INHIBITION OF ASR AND DEF: EVALUATION OF THE MICROSTRUCTURE OF CONCRETE MIXES WITH POZZOLANIC ADDITIONS

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Abstract

The use of pozzolanic mineral additions is a known method to inhibit the expansive chemical reactions in concrete, like the alkali-silica reaction (ASR) or the delayed ettringite formation (DEF).

The ASR is a chemical reaction that occurs between certain types of minerals present in aggregates and alkali and hydroxyl ions present in the interstitial solution of cement paste in concrete. This reaction involve the dissolution of amorphous or poorly crystallized forms of silica, in alkaline medium, with the formation of an alkaline hygroscopic gel that absorbs water and expands, creating internal stresses in the concrete with cracking. The DEF is a pathology related with the formation of expansive ettringite due to an excessive heating of the concrete during the cure that induces swelling, cracking and decrease of the mechanical properties of the hardened concrete.

This paper presents the results of SEM/EDS analysis of concrete mixes with different pozzolanic materials, like metakaolin, biomass fly ash, natural pozzolan and mine sludge from a tungsten mine. The microstructural evaluation is discussed and correlated with the expansion data of each concrete mix.

Keywords: ASR, DEF, Scanning electron microscopy (SEM), microstructure, pozzolanic additions

Introduction

The degradation of concrete structures caused by internal expansive reactions (IER), which includes internal sulphate reaction (ISR) and alkali-silica reaction (ASR) is a problem that affects many concrete structures worldwide. 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.

The ASR is essentially an attack on certain forms of reactive silica, possessing a more or less disordered silica structure and therefore unstable in an environment of high pH, by alkali ions (Na^+ and K^+) and hydroxyl (OH^-) present in the pore solution of concrete.

The concrete degradation by internal sulphate reaction (ISR) 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 delayed ettringite formation (DEF). 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 (clinker, alkalis, SO_3 and C3A contents), water/cement ratio, and environmental conditions, including temperature and humidity.

The use of mineral admixtures to replace a part of the cement can be an effective mitigation measure. It is thought that the additions to react with $Ca(OH)_2$, to form compounds similar to those of hydrated cement hydration, such as hydrated calcium silicates (CSH), to reduce the alkalinity of the medium avoiding the formation of expansive products. Within the context of mitigation of expansive reactions, additions of type II are the ones that are effective. These can be either pozzolanic (e.g. fly ash – FA, metakaolin – MK, etc.) or latent hydraulic (e.g. ground granulated blast-furnace slag – GGBS) (Santos Silva, 2010a; 2010b).

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 mortars and concretes, and presents the results of the accelerated expansion tests which were complemented with the evaluation of the microstructure of the different mortar and concrete compositions.

Test conditions and materials

The study of the effect of mineral admixtures in IER was carried out through specific methods suitable for each type of reaction. In the ASR study we have used the ASTM C 1567 accelerated mortar bar-test (ASTM C 1567-08, 2008), equivalent to the ASTM C 1260 (ASTM C 1260, 2001) or RILEM AAR-2 (RILEM, 2000). The prismatic mortar specimens were casted using a cement CEM I 42.5 R (CEM *a*) and a reactive aggregate (0.30% at 14 days, according to ASTM C 1260). Mineral additions were incorporated as a partial cement replacement by mass.

In the study of DEF concrete cylindrical specimens were cast and tested according to the accelerated method MLPC No. 66 for evaluation of DEF in concrete (Pavoine and Divet, 2007). A cement CEM I 42.5 R from another source (CEM *b*) was used with a nonreactive quartzite aggregate (coarse and fine). Mineral additions were also incorporated as a partial cement replacement by mass.

The chemical compositions of the materials used in this study are given in Table 1. The mineral additions (fly ash (FA), metakaolin (MK), ground granulated blast-furnace slag (GGBS), limestone filler (LF), tungsten mine sludge's (TMS) and biomass fly ashes (BFA1 and BFA2) were dry blended with the cement prior to mixing. In the case of biomass fly ashes, two types were employed: BFA1 from co-generation process of a pulp paper industry and BFA2 from biomass burning in a thermal power plant.

Table 1: Chemical compositions and ignition loss LOI of cement and mineral additions (in wt %), and some calculated parameters.

	CEM *a*	CEM *b*	FA	MK	GGBS	LF	TMS	BFA1	BFA2
main constituents + LOI									
SiO$_2$	18.81	19.74	53.22	54.66	38.09	0.09	62.57	25.10	52.10
Al$_2$O$_3$	5.15	4.14	23.20	37.98	9.38	0.04	18.62	0,07	13.30
Fe$_2$O$_3$-total	3.18	2.69	5.85	1.22	0.89	0.06	9.99	5.18	5.30
CaO	63.70	63.54	5.36	0.01	36.24	55.66	n.d.	40.10	15.90
MgO	1.50	2.42	1.63	0.46	7.40	0.10	2.15	6.63	3.31
SO$_3$	2.69	3.11	1.00	0.01	0.27	0.02	n.d.	1.12	0.45
Cl	n.d.	n.d.	n.d.	n.d.	0.01	n.d.	n.d.	0.25	0.10
TiO$_2$ + P$_2$O$_5$	n.d.	n.d.	1.87	0.49	n.d.	n.d.	1.10	2.64	2.57
K$_2$O	1.02	0.64	1.42	3.09	0.52	0.04	4.01	2.07	4.14
Na$_2$O	0.19	0.08	0.44	0.00	0.25	0.02	0.45	3.61	1.05
LOI	3.18	3.13	5.16	0.94	2.66	43.23	0.34	13.34	3.73
SUM Total	99.42	99.49	99.15	98.86	95.70	99.26	99.23	100.11	101.95
calculated parameters									
Na$_2$O$_{eq.}$	0.86	0.50	1.37	2.03	0.59	0.05	3.09	4.97	3.95
PAI-28d	-	-	87	118	88	76	74	-	-
PAI-90d	-	-	101	119	94	72	85	-	-

PAI: Pozzolanic Activity Index (%) conform EN 450-1:2005+A1:2007

$_2$O$_{eq.}$:.(wt% Na$_2$O + 0.658 wt% K$_2$O)

n.d: not determined

Expansion tests

ASR – Expansion tests in mortar bars

ASTM standard 25 × 25 × 285 mm mortar prisms were cast according the test method ASTM C 1567-08. This test consists in monitoring the variation in length of mortar bars made with a water/cementitious rate of 0.47 (ASTM C 1567-08, 2008). In some blended mixes a water-reducer was used to provide an adequate dispersion and workability of the mixture. The quantity of water-reducer was controlled in order to maintain a flow of ± 7.5% of a control mortar without mineral addition, as determined in accordance with ASTM C 1437

test method (ASTM C1437-07, 2007). The specimens were demoulded 24 hours after mixing, placed in water at 23° C and after in a climatic chamber at 80° C for a further 24 hours, after which it was made the initial measure (zero) for each specimen. Then, the specimens were placed in a solution of NaOH 1M at 80° C where they remained 14 days, and expansion was assessed at standard intervals during this period. For a given reactive aggregate, the rate of incorporation of mineral additions is considered effective when the expansion at 14 days is below 0.10% (ASTM C 1567-08, 2008; Santos Silva, 2005). In this study, the expansion measurements have been extended until at least 28 days in order to evaluate the expansion behavior of the blended mixes at the largest age. The mortar mixes are reported in Table 2.

Table 2: Mortars mixes used in the ASR study.

Designation of mortars mixes	Cementitious material			Aggregate	Water
	Cement (CEM *a*)	Addition (mass replacement in)			
	g	g	%	g	ml
100 CEM	440	0	0	990	207
20 FA	352	88	20		
20 MK	352	88	20		
40 GGBS	264	176	40		
30 TMS	308	132	30		
20 BFA1	352	88	20		
20 BFA1 + 10 MK	308	132	30		
20 BFA2	352	88	20		
20 BFA1 + 10 MK	308	132	30		

DEF – Expansion tests in concrete

The concrete specimens were cast using 440 kg/m^3 of cementitious material, a water/cementitious rate of 0.45, and with a constant alkali content of 5.50 kg of Na$_2$O$_{eq}$/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 development of DEF, specimens were sealed and placed in a climatic chamber with controlled temperature and humidity, to be 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 80º C after 15 hours and was maintained at temperatures above 70º 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).
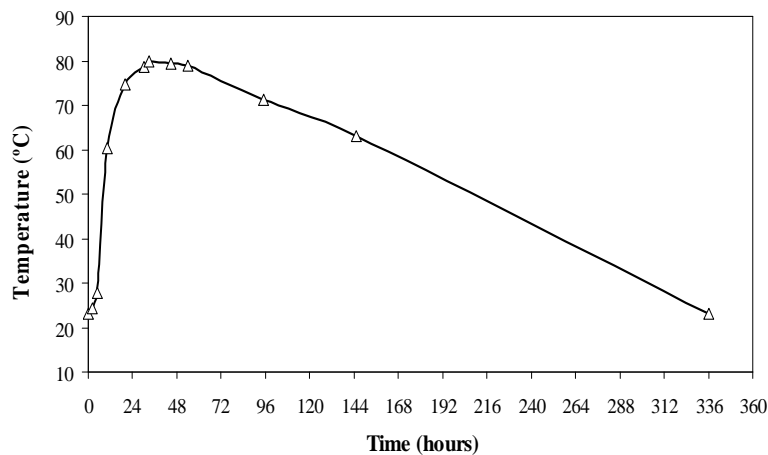

Figure 1: Concrete heat-curing cycle used to promote the occurrence of DEF.

According to the DEF test method, following the heat-curing cycle, the concrete specimens were demoulded and subsequently subjected to two drying-humidification cycles. Each cycle is composed of air drying at 38 ± 2ºC during 7 days followed by immersion in tap water at 20 ± 2ºC. Afterwards, the concrete specimens are kept permanently immersed in water for long-term storage at 20 ± 2º C. Length and mass measurements (3 cylinders per 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 3.

Table 3. Concretes mixes used in the DEF study.

Designation of concrete mixes	Cementitious material			Aggregate		Water
	Cement (CEM *b*)	Addition (mass replacement in)		Coarse	Fine	
	kg/m^3	kg/m^3	%	kg/m^3	kg/m^3	l/m^3
100 CEM	442	0	0			
10 FA	398	44	10			
15 FA	376	66	15			
5 MK	420	22	5			
10 MK	398	44	10	1191	522	200
10 GGBS	398	44	10			
40 GGBS	265	177	40			
20 LF	398	44	20			

SEM/EDS analysis of cement paste in mortars and concretes

SEM/EDS analysis is a widely accessible instrumental technique for reliable assessment of spatial distribution and phase morphology of ASR and DEF in concrete and mortars.

Polished sections of one or more mortar bars from each mix were prepared under vacuum with epoxy in an IU-30 Logitech impregnation unit by vacuum with an epoxy resin. The impregnated samples were pre-polished in a PM5 Logitech lapping/polishing machine with 15 μm and 9 μm Al_2O_3 abrasive, and re-lapped with diamond pastes (6, 3 and 1 μm), prior to sputtering with gold-palladium in a Baltec coater.

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. Besides, to evaluate the morphology and composition of the ASR products SEM observations of broken surfaces were also performed using secondary electron image mode.

The composition of CSH gel was measured by EDS analysis, particularly in terms of Ca/Si and Na_2Oeq content. The analysis were performed on BEI images in location where CSH gel was sufficient thick to minimize the contribution of other phases. To obtain an idea of possible variation and spread in gel composition, approximately 20 to 25 EDS microanalysis were taken for each mix (Santos Silva, 2005).

Results and discussion

Expansion tests

ASR – Expansion tests in mortar bars

Figure 2 presents the mortars expansive behavior according the ASR test method ASTM C 1567-08 for the different mixes shown in table 2.
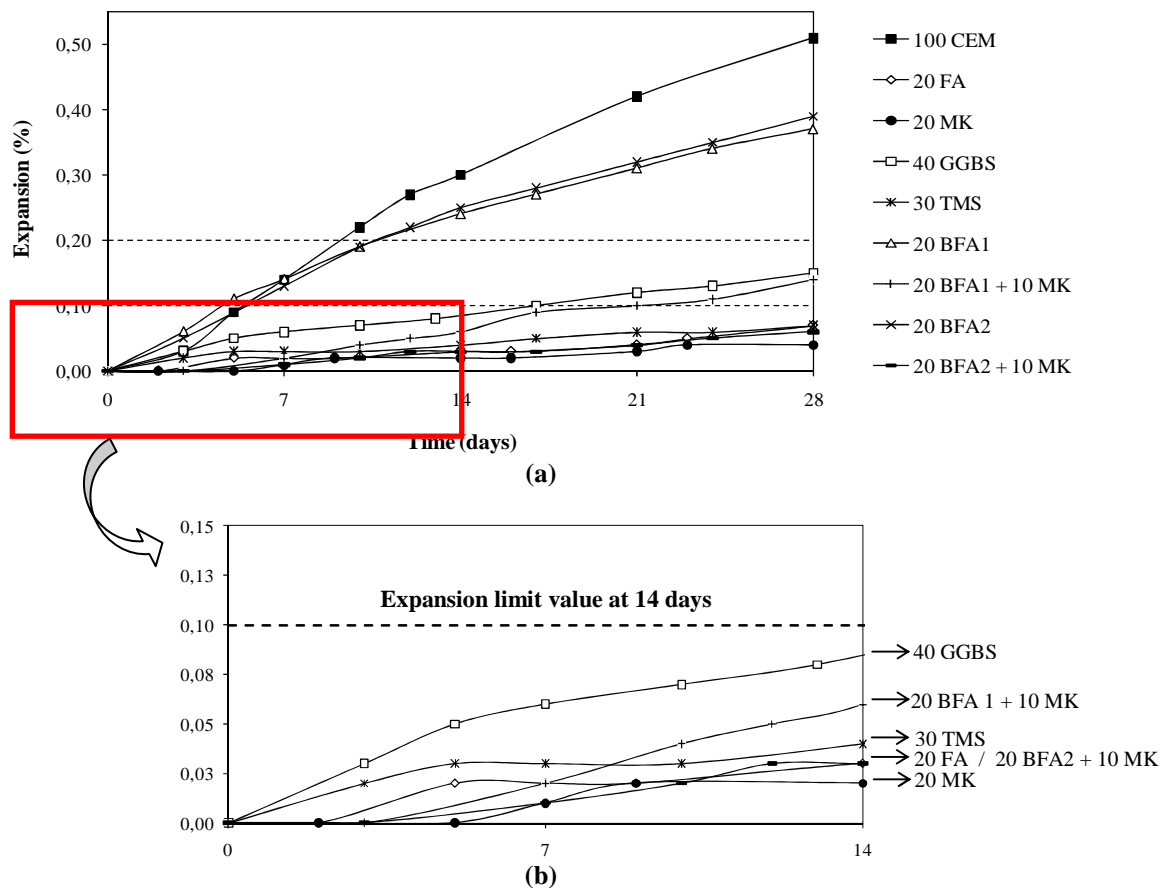
Figure 2: (a) Effect of type and content of mineral addition (% mass) in inhibition of ASR in ASTM C 1567-08 mortar bar method; (b) evidence of the compositions with less than 10% expansion at 14 days of tests.

With exception of BFA1 and BFA2, the results show that all type II mineral additions are effective in mitigation of expansion due to the ASR, related to the type and content of each mineral addition used.

The 20% metakaolin mortar (20 MK), such as 20% fly ash (20 FA), are the mixes that show the higher reduction of expansion, being the MK more effective in this action. The 30% tungsten mine sludge mortar (30 TMS) presents a similar level of expansion reduction, and also the 30% BFA2 fly ash with metakaolin mortar (20BFA2 + 10MK). The reduction in expansion with BFA2 was only possible with the incorporation of MK, proving once again the high mitigation effect of the MK. This MK performance could be related to its high portlandite consumption and alkali binding efficiency through pozzolanic reaction (Ramlochan et al., 2003).

The 40% ground granulated blast-furnace slag mortar (40 GGBS) and the 30% BFA1 biomass fly ash with metakaolin mortar (20BFA1 + 10MK) are both effectives in the mitigation of ASR, however less than the previous mixes. Together, this might suggest that the effectiveness of a given mineral addition at reducing the expansion is related on its chemical composition and pozzolanic activity. In fact, the 20% biomass BFA1 and BFA2 mortars are not effective in the inhibition of the ASR expansion, as noted above. These biomass fly ashes are both the ones with the highest level of Na_2O_{eq} (Table 1), which could explain its lower efficacy in the ASR inhibition. The alkali content of the mineral additions is a well known factor that explains why some materials of same type are more or less effectives in controlling expansion (Shehata and Tomas, 2010). However, it appears that the BFA when used in combination with a very pozzolanic addition, as the MK, can be more efficient in the ASR inhibition. This result indicates a typical behavior of a geopolymer, a material that are known to be effective in the ASR inhibition (Torgal et al., 2007; 2008).

DEF – Expansion tests in concrete cylinders

Figures 3 and 4 present the obtained expansion curves of specimens tested according to the DEF test method MLPC No. 66, for mixes with and without mineral additions (Santos Silva et al., 2010a).
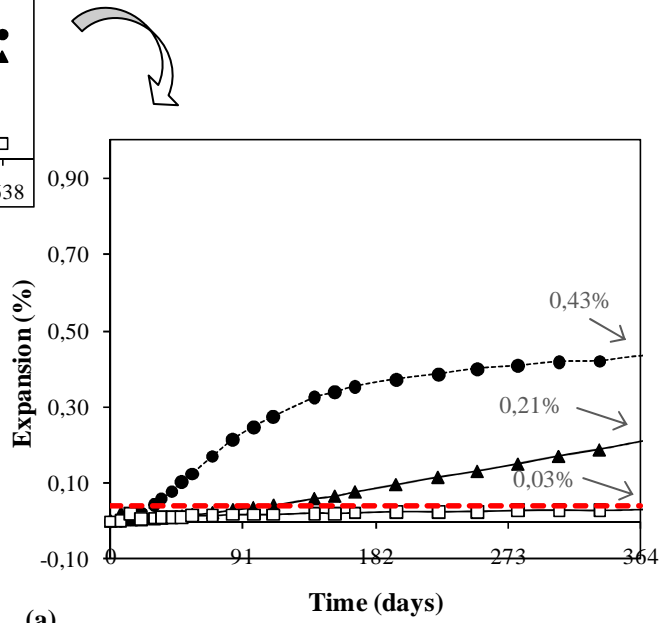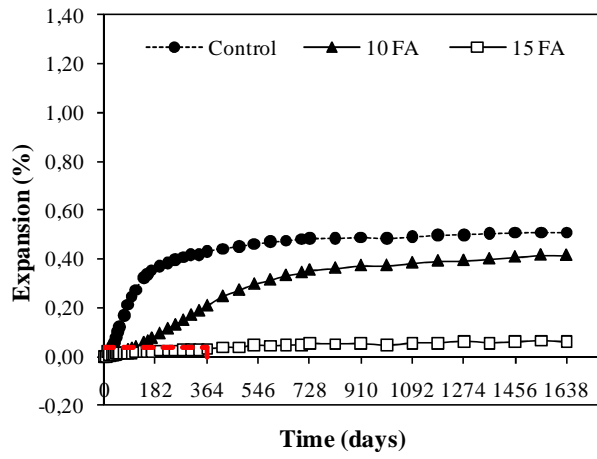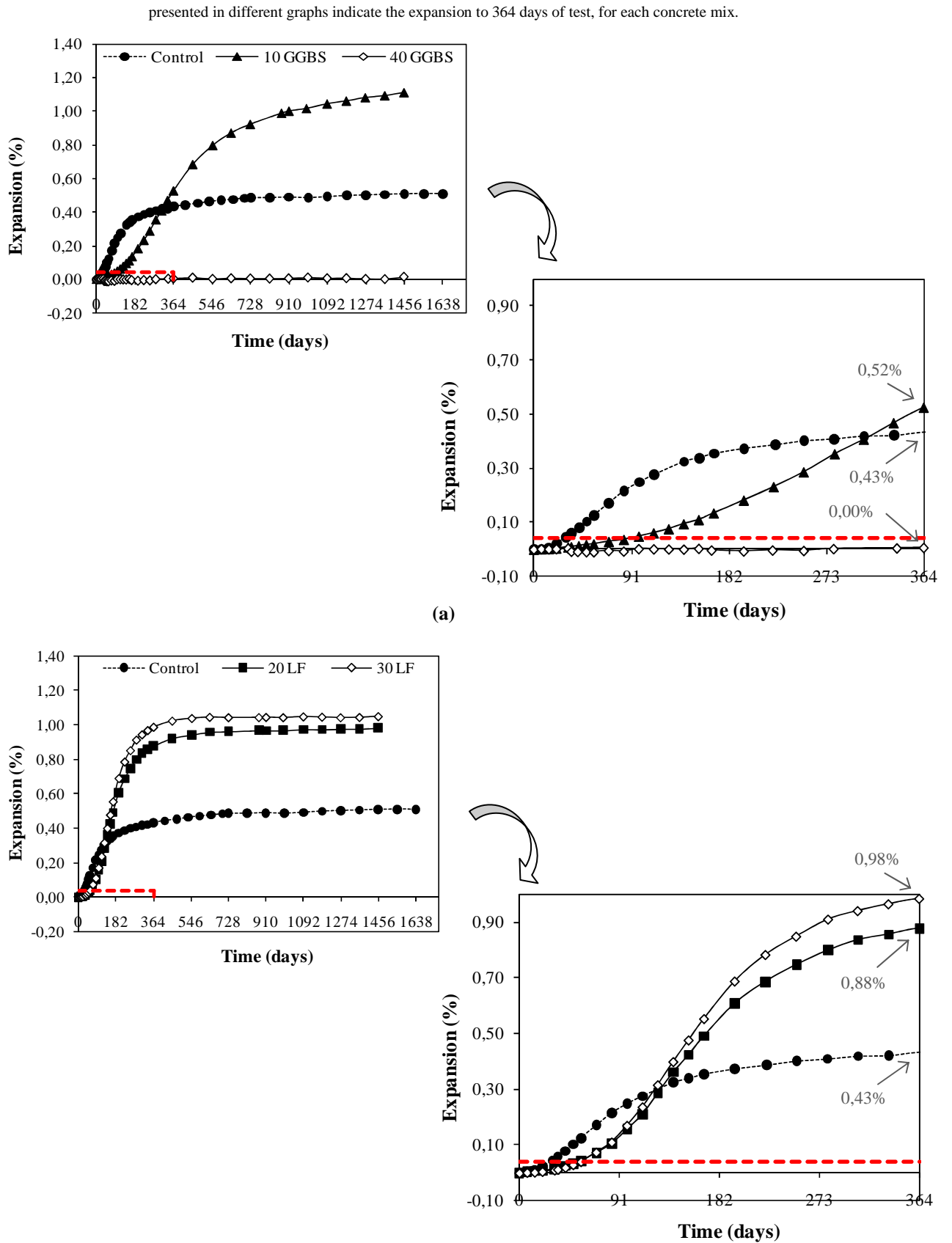
(a)
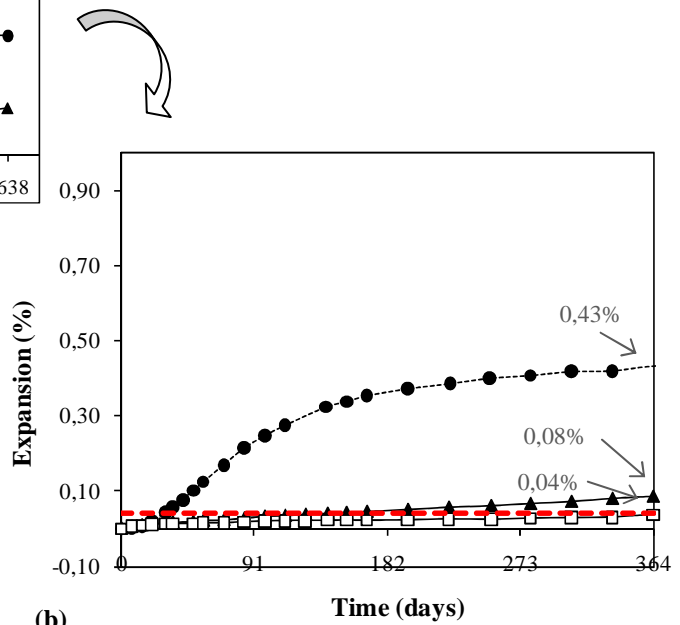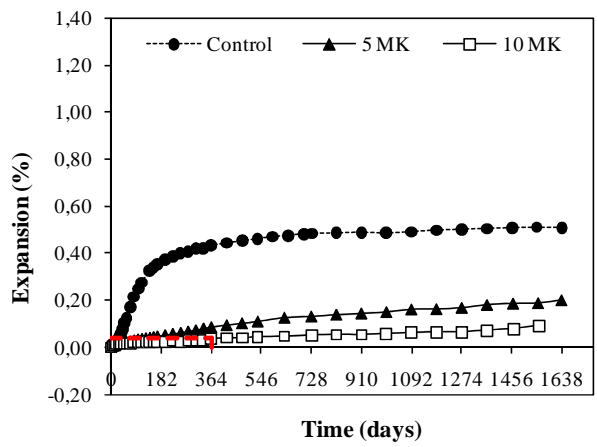
(b)

Figure 3: Effect of different levels of replacement (% mass) of (a) FA and (b) MK, on expansion due to DEF on concrete. The values (in %)

presented in different graphs indicate the expansion to 364 days of test, for each concrete mix.

(a)

(b)

Figure 4: Effect of different levels of replacement (% mass) of (a) GGBS and (b) LF, on expansion due to DEF on concrete. The values (in

%) presented in different graphs indicate the expansion to 364 days of test, for each concrete mix.

The results clearly show that, in general, the mineral additions, when present in sufficient replacement content as have like in ASR process, a strong effect in the inhibition of the expansion due to DEF (Figures 3a, 3b, and 4a), with the exception of LF, for which there is an increase in expansion (Figure 4b).

According to test method, the concrete mixes are considered as being suitable in DEF control, if one of two criteria is met. In the first criteria the average longitudinal deformation of the three samples must be less than 0.04%, and no individual value being greater than 0.06% at 12 months of testing. According the second criteria the test should be extended up to 15 months if the longitudinal deformation of the three individual specimens is between 0.04% and 0.07% at 12 months of testing (Pavoine and Divet, 2007).

At 1 year, the expansion of control mix is 0.43%. The expansion tests are still ongoing, but the results obtained until now seems that 15% of FA (mass cement replacement) is enough for inhibit the expansion due to DEF. With 10% MK, the expansion at 1 year is 0.04%, although at long-term expanded by more than 0.09%. Concretes with GGBS need a 40% replacement level to achieve the DEF inhibition.

From Figure 3 it can be seen that the concrete mixes in which the expansion was below the limit of 0.04% at 1 year, the expansion behavior remains almost constant for long-term ages.

The results obtained with LF mixes 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 LF mixes expand more (0.88% at 1 year) than the control concrete and the expansion seems increase with the replacement level of limestone (Santos Silva, 2010b).

This different behavior of the minerals additions employed could be related with their chemical composition and pozzolanic activity. According some authors (Ramlochan et al., 2003) the disparity in the DEF control is related to the Al_2O_3 content of the additions (Table 1). This could explain why, for the same level of replacement, the MK or FA was more efficient than GGBS in the DEF inhibition. Besides, the pozzolanic activity of each mineral addition is also important, since that controls the alkalinity of the interstitial solution of concrete which plays an important role in the ettringite formation (Divet, 2001; Santos Silva, 2010a).

As was observed for the ASR tests, the inhibition of expansion due to DEF with type II mineral additions depends of the each addition type and cement replacement content.

SEM/EDS analysis

ASR - Mortar bars

It is know that the introduction of mineral additions in concrete changes the Ca/Si ratio in the CSH, usually lowering it. Besides, the alkali binding in the CSH gel has been much investigated in recent years (Hong and Glasser, 1999; Hong and Glasser, 2002; Shehata and Thomas, 2000; Shehata and Thomas, 2002; Ke-Rui et al., 2004), and appears to be related to the decrease in Ca/Si ratio in the blended mixes. It is also known that alumina-rich additions, such as fly ash and metakaolin, can cause a major change in the chemical composition of CSH gel due to the incorporation of a greater amount of aluminum (Santos Silva, 2005).

In the present study we could not access the fixation of alkalis by CSH of cement paste, or its relation with the expansion obtained, since the method used implies a continuous renewal of alkalis over time.

Figure 5 show the EDS taken of the CSH of the mortars tested at 28 days in ASTM C 1567 test conditions, plotted as expansion at 28 days versus atomic Ca/Si ratio. There was a good correlation between a value < 2.45 for Ca/Si ratio and the 0.20% expansion value at 28 days.
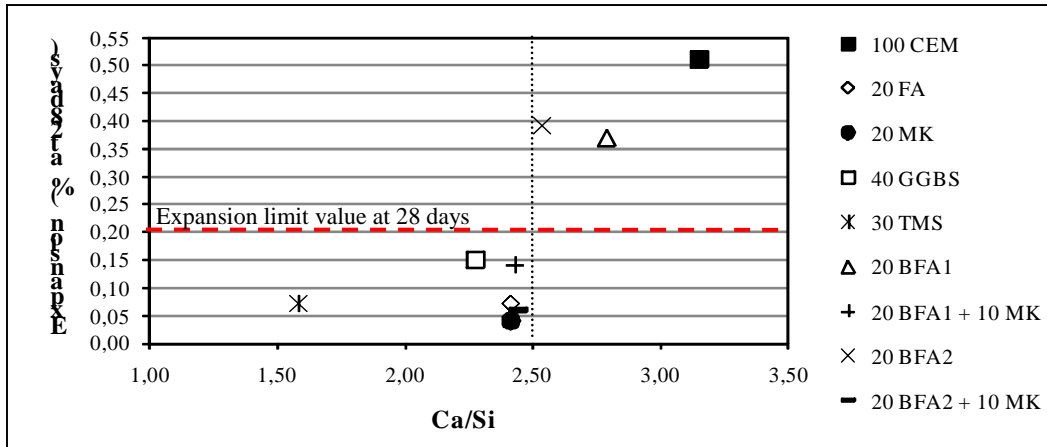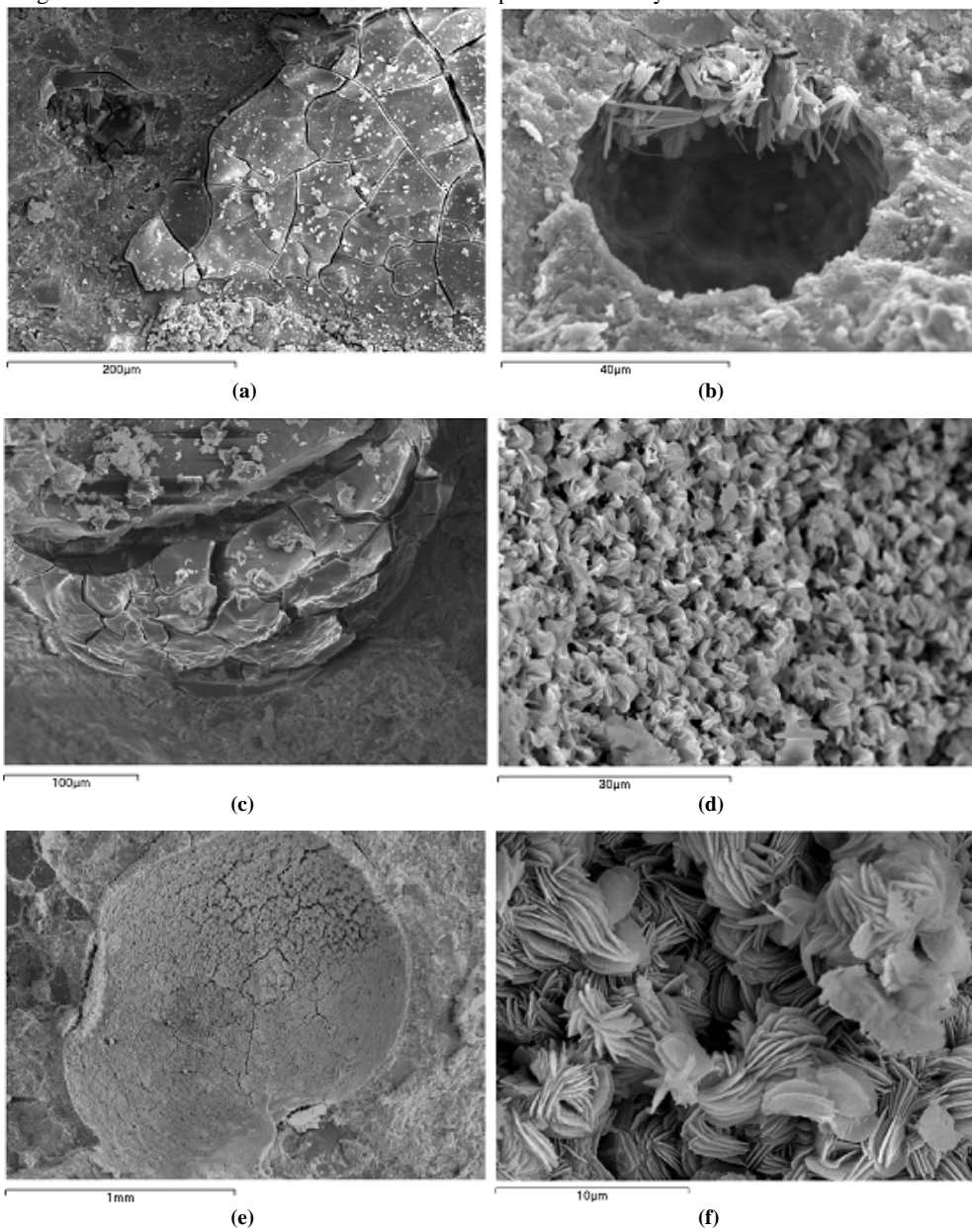
Figure 5: Ca/Si atomic ratio of the CSH and the expansion at 28 days in ASTM C 1567 test method.
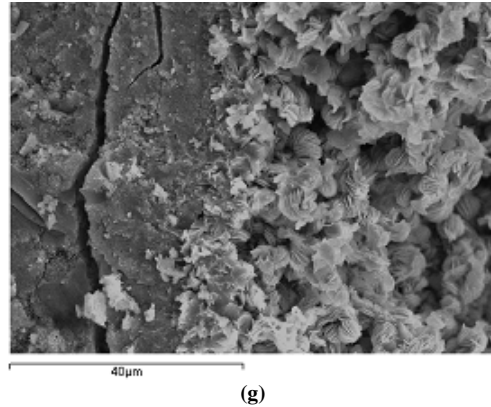

(a)

(b)

(c)

(d)

(e)

(f)

(g)

Figure 6: SEM images of freshly broken surfaces: (a) ASR smoothed gel in the 40 GGBS mortar, (b) ettringite needles in an air void in the 40 GGBS mortar, (c) ASR amorphous gel in the 20 BFA1+10 MK mortar, (d) crystalline ASR in the 20 BFA1+10 MK mortar, (e,f) Crystalline ASR products inside air voids in the BFA2 mortar, (g) crystalline and amorphous ASR gel in BFA2 mortar.

In the all mortars there are microscopic evidences of ASR products (amorphous and crystalline) being much more evident in the blended mortar mixes that have presented higher expansion at 28 days of test (Figure 6). The ASR products are mainly found at aggregate interfaces, filling voids and other porous areas in the cement matrix. The main features in the mortars that presented less expansion are the localization of the expansive ASR products that are mainly located in voids with no evidence that the formation of ASR had caused distress in these specimens.

DEF- Concrete cylinders

As previous mentioned, there are differences in the composition of the CSH with the incorporation of mineral additions. In this study, after 1 year of storage in water a significant amount of sulphate was released from the CSH. This results are similar to those reported elsewhere (Ramlochan et al., 2004) and stopped its correlation with the results of the analysis of CSH, or even expansion results.

Figure 7 shows Al content by EDS versus expansion after 1 year exposure, revealing an inverse correlation in which expansion decreases with increasing Al content. This may be attributed to the cement replacement level in the blended mixes as the mineral additions have a higher aluminum content than Portland cement, except LF. This could explain why alumina-rich additions, such as fly ash and metakaolin, were the more effective ones in DEF inhibition, as mentioned by others authors (Ramlochan et al., 2003).
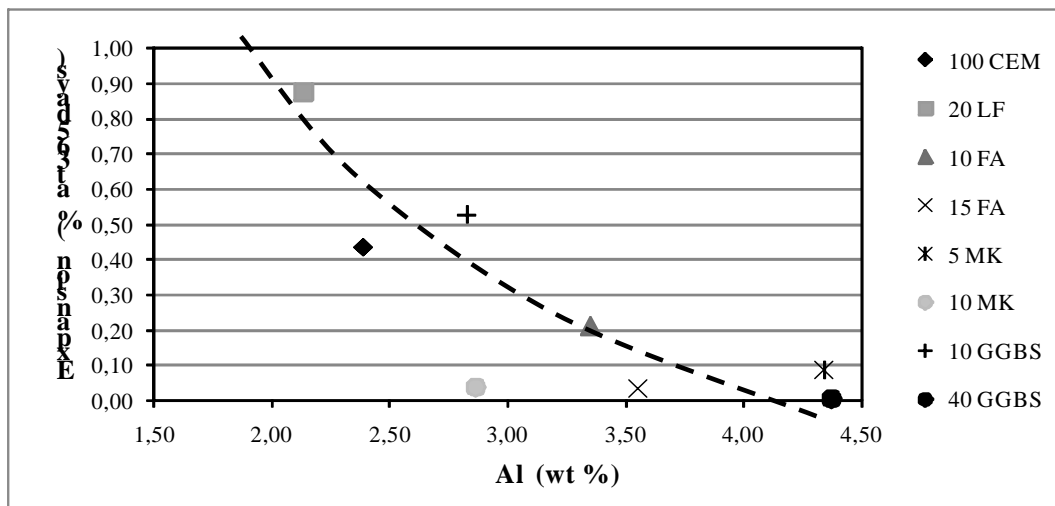

Figure 7: Chart showing the relation between Al in CSH and expansion at 365 days of immersion in water.

SEM observation made on polished sections of concrete at 28 and 365 days of immersion reveals an improvement of the compactness of the cement paste with age, besides some differences in the microporosity between the different mixes (Figures 8 and 9).

At 28 days of immersion it was detected in all blended mixes the presence of calcium monosulfoaluminate (Afm) and traces of ettringite, but the ettringite only in the mixes that show expansion at 28 days, e.g. 10 FA (Figure 10).

At 1 year, with the release of sulphate from the CSH copious amounts of ettringite was detected on the blended concretes that have presented the highest expansion values (>0,04%). The ettringite was found in voids, around aggregate particles and in the cement paste (Figure 11).
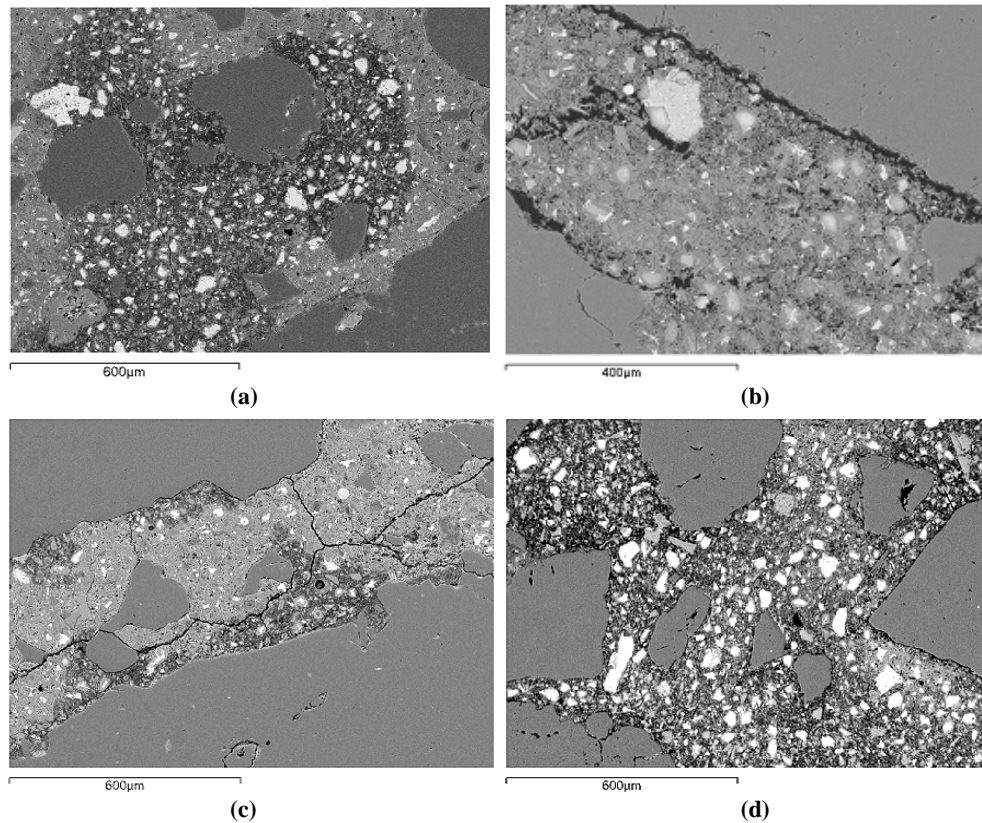

Figure 8: SEM images of polished sections of concrete at 28 days of immersion, where it is possible to observed the heterogeneity in compactness of the blended cement pastes: (a) 5 MK, (b) 10 GGBS, (c) 15 FA, (d) 10 LF.
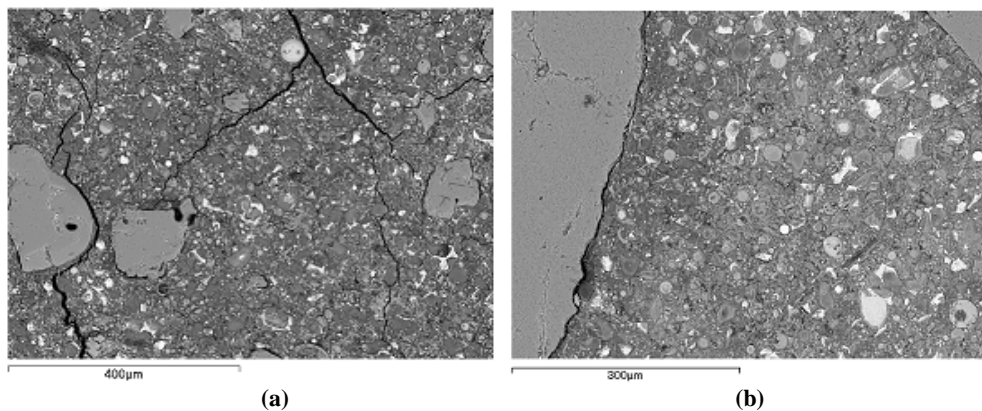

Figure 9: SEM images of polished sections of concrete at 365 days of immersion: (a) 10 FA, (b) 15 FA.
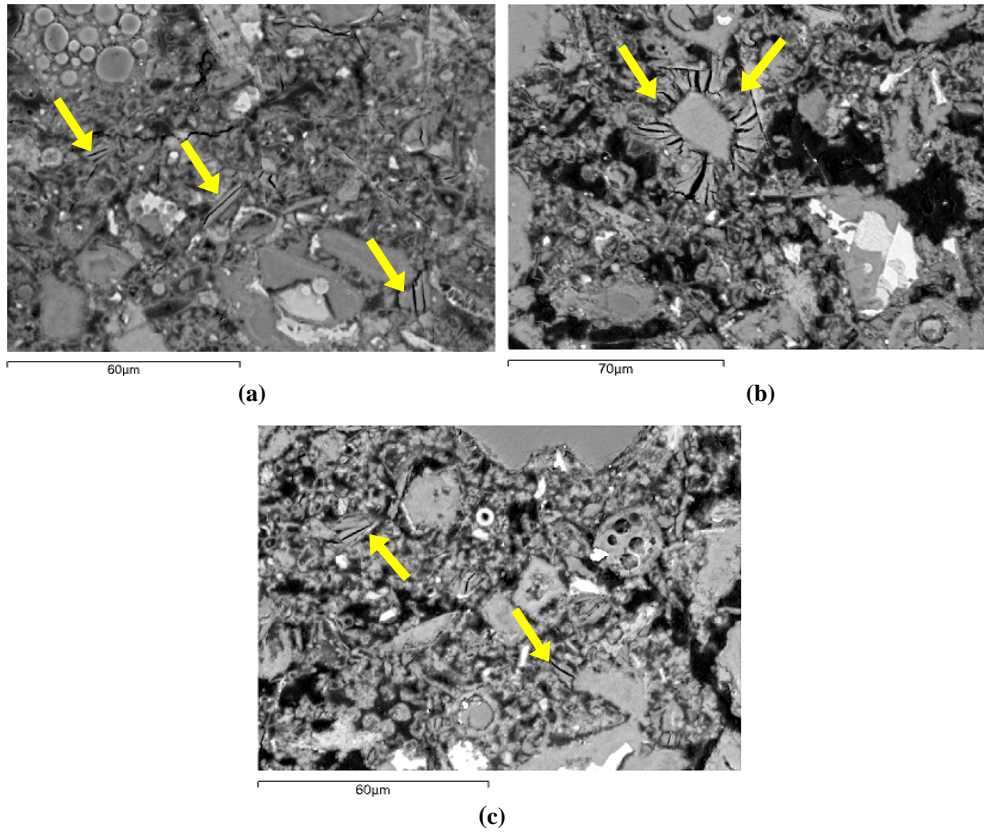
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Figure 10: SEM images of polished sections of concrete at 28 days showing calcium monosulfoaluminate (Afm) and ettringite (Aft) dispersed in the cement paste: (a)Afm in 15 FA mix, (b) Aft in 10 FA mix, (c) Afm in 10 FA.
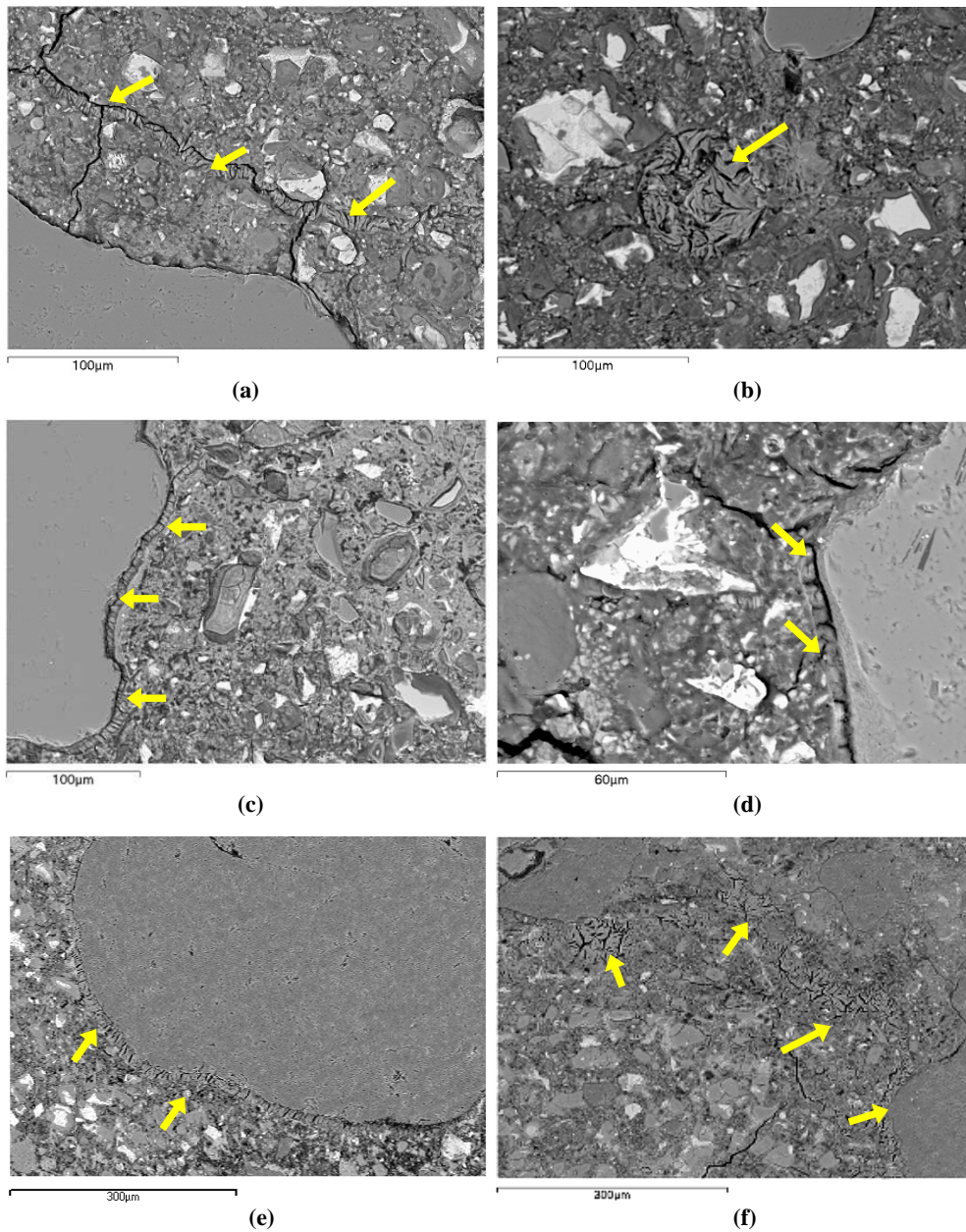
Figure 11: SEM images of polished sections of concrete at 365 days of test showing the presence of DEF: (a, b) 5 MK, (c) 10 GGBS, (d) 10 FA, (e) 10 LF, (f) 100 CEM.

Conclusions

The results obtained in this study points out the existence of a relationship between the mineral addition type and the inhibition of IER, being only the type II additions effective in this purpose. This efficiency is related to the chemical composition and pozzolanic activity of the addition.

According our results the mitigation effect of the mineral additions in ASR seems mainly due to the pozzolanic activity, CaO and alkalis content of the mineral additions. The materials studied that show the best ASR inhibition effects are: MK > FA > TMS > GGBS. Due to their high CaO and alkalis content the biomass fly ashes could be effective in ASR mitigation by incorporating a small amount of metakaolin (e.g. ~10%). The microscopic observations confirmed the presence of ASR products in all blended mortars, however in the mortars that have less expanded during test these expansive products are mainly located in voids with no evidence of distress in the specimens.

In terms of DEF inhibition their efficiency is mainly related to the Al_2O_3 content and also pozzolanic activity. Although the occurrence of ettringite their formation in some of the blended concretes was not accompanied by expansion. By microscopy we have observed that the concretes that more expanded during immersion storage the monosulfoaluminate was replaced by ettringite, this did not happen in the blended concretes with sufficient Al_2O_3-bearing mineral addition. The use of a non pozzolanic mineral addition in blended concretes, e.g. limestone filler, could be worse than only Portland cement. This seems occur due to a refinement of the cement microstructure, reducing the porosity, which is not more sufficient to accommodate the expansive ettringite.

Acknowledgements

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