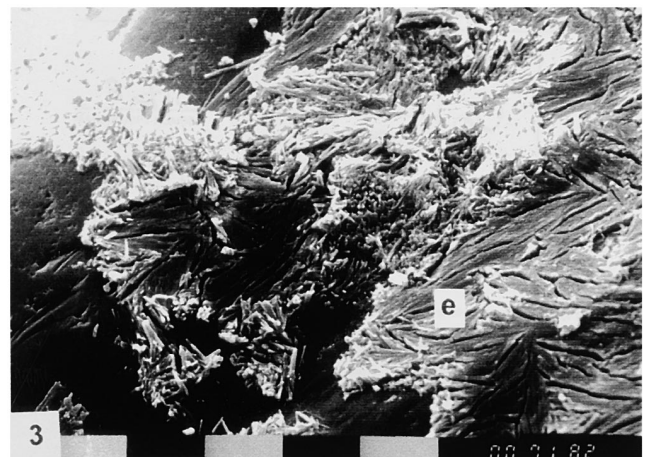


Fig. 3. SEM micrograph. Specimen FT made with Type I cement.

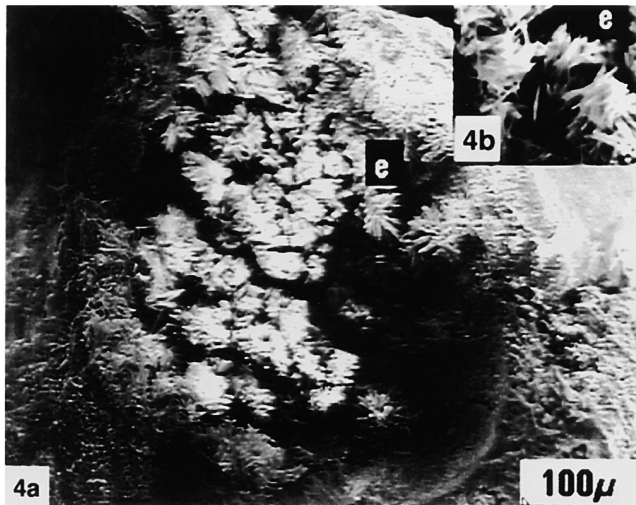


Fig. 4. SEM micrograph. Specimen WD made with Type I cement, ettringite-filled void (e).

and 5). It was also observed in the matrix–aggregate transition zone (massive ettringite) (Fig. 5).

ASR: All concretes under study exhibited a high degree of deterioration. In general, ettringite was abundant inside voids as well as in cracks and on the surface of the coarse aggregates. It was generally related to calcite and portlandite (Fig. 6).

#### 4. Conclusions

From OM and SEM analyses, the formation of two types of ettringite could be detected: (a) primary ettringite of a crystalline nature, formed at early ages as a result of cement hydration processes, and (b) secondary ettringite, of changing morphology, either massive or crystalline, formed later (6 months or more) by the recrystallization of the primary components ( $\text{SO}_4^{2-}$ ,  $\text{Al}^{+3}$ , and  $\text{Ca}^{+2}$ ) that were present in



Fig. 5. SEM micrograph. Specimen WD made with Type I cement, ettringite-filled void (e).

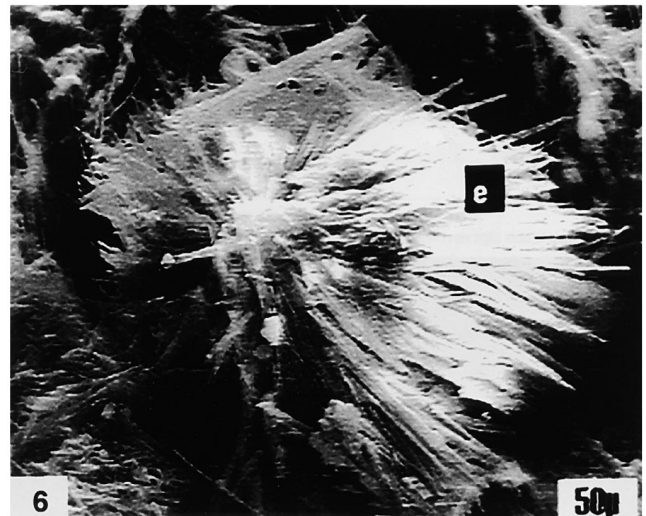


Fig. 6. SEM micrograph. Calcite and portlandite-related ettringite-filled void (e).

the concrete pore fluid, without the external contribution of sulfate ions.

It is well known that the migration of reactive ions towards nucleation sites through the pore aqueous phase requires a transport mechanism. In the case of concretes affected by ASR, for instance, both alkali reactions at the interface level (giving rise to concentration gradients) and the subsequent formation of gels with high surface energy (resulting in phenomena of an osmotic nature), would be two of the major mechanisms that can cause the mobility of these ions. In concretes subjected to FT, similar mechanisms of thermodynamic and osmotic nature would be caused by water crystallization.

In this way, the amount of secondary ettringite crystallized in concretes will largely depend on the environment surrounding the specimens: it is minimum under permanent saturation conditions (as in C and CL specimens), it is somewhat larger in concretes subjected to FT, and it is substantially increased due to the action of WD cycles (pore fluid concentration).

Moreover, SEF is dependent on the mineralogical composition and source of portland cement. However, in this case (Type I cement), the  $\text{SO}_3/\text{Al}_2\text{O}_3$  ratio does not seem to be a good factor to predict how susceptible cement will be to this failure mechanism.

When spaces available inside the concrete are small, ettringite develops thin and rather short crystals; inside pores or cracks crystals have greater development and in some cases dense clusters are formed, which would indicate that crystalline ettringite fits into the available space without exerting any expansive action.

Deterioration mechanisms operating in concretes affected by ASR seem to be linked only to the formation of siliceous gels of an amorphous nature. Ettringite crystal formation in

these concretes does not participate in the expansive mechanisms of the material. In fact, even though the first crystals start to be observed only after 6 months, the structure of the material is already severely deteriorated and its deposition does not contribute, at least appreciably, to the increase in expansions.

Deterioration mechanisms operating in concretes subjected to FT cycles are caused by the contribution of two factors: water crystallization and the appearance of hydraulic pressure from osmotic phenomena [17]. There are some doubts, however, about the role played by massive ettringite, found at the matrix–aggregate interface, in the deterioration process of the material.

The WD process causes large expansions and cracking in concretes made with normal cement. Even though this can be attributed to the action of water inside pores and cracks, especially in the smallest ones, due to the orientation of water dipoles that exert great pressure, the extent of damage observed leads to the assumption that another damaging action should be involved, such as the one caused by massive ettringite formation.

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