

Mineral Additions for the Inhibition of Delayed Ettringite Formation in Concrete: The Role of Limestone Filler

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Abstract

One of the most popular preventive measures to minimize the occurrence of chemical expansive reactions, namely the internal sulphate reaction (ISR), in hardened concrete is the use of mineral additions. This pathology is due to the formation of expansive ettringite (delayed ettringite formation - DEF) 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. Nowadays, it's recommended the use of mineral additions to sustain this type of degradation. Moreover, their effect depends on the chemical and mineralogical composition and also the cement replacement.

The research work presented in this paper deals with the influence of limestone filler, a type I mineral addition, in the inhibition of DEF (Santos Silva et al., 2010a, 2010b), and is part of an extensive study to elucidate the role that the mineral additions have in the mechanism of inhibition of DEF in concrete. For this purpose different concrete mixes were produced by using the same cement type (CEM I 42.5Ra with 3.11% SO₃ and 6.4% C₃A) and water/cement ratio (0.45), incorporating different amounts of mineral additions, like fly ash, metakaolin, blast-furnace slag, silica fume and limestone filler. The filler influence was followed by expansion and microstructure evaluation of concrete mix at several ages. These studies showed an interesting behaviour of limestone filler, which motivated new concrete formulations with different cement types (CEM I 42.5Rb and CEM I 52.5) that differ in SO₃ and C₃A contents, in order to investigate its influence in development of DEF. This research includes also a concrete composition with a cement type II (CEM II A-L 42.5R). The results obtained were compared and the conclusions were extracted.

It was found that the concrete mixes with limestone filler showing higher expansions than the control composition. According to these results it seems that the limestone filler does not inhibit rather it promotes the expansion due to DEF. Thus, for concretes subjected to high temperatures in early ages, the limestone filler is not adequate to sustain DEF development rather it may even increase the expansion behaviour in concrete mixes. According to these findings, it was proposed that the ISR recommendations must prohibit this kind of mineral addition.

Originality

The degradation of concrete structures due to delayed ettringite formation (DEF) is a problem that affects nowadays growing number of concrete structures (mainly dams and bridges), where the concrete is subjected to high temperatures during its cure. When this pathology occurs, its effects are particularly dangerous because DEF is extremely expansive causing cracking of the concrete, thus contributing to the reduction of life-time due to early degradation of concrete structures and in extreme cases can lead to its demolition. This reaction is also difficult to detect early, requiring expensive diagnostic tools and highly specialization, and when detected in a concrete the repair is not guaranteed. In this context, it is urgent to find preventive methods that allow the inhibition of DEF in the new concrete structures. It is already known that some mineral additions could be used as partial replacement of cement in concrete to mitigate the effects of these reactions. However, the behaviour of each mineral addition depends on its mineralogical composition and cement replacement content. The present work shows that limestone filler additions do not mitigate the DEF as expected instead they promote the deleterious expansion due to this reaction.

Chief contributions

Nowadays, one of the biggest challenges is to reduce the environmental impact of Portland cement, which is the most consumed material manufactured in the world. Some cements, like CEM II that have already a reduction in the portland clinker content are normally recommended for concretes that could be subjected to internal expansive reactions.

Besides the use of cements with less Portland clinker, the employment of mineral additions is a well known mitigation measure to inhibit the expansion due to internal expansive reactions in concrete. However, the chemical, mineralogical and replacement content of a certain type of mineral addition are important factors to take into account at this respect.

The study presented in this paper is part of an extensive work developed in LNEC, Portugal, aiming to study expansion rate and microstructure of heat-cured concretes with different amounts of mineral additions, like fly ash, metakaolin, blast-furnace slag, silica fume and limestone filler. The results obtained show that only type II mineral additions are effective in DEF suppression. According to these findings the recommendations for DEF inhibition must prohibit the use of additions or cements with limestone filler, like CEM II A-L, in concrete.

Keywords: ISR, DEF, limestone filler, mineral additions, microstructure

Introduction

The concrete degradation by internal sulphates seems to be related to the remobilization of sulphates included in the cementitious matrix due to excessive heating of the concrete during its early ages leading to the formation of DEF. It has been found that DEF appears in concretes exposed to frequent humidity and subjected to a relatively high thermal treatment ($> 65^{\circ}\text{C}$) or having reached equivalent temperatures for other reason (massive cast-in-place concrete, concreting during summer, etc). The effect of DEF may be enhanced by the initial development of cracks due to alkali-aggregate reaction or by some other factor, with ettringite crystallizing in these cracks and leading to additional expansion of the concrete. The development of DEF in concrete depends on several factors that influence not only the beginning of their formation, but also the progression of the reaction, examples of these factors are related to the composition of concrete, such as the aggregate nature, type of cement (SO_3 and C3A contents), water/cement ratio, and environmental conditions, including temperature and humidity.

The prevention of DEF is normally carried out having in mind the elimination of at least one of the influencing factors that promotes, namely, by controlling the alkali content of the concrete, the maximum temperature of the concrete, the aluminates and the sulphates of the binder, the humidity and the portlandite content of the concrete. Another way to prevent the DEF is through the use of mineral additions in substitution or replacement of cement. It is believed that the pozzolanic additions have the ability to react with $\text{Ca}(\text{OH})_2$ 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 the expansive products (Santos Silva *et al.*, 2010a).

The mineral additions are classified into two types: type I, “almost inert” additions (e.g. limestone filler – LF) and type II, pozzolanic (e.g. fly ash – FA, metakaolin – MK and silica fume – SF) or latent hydraulic additions (e.g. ground granulated blast-furnace slag – GGBS). Nowadays it is already known that the type II additions may, in sufficient quantity, mitigate the effects of these reactions, although their action depends on their composition and pozzolanic reactivity (Santos Silva *et al.*, 2010a). Despite the good results already obtained by some additions, the type I additions do not show the same behaviour. This work presents the results of the accelerated expansion tests which were complemented with the evaluation of the microstructure, alkali and calcium hydroxide contents, of the different concrete mixes, and is part of an extensive study to elucidate the role that the mineral additions have in the mechanism of inhibition of DEF in concrete.

Experimental

Test Conditions. Materials

Cylindrical concrete specimens (22 cm length by 11 cm diameter) were casted and tested according to the accelerated MLPC No. 66 test method (Pavoine and Divet, 2007). In this study a Portland cement (OPC), CEM I 42.5 R, and a non reactive alluvial quartzitic coarse and fine aggregates, were used. The cement replacement by different amounts of mineral additions, namely FA, MK, GGBS, SF and LF, was already described in previous works (Santos Silva *et al.*, 2010a, 2010b). These studies emphasized the behaviour of limestone filler, which motivated new concrete formulations but with different cement types. These cements differ in SO_3 and C_3A contents, and include a filler CEM II type. The chemical compositions of the materials used, obtained by XRF, are presented in Table 1.

Expansion Tests

The concrete specimens (cylinders) were cast using 440 kg/m^3 of cementitious material, a water/binder = 0.45, and with an similar alkali content of $5.50\text{ kg of Na}_2\text{O}_{\text{eq}}/\text{m}^3$ of concrete, calculated on the basis of available alkalis from the cement, additions and added NaOH.

Immediately after casting, in order to promote the occurrence of DEF, the specimens were sealed and placed in a climatic chamber with controlled temperature and humidity, to be heat-cured. The heat-curing cycle used (Santos Silva *et al.*, 2010a) 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 80° C after 15 hours and was maintained at temperatures above 70° C during 3 days. This cycle was computed by the TEXO program part of the CESAR-LCPC finite element design code (Divet *et al.*, 1998).

According to the DEF test method, following the heat-curing cycle, the concrete specimens were demolded and subsequently subjected to two drying-humidification cycles. Each cycle is composed of air drying at $38 \pm 2^\circ\text{C}$ during 7 days followed by immersion in tap water at $20 \pm 2^\circ\text{C}$. Afterwards, the concrete specimens are kept permanently immersed in water for long-term storage at $20 \pm 2^\circ\text{C}$. Length and mass measurements (3 cylinders by mix) were taken periodically in accordance to the accelerated test method MLPC No. 66 (Pavoine and Divet, 2007). The concrete mixes are reported in Table 2.

Table 1: Chemical and Bogue compositions of the materials used

	CEM I 42.5R <i>a</i>	LF	CEM I 42.5R <i>b</i>	CEM I 52.5R	CEM II A-L 42.5R
Chemical analysis (%)					
<i>SiO₂</i>	19.74	0.09	19.66	20.01	18.82
<i>Al₂O₃</i>	4.14	0.04	5.51	4.08	4.16
<i>Fe₂O₃</i>	2.69	0.06	3.40	4.14	2.94
<i>CaO</i>	63.54	55.66	63.12	64.29	61.97
<i>MgO</i>	2.42	0.10	1.90	0.86	0.83
<i>SO₃</i>	3.11	0.02	2.70	3.17	3.18
<i>K₂O</i>	0.64	0.04	1.03	0.65	0.64
<i>Na₂O</i>	0.08	0.02	0.22	0.41	0.41
<i>Na₂O_{eq.}</i>	0.50	0.05	0.90	0.84	0.83
<i>LOI</i>	3.13	43.23	2.44	1.85	8.12
Bogue Potential Compound Composition					
<i>C₃S</i>	62.7	-	50.4	60.8	60.7
<i>C₂S</i>	9.3	-	13.8	5.6	2.4
<i>C₃A</i>	6.4	-	9.1	3.9	6.6
<i>C₄AF</i>	8.2	-	10.6	12.8	9.7

Table 2: Concrete mixes

Designation of concrete mixes	Binder (14% v/v)		Aggregate		Water (20% v/v) (kg/m ³)
	Cement (kg/m ³)	Limestone filler (kg/m ³)	Coarse (46% v/v) (kg/m ³)	Fine (20% v/v) (kg/m ³)	
CEM I 42.5R <i>a</i>	442	-	1191	522	200
80CEM I 42.5R <i>a</i> + 20LF	354	88			
CEM I 42.5R <i>b</i>	444	-			
CEM I 52.5R	435	-			
CEM II A-L 42.5R	427	-			

Chemical Bulk Analysis of Concrete Samples

At different ages, concrete samples were removed from the water tank and, after drying at 40° C, they were crushed and ground to particle size < 106 μm. The alkalis and portlandite content determinations were done by atomic absorption spectrometry (AAS) and by thermogravimetric analysis (TGA), respectively.

Petrographic Examination and SEM-EDS Analysis of Concrete Samples

Fluorescence optical microscopy and scanning electron microscopy, coupled with X-ray energy dispersive microanalysis (SEM/EDS), were used to analyze the microstructural characteristics associated with the formation of DEF.

Polished and thin sections of each concrete composition were prepared after impregnation by vacuum with an epoxy resin with a fluorescent dye, to allow the observation at fluorescence microscopy. The impregnated samples were initially polished with 15 μm and 9 μm Al_2O_3 abrasive, and re-lapped with diamond pastes (6, 3 and 1 μm). After, they were sputtering with gold-palladium sputter-coater.

The thin section observations were performed on an Olympus BX60 petrographic microscope in polarized and fluorescent light, and images were recorded digitally.

SEM observations of polished sections were performed on a scanning electron microscope (SEM) JEOL JSM-6400 coupled with an OXFORD energy dispersive spectrometer Si(Li) X-ray detector (EDX), using backscattered electron – BEI images.

Results and Discussion

Expansion Tests

Figure 1 presents the obtained expansion curves of the concrete specimens tested according to the DEF test method, for the different cements types shown in table 1.

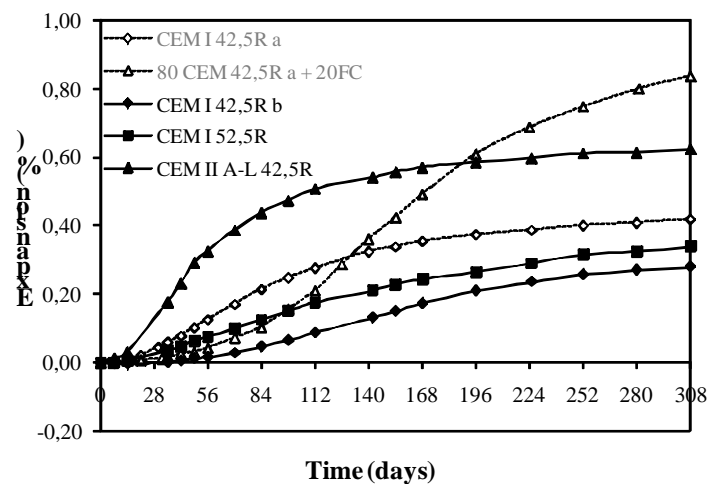


Figure 1: Expansion curves of the studied concrete mixes.

The expansion curves of the three CEM I types are quite similar. The final expansion appears to be related to both the SO_3 content and to the alkalis added to achieve a dosage of 5.50 kg/m^3 of $\text{Na}_2\text{O}_{\text{eq}}$. Comparing the two *a* and *b* CEM I 42.5R cement types it appears that the higher SO_3 cement content provides the highest expansion. When comparing the two cements with the same SO_3 content, “CEM I 42.5Ra” and “CEM I 52.5R”, the cement CEM I 42.5Ra present the highest expansion, which could be related to its highest C_3A content. However, it also appears that, for a SO_3 content of 3% a C_3A content of 3.9% is still not enough to prevent the expansion due to DEF, confirming the results already published by some authors (Taylor *et. al.*, 2001).

For the concrete mixes with limestone filler, the expansion kinetics was different that of mixes without limestone filler. The concrete with the CEM II A-L 42.5R has presented the shortest induction period, while the concrete composition 80CEM I 42.5Ra + 20LF has the highest expansion at 308 days (0.84%). This expansion behaviour may be related to the limestone filler content in these cements. The CEM II A-L 42.5R has about 14% of limestone filler, according the weight loss of 6.23% obtained between $500\text{-}900^\circ \text{C}$ by TGA, while the composition 80CEM I 42.5Ra + 20LF has 20% (by weight) of limestone filler. The particle size of limestone filler added to the concrete and the limestone in cement should not be the same. This difference may also have an effect on the final expansion. Fu *et al.* 1997 show greater swelling in the use of fine particles. According to Grattan-Bellew *et al.*, 1998, the swelling rate of mortars is inversely proportional to the average grain size.

Comparing all concrete mixes, we can verify that the limestone filler concrete mixes do not only inhibit the DEF formation, but instead increase the final expansion (0.84% for 80CEM I 42.5Ra + 20LF versus 0.41% for CEM I 42.5Ra).

The synergetic effect of the limestone filler on DEF, may be related to its role in the hydration reactions of portland cement. Some authors mention that the setting kinetics is improved, being the dormant period reduced and the hydration process accelerated (Poppe *et al.*, 2005). This situation increases the heat of hydration, and could promote a faster formation of DEF (Ye *et al.*, 2007).

To explain these phenomena two different hypotheses can be proposed. The first considers that the limestone filler is inert and therefore does not take part in the reactions during the hydration. Besides, the filler act as nucleation for hydration reaction of C₃S and C₂S around the cores of filler particles hydrate more quickly (Brunetaud *et al.*, 2005; Ye *et al.*, 2007). Another approach is starting from the principle that limestone filler is not inert and takes part in the hydration reactions. The limestone filler modifies the reactions, namely accelerating the ettringite formation, and secondly delays or even stop the ettringite conversion to monosulphoaluminate. After 3 days the carboaluminate is detected in the cement paste, providing a new source of sulphate ions in solution with possible DEF as consequence (Poppe *et al.*, 2005).

Chemical Analysis of Concrete Samples

The consumption of Ca(OH)₂ over time was followed by TGA - Figure 2. The limestone filler mixes do not show any reduction in Ca(OH)₂ content over time, as opposed to what happens when pozzolanic additions are used (Santos Silva *et al.* 2010b). Also, as expected, the Ca(OH)₂ content in the mixes with limestone filler is lower than in OPC mixes.

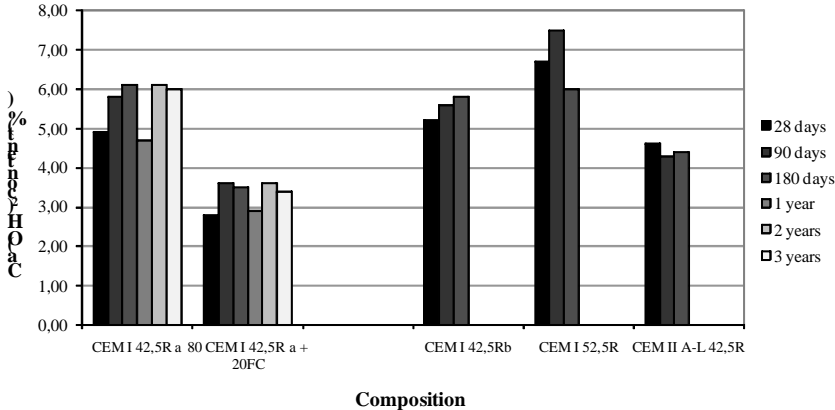


Figure 2: Evaluation of Ca(OH)₂ content by TGA of different concrete mixes over time.

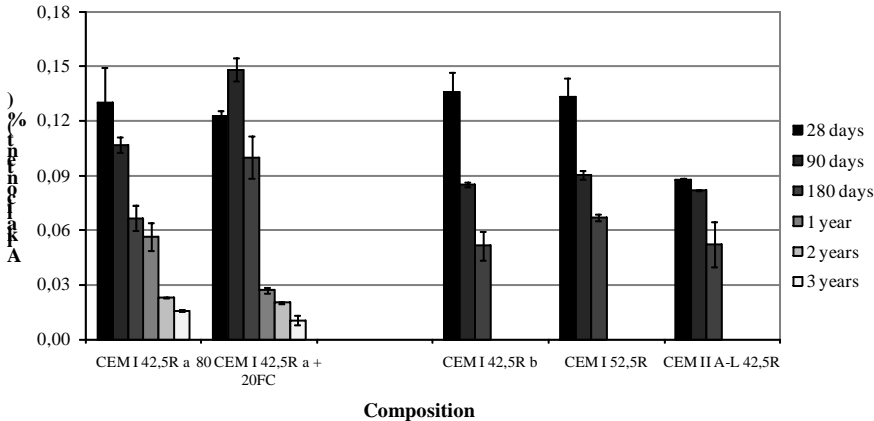


Figure 3: Evaluation of alkalis content by AAS of different concrete mixes over time.

The two mixes with limestone filler presents different Ca(OH)₂ contents, being higher in CEM II A-L 42.5R which showed higher kinetics expansion rate. According to this behaviour, the Ca(OH)₂ content

in cement paste seems to be also a crucial factor in the DEF kinetics, which is in accordance with the reduction in portlandite content by the pozzolanic additions, provided they are used in sufficient quantity..

The evolution of free alkalis content in the concrete cement paste is present in Figure 3. The obtained results didn't show any correlation with the expansion concrete behaviour, contradicting the hypothesis of the inhibition mechanism regarding the pozzolanic additions on DEF (Shehata and Thomas, 2000). Nevertheless for all concrete mixes, a strong alkaline leaching was observed during testing.

Petrographic Examination of Concrete Samples

The evolution in microporosity of cement paste was followed through petrographic observations in fluorescence mode. At the end of 28 days of expansion the CEM I 42.5Rb present the highest porosity, while the CEM II A-L 42.5R showed the highest compactness of the cement paste. It was clearly observed the densification of the cement paste with the age increase for all samples.

SEM Examination and EDS Analysis of Concrete Samples

As mentioned in petrographic observation, the concrete with the CEM I 42.5Rb is the less compact of all at the end of 28 days. At this age, the CEM II A-L 42.5R composition showed, besides being the most compact ones, having the greatest amount of calcium monosulfoaluminate in cement paste (Figure 5a). No ettringite was observed in any concrete composition. At the end of 90 days of testing, it is visible the presence of ettringite in all samples, being its major occurrence in the composition CEM II A-L 42.5 (Figure 5b). At the end of 80 days of testing, all the mixes show ettringite in considerable amount, but their location differs from composition to composition. In the composition CEM I 42.5Rb, the ettringite is mainly located in the paste/aggregates interfaces (Figure 5c), while in CEM II A-L 42.5R the ettringite is everywhere (Figure 5d).

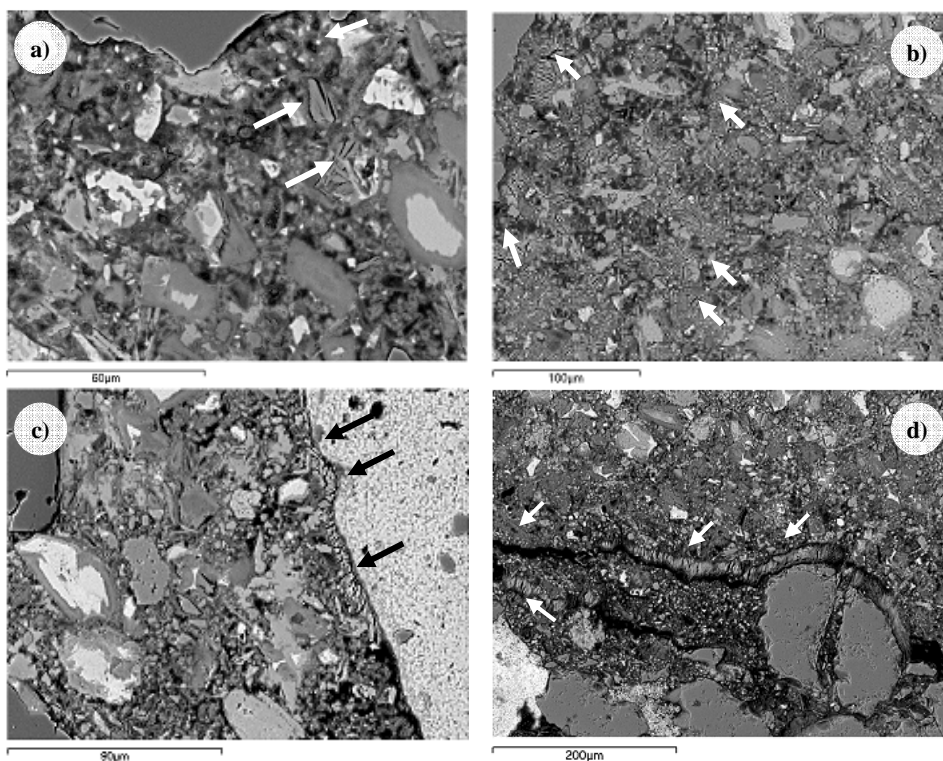


Figure 4: SEM images of concrete samples at several testing ages showing the different properties of the composition studies: a) CEM II A-L 42.5R _28 days; b) CEM II A-L 42.5R _90 days; c) CEM I 42.5Rb _180 days; d) CEM II A-L 42.5R _180 days.

Conclusion

The results show that the concrete mixes containing CEM II A-L or filler in substitution of OPC do not inhibit, but rather accelerate the expansion due to DEF using a thermal cycle to simulate the heating of a massive piece of concrete ($> 70^{\circ}\text{C}$ for 3 days). The synergetic effect of the limestone filler on DEF, which increases with the filler content, may be related with several phenomena associated to cement hydration, homogeneous cement paste swelling, pore distribution, morphology and location, and the amount of ettringite formed in the presence of fillers. It was confirmed that the SO_3 and C_3A cement contents are factors that must be taken in account regarding the inhibition of DEF. In particular, for cements containing 3% of SO_3 , a C_3A content of 3.9% is not sufficient to inhibit the formation of DEF. This research is on-going and the results obtained until now are only partially completed, however according to these findings, it was proposed that the ISR recommendations should prohibit this kind of mineral addition or limestone filler cements.

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