

INHIBITION OF INTERNAL EXPANSIVE REACTIONS IN CEMENT BASED MATERIALS WITH MINERAL ADDITIONS

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Keywords: RAS, DEF, Fly Ash, Metakaolin, Ground Granulated Blast-Furnace Slag, Silica Fume, Limestone Filler.

Abstract: The degradation of concrete structures caused by internal sulphate reaction, with delayed ettringite formation (DEF) and alkali-silica reaction (ASR) is a problem that affects many concrete structures worldwide (Divet et al., 2004). When these reactions occur their effects are particularly dangerous since their reaction products are extremely expansive causing the cracking of the concrete, contributing for a large reduction in the lifetime of the structure and in some extreme cases forcing its demolition. Hence, there is an urgent need to find preventive methods that may inhibit such reactions in new concrete structures. Today, it's well known that the use of supplementary cementitious materials, e.g. type II mineral additions, could sustain this degradation form. Moreover, their effect depends on the chemical and mineralogical composition and also the cement content replacement. This paper presents the findings of a long-term study (Santos Silva et al., 2006; Divet et al., 2006) on the expansion rate and microstructure of 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 by using the same cement type (CEM I 42.5R) and water/cement (w/c) ratio. The results of the blended-concrete compositions were compared with those of control compositions, and the conclusions were extracted.

1 INTRODUCTION

In the last years, around world, an increased number of concrete structures affected by expansive chemical reactions of internal origin have been diagnosed, namely by Alkali-Silica Reaction (ASR) and Delayed Ettringite Formation (DEF).

These reactions, which could be present simultaneously, origin products those are responsible for expansive stresses in the cement-based building materials, leading to severe cracking and loss of strength. The reaction products are also often amorphous or badly crystallized, or even present in very low content that they are very difficult to identify by current analytical physico-chemical techniques. The main macroscopic evidence of these degradation phenomena in concrete structures are the superficial occurrence of map-cracking, pop-outs and exudations.

ASR in concrete is a reaction that occurs between certain type of silica minerals in the aggregates and the alkaline pore solution of the cement paste. The reaction produces an alkaline

hygroscopic gel that absorbs water and expands, causing internal stresses in the concrete with cracking.

Degradation of concrete by internal source of sulphates seems to be related to the remobilization of sulphates included in the cementitious matrix due to excessive heating of the concrete during its initial 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, concrete preparation during summer, etc). The effect of DEF may be enhanced by the initial development of cracks due to alkali-silica reactions (ASR) or by some other factor, with ettringite crystallizing in these cracks and leading to additional expansion of the concrete.

The development of ASR and/or DEF in concrete depends on several factors that influence not only the beginning of their formation, but also the progression of these reactions. As an example of are some factors related to the composition of

concrete, such as the aggregate nature, type of cement, water/cement ratio, and environmental conditions, including temperature and humidity.

The prevention of these internal expansive reactions are normally carried out having in mind the elimination of at least one of the factors that promote them, namely, by the control of: the alkali reactivity of the aggregates; the alkali content of the concrete; the maximum temperature of the concrete; the aluminates and the sulphates of the binder; the humidity (the maintenance of the concrete in a relatively dry state); and the calcium hydroxide content of the concrete.

Another way to prevent the ASR and DEF is through the use of mineral additions in replace of one part of cement. It is believed that the 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.

The additions may be 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).

The work presented in this paper is part of an extensive study to elucidate the role that the mineral additions have in the mechanism of inhibition of ASR and DEF in concrete, presenting the results of the accelerated expansion tests which were complemented with the evaluation of the microstructure of the different concrete compositions.

2 EXPERIMENTAL PROGRAM

2.1 Materials

The chemical compositions, obtained by WD-XRF, of the materials used in concrete formulations are presented in Table 1, namely, two CEM I, and the mineral additions: FA, MK, GGBS, SF and LF.

Two control concrete compositions were produced: the first one using the CEM I *a*, a reactive siliceous limestone (0.22 % at 14 days according to RILEM AAR-2 method (RILEM, 2000) as coarse aggregate together with a non reactive limestone sand (0.00 % at 14 days according AAR-2); the second one with the CEM I *b* using a non reactive alluvial quartzitic as coarse and fine aggregate.

Table 1: Chemical composition and pozzolanic activity index of cement and mineral additions (% mass)

	CEM <i>I a</i>	CEM <i>I b</i>	FA	MK	GGBS	SF	LF
Chemical analysis							
SiO ₂	18.81	19.74	53.22	54.66	38.09	96.9	0.09
Al ₂ O ₃	5.15	4.14	23.20	37.98	9.38	0.52	0.04
Fe ₂ O ₃	3.18	2.69	5.85	1.22	0.89	0.14	0.06
CaO	63.70	63.54	5.36	0.01	36.24	0.58	55.66
MgO	1.50	2.42	1.63	0.46	7.40	0.00	0.10
SO ₃	2.69	3.11	1.00	0.01	0.27	0.13	0.02
K ₂ O	1.02	0.64	1.42	3.09	0.52	0.42	0.04
Na ₂ O	0.19	0.08	0.44	0.00	0.25	0.04	0.02
Na ₂ O _{eq.}	0.86	0.50	1.37	2.03	0.59	0.32	0.05
LOI	3.18	3.13	5.16	0.94	2.66	1.47	43.23
Poz.. Act. Index (%)							
28-day	-	-	87	118	88	41	76
90-day	-	-	101	119	94	45	72

The concrete compositions were prepared in accordance with RILEM AAR-3 test method for ASR (RILEM, 2000) (equivalent to ASTM C 1293). During this test the concrete remains in a climatic chamber at $38 \pm 2^\circ \text{C}$ and a relative humidity $> 95\%$.

Besides the ASR test conditions, some concrete compositions prepared with the CEM I *a* and *b* were casted and tested in accordance to the French concrete performance test for DEF accelerated concrete performance LPC test method (Pavoine et al., 2003).

2.2 Expansion testing

The concrete specimens (prisms and cylinders) were cast using 440 kg/m^3 of cementitious material, a water/binder = 0.45, and with an alkali content of 5.50 kg of Na₂O_{eq.} by cubic meter of concrete, calculated on the basis of available alkalis from the cement, additions and added NaOH. Mix compositions are reported in Table 2.

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 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. After, concrete specimens are kept permanently immersed in water for long-term storage at $20 \pm 2^\circ \text{C}$. Length and mass measurements were taken periodically in accordance to the accelerated concrete performance French test LPC n° 66 (LCPC, 2007).

Table 2: Concrete mixtures

Cement, aggregate and replacement type	Control	FA	MK	GGBS	SF	LF
		(%)	(%)	(%)	(%)	(%)
CEM I a, siliceous limestone, % volume	1	20	20	-	-	-
		40	-	-	-	-
		60	-	-	-	-
		-	5	-	5	-
CEM I b, quartzitic aggregate, % mass	2 ($T_{\text{max}}=80^\circ \text{C}$ C e 20°C)	10	10	10	10	10
		15	15	15	-	15
		20	20	20	-	20
		30	-	-	-	30
		-	-	40	-	-

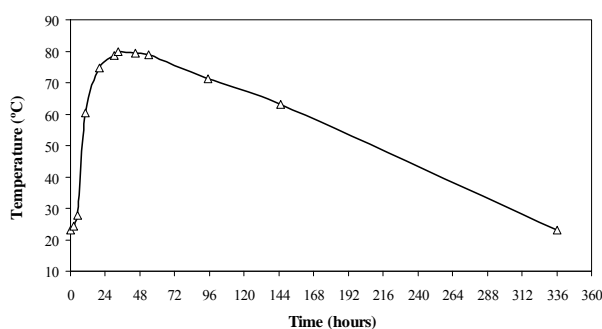


Figure 1: Concrete heat-curing cycle used to promote the occurrence of DEF.

2.3 Petrographic examination and SEM-EDS analysis, of concrete samples

Microscopy is the only technique capable to clearly identify the features associated with ASR and DEF in concrete, namely the distribution and the morphology of the reaction products in cement paste.

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

Thin and polished sections of each concrete mix were prepared in an IU-30 Logitech impregnation unit by vacuum with an epoxy resin. The impregnated samples were polished in a PM5 Logitech lapping/polishing machine with 15 μm and 9 μm Al_2O_3 abrasive. Besides that, polished sections were re-lapped with diamond pastes (6, 3 and 1 μm). After, they were sputtering with gold-palladium in a Baltec sputter-coater.

The observations of thin sections 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.

3 RESULTS

3.1 Expansions testing

Figure 2a and 2b present the expansion curves according, respectively, ASR and DEF test methods, for concrete mixtures with limestone aggregates with 440 kg/m^3 of cementitious material and a water/binder = 0.45. Each value on these curves represents the average of 3 measurements on three specimens.

As shown in figure 2a, at one year, the expansion of control specimens is lower than 0.04 %, the threshold limit established by RILEM AAR-3. The result of the test is negative, concerning potential risk of ASR, and could be explained by a possible marginally reactive composition as predicted in the AAR-3 method. However, the measurements after one year have shown an increase in the expansion that confirms the reactive behaviour of coarse

aggregate, previously evaluated by petrographic analysis and by the mortar-bar accelerated AAR-2 test method.

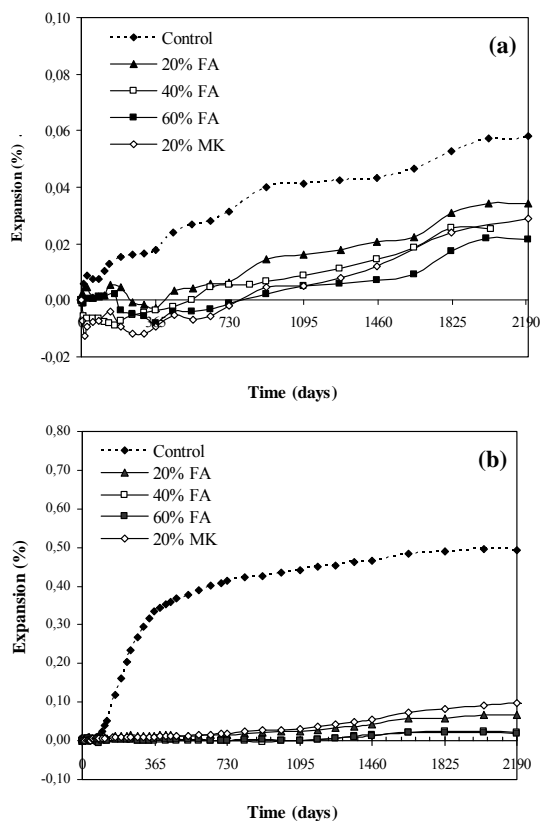


Figure 2: Effect of various levels of replacement (% volume) of FA or MK on expansion of concrete with limestone aggregates with 440 kg/m^3 of cementitious material and a water/binder = 0.45. Expansion due to (a) ASR and (b) DEF.

From figure 2a it can also be observed that 20% of FA or MK was effective in inhibiting the expansion by ASR, since a threshold expansion level of 0.06% at 6 years is normally used to evaluate the effectiveness of the additions in the ASR control (Bleszynsky et al., 2000). Results indicate that 20% of MK is more effective than 20% of FA in ASR control.

Figure 2b summarizes the 6-years expansion results of heat-cured concrete, tested accordingly LPC method (LCPC, 2007). As shown in the figure 2b, 20% of FA or 20% of MK (volume replacement) were effective in reducing the expansion by DEF when compared with control mixture. The control concrete expanded more than 0.50% at 6 years, while mixtures with FA or MK present no

appreciable expansion (not more than 0.10% with 20% MK and 0.08% with 20% FA). These results are in agreement with the results of Ramlochan (Ramlochan et al., 2003) obtained for mortar samples.

Figure 3a to 3e present the obtained expansion curves of specimens tested according to the DEF test method, for mixtures with or without mineral additions (mass replacement) with quartzitic aggregates. In these concrete compositions the content of binder and water/binder ratio are the same of the concrete mixes with cement volume replacement. The results clearly show that, in general, the mineral additions have a strong effect in the inhibition of the expansion due to DEF (Fig. 3a, b, c and d), with the exception of LF, for which there is an increase in expansion (Fig. 3e).

At 3 years (approximately 1092 days), the expansion of control specimens is 0.50%. The expansion tests are still ongoing, but the results obtained until now show that 15% (% mass) replacement of cement by FA is enough (0.06%) for inhibition of expansion due to DEF. With MK or SF, the same effect is obtained with 10 % replacement (0.06% and 0.03% of expansion, respectively). With GGBS, we need a 40% replacement to achieve the approximately the same level of inhibition (0.01%). These different behaviours of minerals additions, concerning the percentage content of cement replacement, seems to be related with their pozzolanic activity, which is more intense for SF and MK (Table 1).

The results obtained with LF mixtures show that this addition is not capable of inhibit the expansion by DEF. This absence of effectiveness could be attributed to the non pozzolanic action of this addition. The results also show that mixtures with LF expand more ($\sim 1.00\%$ of expansion) than the control concrete and the expansion increase with the amount of cement replacement.

Figure 4 shows the expansion curves obtained for control composition, with and without heat-curing treatment. The results obtained show that the concrete without heat-treatment as an expansion of 0.05%, in opposition to the heat-treated that as 0.50% expansion at 3 years. These results clearly validate, for the same concrete composition, the DEF dependence on the imposed external heat-curing conditions.

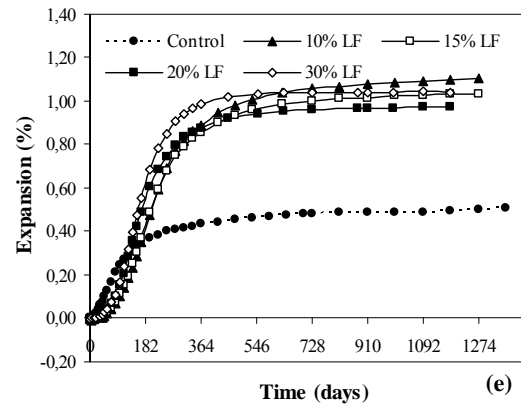
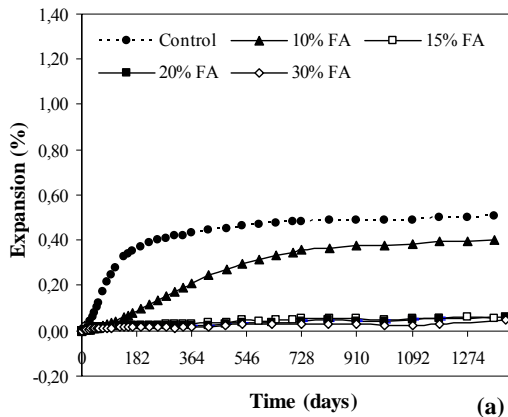


Figure 3: Effect of different levels of replacement (% mass) of FA (a), MK (b), GGBS (c), SF (d) or LF (e) on expansion due to DEF on concrete with quartzitic aggregates with 440 kg/m^3 of cementitious material and a water/binder = 0.45.

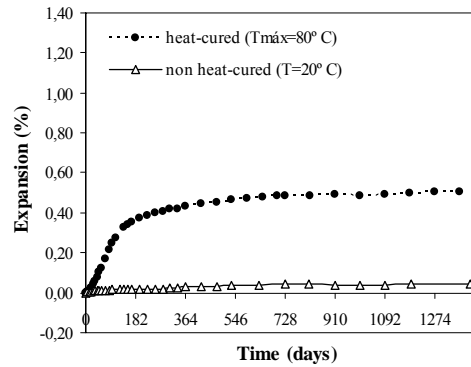
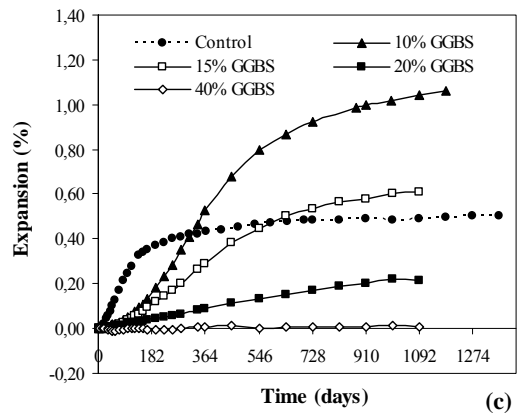
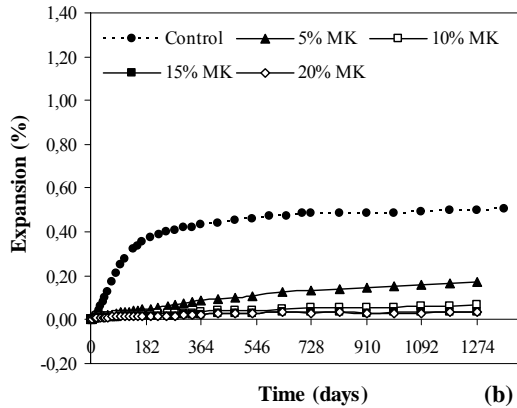
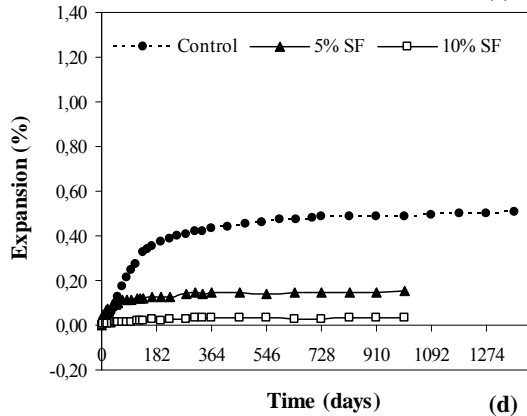


Figure 4: Effect of thermal treatment on expansion due to DEF on concrete with quartzitic aggregates with 440 kg/m^3 of cementitious material and a water/binder = 0.45.



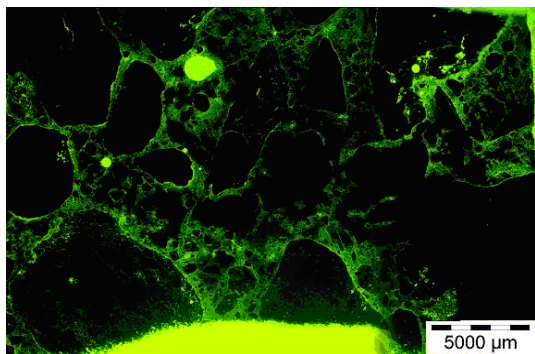
3.2 Petrographic examination of concrete samples

The polarized microscopy is normally used to detect ASR symptoms, namely microcracks and gels around or inside aggregate particles. But 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, but comes more easily detected in the fluorescent mode.

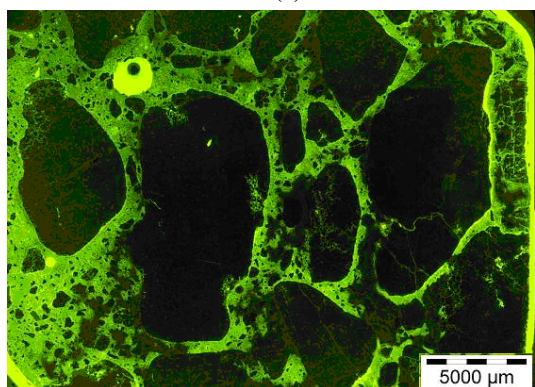
The observations performed by optical microscopy in the fluorescence mode, shown easily that the limestone filler compositions have at 28 days of test, in comparison with the others mixes

and for the same level of cement replacement, the higher porous pastes (Figure 5).

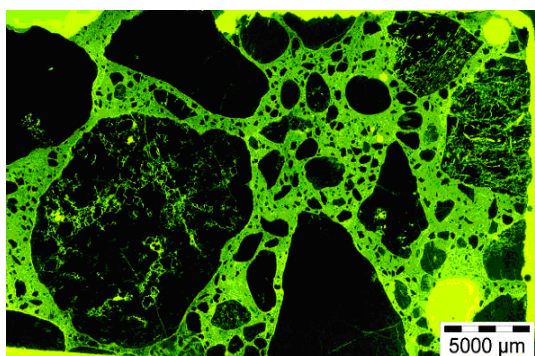
Besides, the compositions that have presented the biggest expansion values showed at petrographic microscope the occurrence of veins of ettringite around aggregate particles and in the paste (Figure 6).



(a)

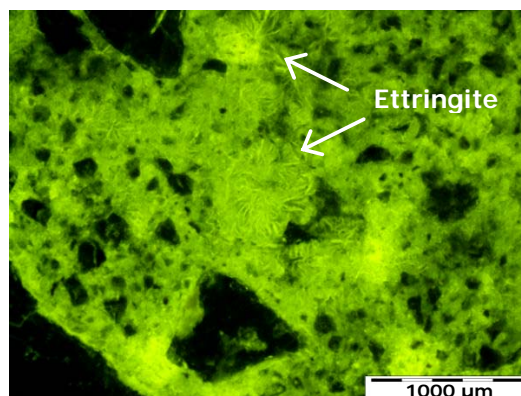


(b)

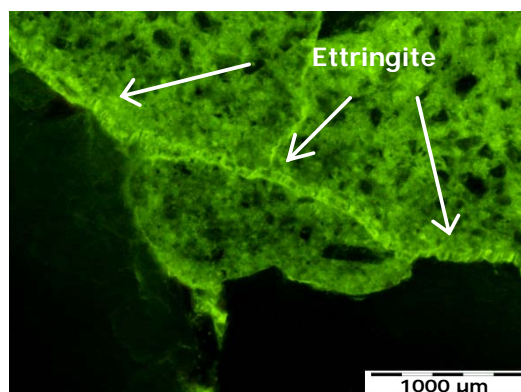


(c)

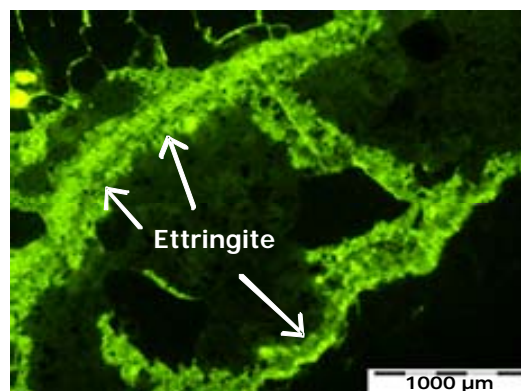
Figure 5. Images of a concrete samples, in fluorescence mode, showing microporosity: (a) Control with 28 days of test; (b) 10GGBS with 28 days of test; (c) 10LF with 28days of test.



(a)



(b)



(c)

Figure 6: Images of a concrete samples, in fluorescence mode, showing ettringite (Et): (a) 10 LF with 2 years of test; (b) 20 LF with 1 year of test; (c) Control with 2 years.

The results allow identifying some correlations between some properties studied, namely 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 the

middle of paste. 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 LF and Control compositions have, in comparison with the others mixes and for the same level of cement replacement, the less compact paste and also with the lowest air-voids content.

3.3 SEM examination and EDS analysis of concrete samples

The observation of samples of the concrete petrographic microscope were complemented by their observation by SEM/EDS, which allows the confirmation of the chemical composition of expansive products, its morphology and the microporosity and the amount of clinker grains in the hydrated cement paste.

In Figure 7, we observe the microporosity of the samples at 28 days of test, which decreases in the order: Control < 10GGBS < 10LF, confirming the petrographic observations (figure 5).

Accordingly these results we didn't have an explanation for the expansive behaviour of the limestone filler compositions.

From the literature, the influence of the filler materials on the hydration of the cement, in particular limestone filler, is in most cases considered to be limited to the rate of the cement hydration. 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 C_3S and C_2S around the cores of filler particles hydrate more quickly (Ye et al., 2007).

On the other hand, another approach is starting from the principle that limestone filler is not inert and does not only act as an activator for some reactions, but actually takes part in the hydration reactions. Firstly, ettringite formation is accelerated by the presence of the filler, and secondly, the ettringite conversion to monosulphoaluminate is delayed or even stopped when a large amount of carbonate is present in the paste. This compound

was also found by other researchers at different times related to the C3A content of the cement. This hydration product is probably supplied by the transformation of monosulphoaluminate to monocarboaluminate, the latter compound being more stable (Poppe et al., 2005).

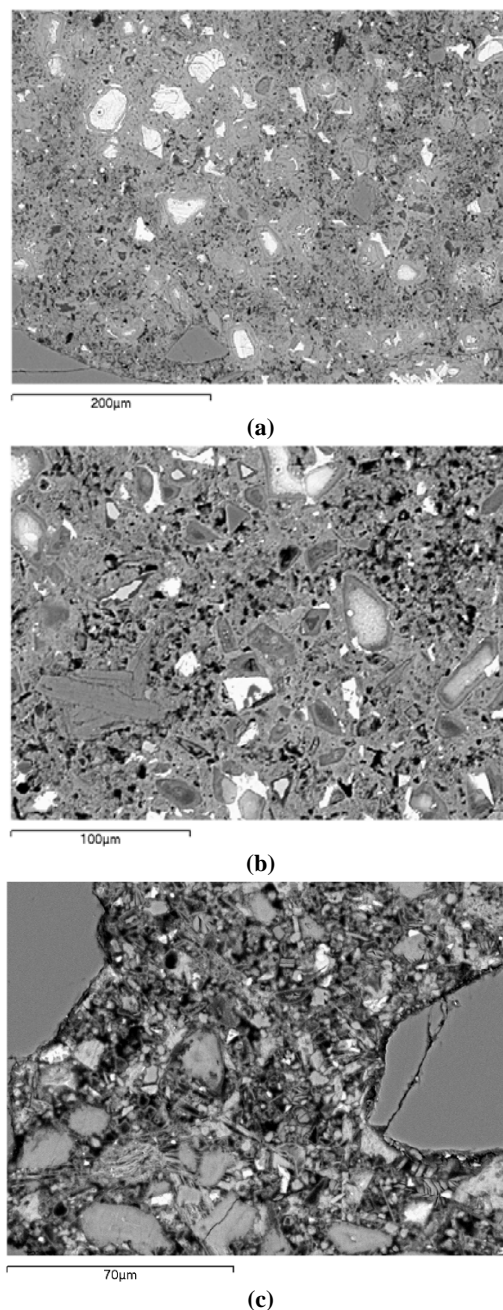


Figure 7: SEM images of samples of concrete showing different microporosity of the samples: (a) Control with 28 days of test, (b) 10 GGBS with 28 days of test, (c) 10LF with 28 days of test.

4 CONCLUSIONS

The results obtained at present suggest that the efficiency of mineral additions in the inhibition of ASR and DEF depends on the type of mineral addition, and only those of additions type II are effective.

For DEF inhibition a replacement cement rate (% mass) of 15% FA, 10% MK, 40% GGBS and 10% r SF seems to be, at moment, sufficient.

The mechanism of ASR and DEF suppression, and how the mineral additions act at this level, could be related with their efficiency in the alkalinity of the cement paste reduction, but these findings are still ongoing.

The most important feature observed until now is that the limestone filler is not efficient in the DEF mitigation, and even seems that improves the expansion due to ettringite formation. The reaction mechanism of the Portland cement is clearly influenced by the limestone filler and it's supposed that this occurs due to an acceleration of the hydration reactions, increasing the heat of hydration and that promotes the formation of DEF.

ACKNOWLEDGEMENTS

The authors wish to acknowledge the Fundação para a Ciência e Tecnologia (FCT) for the financial support under project EXREACT (PTDC/CTM/65243/2006) and project DURATINET for Transnational Programme of Atlantic Area 2007-2013, co-financed by FEDER.

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