Prevention of internal sulphate reaction in concrete. Long-term results of the effect of mineral additions

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Abstract

In Portugal and France, several cases of premature degradation of concrete structures due to internal expansive reactions (alkali-aggregate reactions – AAR - and internal sulphate reaction due to delayed ettringite formation - DEF) have been reported.

In Portugal both types of reactions are in generally present in affected structures, while in France the DEF is presently the main concern. In France the AAR control was very effective after the publication in 1994 of the first recommendations for the prevention of disorders due to AAR by LCPC (now Université Gustave Eiffel). In Portugal the first recommendations for the prevention of internal swelling reactions were published in 2004, and even so several cases of concrete structures affected by AAR and DEF still continue to be diagnosed.

It is well known that some mineral additions have the ability to react with the calcium hydroxide from the hydration of the cement, to form cementitious hydrated compounds, and thus being able to reduce the alkalinity of the pore solution of cement paste, inhibiting the formation of AAR expansive products. However, there is still insufficient data on the long-term performance of different types of additions, and particularly in the DEF control.

This paper presents the results of concretes incorporating different types of mineral additions (fly ash, metakaolin, granulated blast furnace slag, silica fume, tungsten mine tailing, biomass ash and limestone filler) for approximately 8 years of follow-up, and some considerations are made on the levels to be considered in the prevention of DEF.

***Keywords**: concrete; DEF; prevention; mineral additions*

1. INTRODUCTION

Deterioration by internal expansive reactions (IER) is a problem for concrete durability, which affects an increasing number of concrete structures in several countries. In addition, these reactions are difficult to detect early, usually requiring expensive and highly specialized means of diagnosis.

IER is so named because its causes are related to the internal constituents of concrete (silica, alkalis, aluminates and sulphates, essentially), and are due to two distinct mechanisms: Alkali-Aggregate Reaction (AAR) and Internal Sulphate Reaction (ISR).

The delayed ettringite formation (or DEF), the ISR that causes greatest concern, may be defined as the formation of ettringite in the concrete material after its hardening. It has been known for two dozen years [1, 2], and has been found in concrete produced with cement having sensitive composition, exposed to a favorable environment (frequent humidification) and having undergone a relatively high heat treatment (> 65 ºC) or having reached equivalent temperatures for another reason (solid pieces of concrete, concreting in summer, etc.). The degradations due to DEF were observed mainly on prefabricated concrete elements (railway sleepers, concrete pipes, concrete masts, ...) and on massive pieces of concrete bridges [3, 4].

This situation motivated the need to study preventive measures to avoid the occurrence of DEF in new structures. The use of pozzolanic mineral additions, as partial cement replacement, can mitigate the expansion due to AAR, if they are used in sufficient quantity [5], although their action depends on its composition and pozzolanic reactivity.

Despite the good results in preventing deleterious expansions obtained with some additions [6], such as fly ash, its use may be compromised in the short/medium term taking into account the growing concern with CO_2 emissions, which may led to the massive use of “clean” energies. This trend will result in a decrease or even the depletion of some industrial by-products and, in the case of natural products, limitations of exploitation and their treatment. This is the context for the evaluation of the use of type I and type II mineral additions [7], capable of meeting the needs of the concrete industry in the short/medium term and capable of mitigate/inhibit the IER. This paper presents results that have been obtained on the medium/long term effect of mineral additions in the inhibition of DEF.

2. MATERIALS AND METHODS

2.1 Materials

Table 2.1 presents the chemical composition of the tested materials: portland cement CEM I 42,5R (CEM), coal fly ash (CFA), metakaolin (MK), ground-granulated blast-furnace slag (GGBS), silica fume (SF), tungsten mine sludge (TMS), biomass fly ash (BFA) and limestone filer (LF).

The mineral additions were used as a partial cement replacement (by mass) maintaining a constant water/binder ratio (Table 2). A binary mixture (CFA + LF) was also tested to assess the possibility of a possible synergistic effect of this combination.

Table 2.1: Chemical composition of the tested materials (mass %)

Composition	Materials							
	CEM	CFA	MK	GGBS	SF	TMS	BFA	LF
SiO_2	19.74	53.22	54.66	38.09	96.9	60.78	31.0	0.09
Al_2O_3	4.14	23.20	37.98	9.38	0.52	18.26	8.5	0.04
Fe_2O_3	2.69	5.85	1.22	0.89	0.14	9.46	3.0	0.06
CaO	63.54	5.36	0.01	36.24	0.58	0.61	24.0	55.66
MgO	2.42	1.63	0.46	7.40	0.00	2.16	4.8	0.10
SO_3	3.11	1.00	0.01	0.27	0.13	-	-	0.02
K_2O	0.64	1.42	3.09	0.52	0.42	3.93	2.7	0.04
Na_2O	0.08	0.44	0.00	0.25	0.04	0.46	6.6	0.02
$Na_2O_{eq.}$	0.50	1.37	2.03	0.59	0.32	3.05	8.38	0.05
LOI*	3.13	5.16	0.94	2.66	1.47	3.12	13.5	43.23

* Loss on ignition at 1000 °C

2.2 Mix design

Concrete specimens (cylinders with 110 mm in diameter and 220 mm high) were prepared using CEM I 42.5R cement (Table 2.1) and quartzitic aggregate (gravel and sand) of French origin, known for its non-reactivity to alkalis. The specimens were cast following the concrete mix design of RILEM AAR-3 test-method [8], using 440 kg/m^3 of cementitious materials, with a water/binder ratio of 0.45 and with an constant alkali content of 5.50 kg/m^3 of Na_2O_{eq}, which was adjusted by adding sodium hydroxide (NaOH) to the mixing water. A non-boosted mixture was also prepared to assess the effect of decreased alkalinity on DEF development. The binders of the studied concrete mixtures are shown in Table 2.2.

In order to promote the formation of DEF, immediately after casting the concrete cylindrical specimens were sealed and subjected to a heat treatment (Figure 2.1). This heat curing aims to reproduce the temperature core rise obtained during setting inside a massive cast-in-place concrete with dimensions of 14 m length, 3.5 m width and 1.5 m high, with an average external temperature of 23 °C. The concrete reaches a maximum temperature of 80 °C after 15 hours and is maintained at temperatures above 70 °C for 3 days. The temperature program was modeled by the TEXO program of the CESAR-LCPC calculation program [6,8]. After the thermal cycle, the concrete specimens were demolded and subsequently subjected to two drying-humidification cycles in order to accelerate the kinetics of the ettringite formation. Each cycle lasted 14 days and consists of two phases: drying for 7 days at 38 ± 2

°C and RH < 30%, followed by immersion for 7 days at 20 ± 2 °C. After the drying-humidification cycles, the specimens were immersed in water at 20 ± 2 °C for long-term storage.

Additionally, a reference mixture was made (without additions) that was not subjected to heat treatment to assess the influence of temperature on the development of DEF.

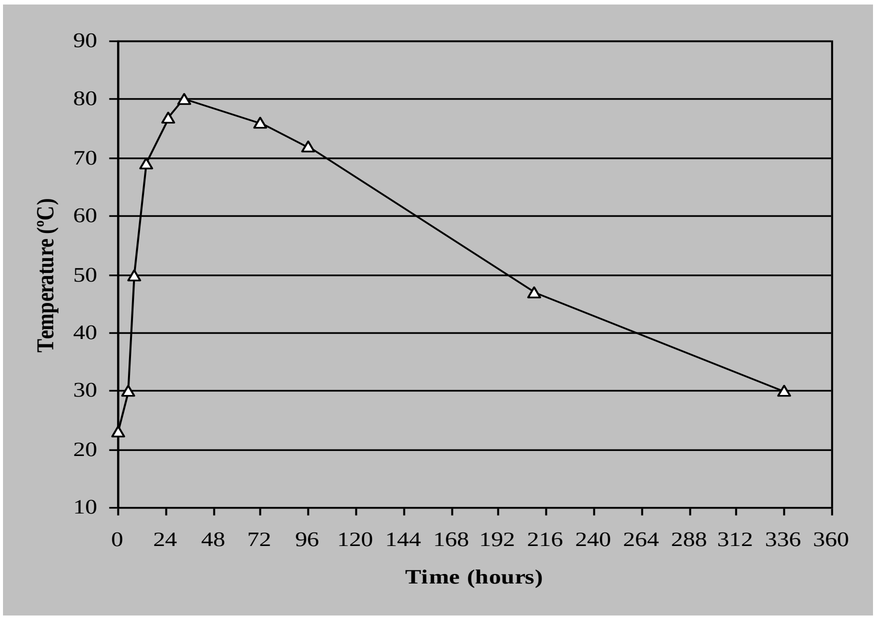

Figure 2.1: Heat-curing cycle used for concrete to promote the occurrence of DEF

Table 2.2: Binders of the concrete mixtures tested

Mixture		Addition type and substitution content (mass %)							
		FA	MK	GGBS	SF	TMS	BFA	LF	FA+LF
Reference	with heat treatment	-	-	-	-	-	-	-	-
	without heat treatment	-	-	-	-	-	-	-	-
Mineral addition content		-	5	-	5	-	-	-	20+10
		10	10	10	10	-	-	10	
		15	15	15	-	-	-	15	
		20	20	20	-	-	-	20	
		30	-	-	-	30	30	30	
		-	-	40	-	-	-		
		-	-	-	-	-	-	10 (non alkali-boosted)	-

2.3 Expansion tests

Expansion tests, accompanied by the measurement of the mass of the concrete specimens, were carried out in accordance with the LPC accelerated method Nº. 66 [10-12]. According to this test method, three series of two steel studs are glued in each test specimen between the 3rd and the 7th day of the immersion of the second drying and humidification cycle. The studs are 100 mm apart and equidistant from 120° according to the diameter of each concrete specimen. The expansion at each period corresponds to the average of the readings in each of the three generatrices of three specimens.

2.4 Evaluation of water-soluble alkali content

In AAR inhibition, one of the mechanisms proposed to explain the effectiveness of supplementary cementing materials is the reduction of alkalinity of the pore solution of cement paste by the formation of calcium silicate hydrates (CSH) with alkali binding capacity. In the case of ISR, it is believed that this alkalinity decrease may affect the solubility of ettringite, thus increasing the potential for the formation of DEF in concrete [13-15].

In order to evaluate the evolution of alkalinity over time, the determination of the content of soluble alkalis in concrete mixtures containing CFA, MK, GGBS, SF and LF was carried out over 3 years, using the hot-water extraction method [16]. The sodium (Na) and potassium (K) contents of the extracted solutions were determined by atomic absorption spectrometry (AAS), and subsequently expressed as % Na_2O_{eq}..

2.5 Evaluation of calcium hydroxide content

The consumption of calcium hydroxide (portlandite) when pozzolanic materials are used is also considered one of the mechanism for controlling the deleterious expansion due to AAR. With regard to the inhibition of DEF, some studies [17] have shown that the consumption of portlandite can also be beneficial. In addition to the alkali content, the content of portlandite was determined in the same concrete mixtures for 3 years, by thermogravimetry in a TGA Setaram apparatus using an inert atmosphere (argon - 3 L/h), with a heating rate of 10 °C / min, from room temperature to 1000 °C. The portlandite content was obtained from the mass loss between 450 and 600 °C and then calculated according to the reaction:

Portlandite (%) = ((Mass $\text{loss}_{450\text{-}600}$ x Molecular mass of Portlandite) / Molecular mass of water) x 100

3. RESULTS AND DISCUSSION

3.1 Expansion results

Figure 3.1 shows the expansion curves obtained for the reference mixture with and without heat treatment. The concrete that has undergone the heat treatment shows an expansion of 0.54% after 8 years of testing, against 0.06% of the same concrete without heat treatment. This difference shows the importance of the curing temperature in the DEF expansion potential [18].

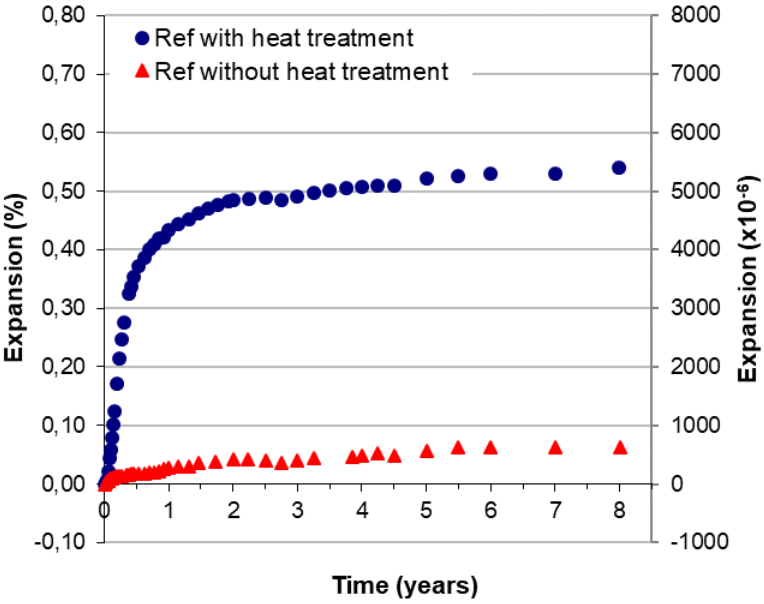

Figure 3.1: Expansion curves for the reference concrete mixture with and without heat treatment

According to the LPC test method, concrete mixtures, when subjected to heat treatment, are considered non-reactive if one of the following criteria is met: the average expansion is less than 0.04 % at 1 year of testing, and no individual value is greater 0.06 %; or in case the average expansion to 1 year is between 0.04 to 0.07 % the test must be extended up to 15 months, and in this case the accumulated expansion between 12 and 15 months must be less than 0.006 % [12].

Figures 3 and 4 show the expansion curves of the various concrete mixtures with mineral additions as partial cement replacement.

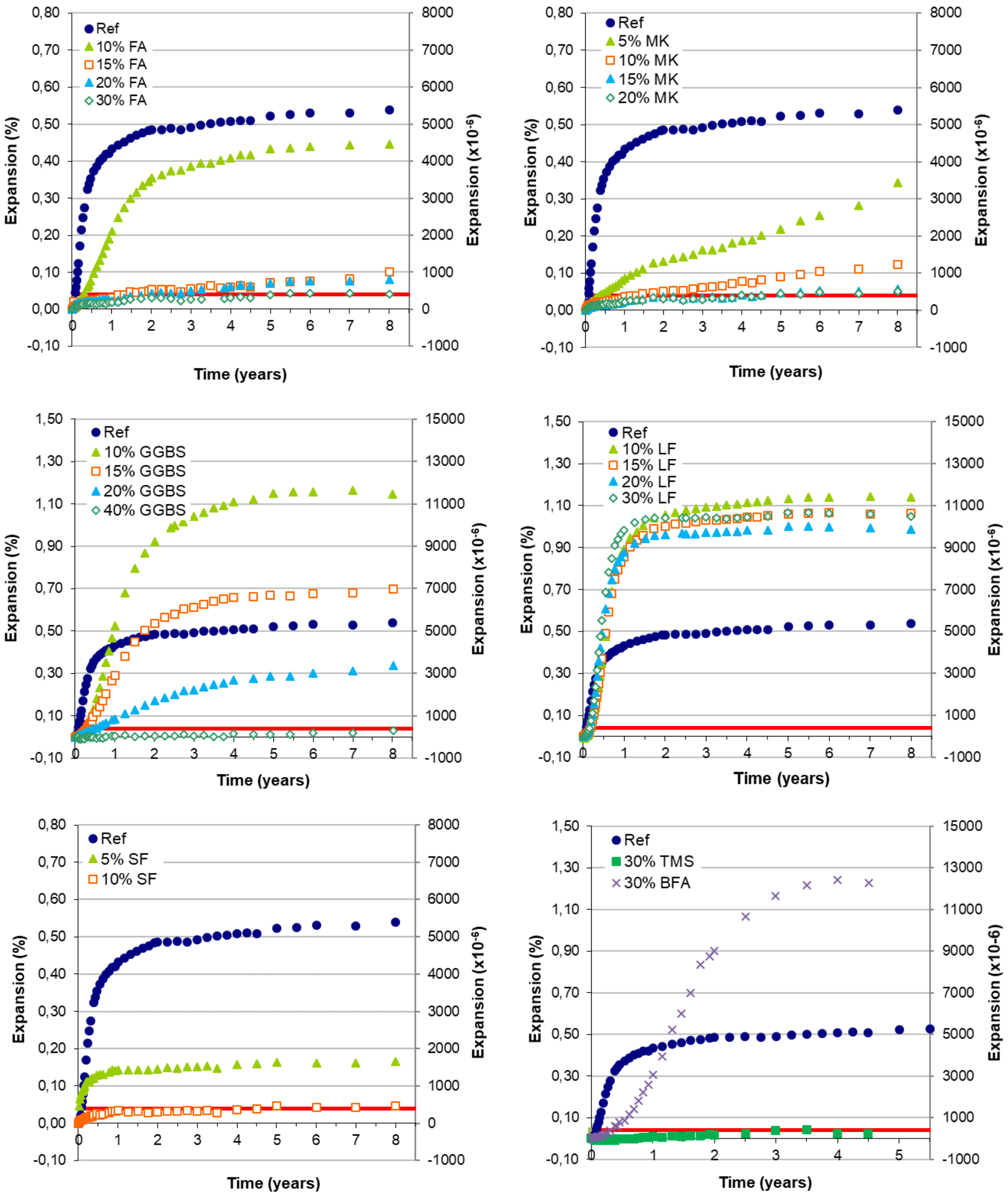

Figure 3.2: Expansion curves for the concretes with mineral additions (FA, MK, GGBS, LF, SF, TMS and BFA)

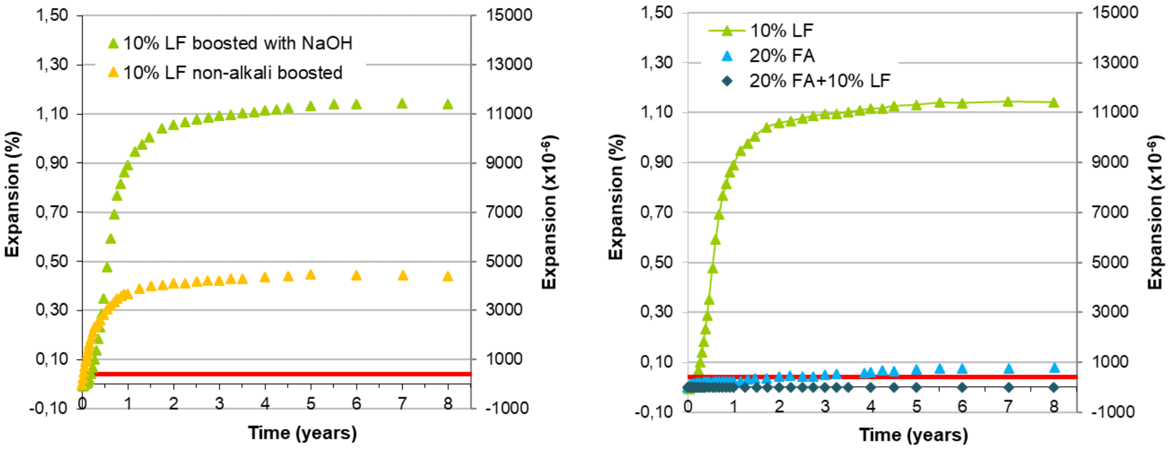

Figure 3.3: Expansion curves for the concretes with limestone filler (LF), and the effect of alkalis boosting and synergetic effect of binary mixtures on expansion behavior

It is found that, in general, mineral additions, if present in sufficient substitution contents, have a strong effect of inhibiting the expansion due to DEF. Mixtures with CBS and with LF are excluded from this behavior, since the final expansion is greater than that of the reference mixture. This is a reflex of the non-pozzolanic behavior of these two mineral additions [19].

In the case of BFA, the curve is S-shaped, showing small rate of expansion until about 6 months of testing, after which there is a strong increase in rate of expansion (reaching a swelling of 1.22 % at 4.5 years). This delayed expansion may be related to the high alkali content of the BFA (Table 2.1). Without significant binding capacity, the BFA particles are better able to release alkalis into the porous solution. This likely higher alkali content creates conditions to prevent the formation of ettringite in the first months. Later, the gradual release of the alkalis from the BFA specimens to the storage solution allows for expansion due to DEF [20].

LF addition does not inhibit the expansion due to DEF even doubling the expansion values (1.15 % at 8 years) in relation to the reference mixture. The effect of LF on DEF may be related to its role in the hydration reactions of Portland cement. Is usually mention in the literature, e.g. [21], that filer particles acts as reaction nuclei for the hydration of C_3S and C_2S, which leads to a faster hydration of the cement particles. When filler is used as cement addition, and not as cement replacement, there is a decrease in the porosity of the cement paste, and consequently less space for accommodates the expansive products. Some authors, e.g. [22], refer that the hydration of cement in the presence of limestone filer accelerates the formation of ettringite, reducing or even stopping its conversion to monosulfoaluminate, when a large amount of carbonate is present in the paste.

At 3 months, the LF mixture boosted with alkalis showed less expansion than the non-boosted mixture, Figure 3.3. This behavior is in accordance with the role of alkalis presented above, that the initial high alkali content of the mixture has an inhibiting effect in the expansion (0.23 % with 1.60 kg/m^3 $Na_2O_{eq.}$ versus 0.10 % with 5.50 kg/m^3 at 3 months of testing), also in agreement with the results shown by Sellier and Multon [20]. With ageing, the opposite behavior is observed, as occurred when comparing the reference mixture with the BFA mixture, with a higher expansion in the mixture with the highest initial alkali content (0.44 % with 1.60 kg/m^3 $Na_2O_{eq.}$ versus 1.14 % with 5.50 kg/m^3 at 8 years of testing). This can be due to higher sorption of sulphates with the increase in the alkali content [18, 20, 23]. In view of the LF behavior, a mixture with FA was tested in the proportion of 20 % FA + 10 % LF. This mixture (Figure 3.3) showed an much lower expansion after 8 years of testing (0.02 %) than that of the 10 % LF (1.14 %), and even lower than 20 % FA (0.08 %). This result suggests that there is a synergistic effect of binary mixtures with these two mineral additions in DEF mitigation, has it happens in ASR with other binary mixtures [24].

The expansion results of the FA mixtures (Figure 3.2) show that from 15 % cement replacement there is an evident inhibition of expansion (0.03 % at 1 year). However, long-term results show that the expansion rate is not zero, being safer to use at least 30 % cement replacement by FA (0.04% at 8 years).

MK shows, in comparison to FA, a greater efficiency in reducing expansion (0.04 % at 1 year, with 10%), although at long-term 15 % is more effective (0.05 % at 8 years).

In GGBS mixtures, the results indicate that only a replacement of 40 % (0.03 % at 8 years) is sufficient to inhibit expansion. Silica fume shows a comparable behavior with only 10% replacement (0.04 % at 8 years) while for the tungsten mine sludge a content of 30% is required.

The different behavior obtained for the various mineral additions employed may be related to their chemical composition and pozzolanic activity. According to some authors [25] the effectiveness of the pozzolans and slags may be related to its Al_2O_3 content. With the exception of silica fume, the Al_2O_3 content of the materials used (Table 1) are in agreement with this assumption, and may explain why, for the same level of substitution, MK or FA was more effective than GGBS in DEF expansion inhibition. In addition, the pozzolanic activity of additions is also an important factor, since it controls the alkalinity of the concrete interstitial solution, which plays an important role in the formation of ettringite [26-29].

3.2 Evolution of water-soluble alkali with ageing

Figure 3.4 shows the results of the evolution of the content of soluble alkalis (expressed as $Na_2O_{eq.}$) for concrete mixtures with FA, MK, LF, GGBS and SF.

As can be seen, there is in general a decrease in the alkali content with ageing, that can be attributed to the incorporation in cementitious hydrated products formed by the reaction of cement and some mineral additions [30], but mainly due to alkali leaching as a result of the long immersion of the specimens in water.

The differences observed at 28 days in the soluble alkali content of the tested mixtures can due to the alkali binding in cement hydrates and also to the differences in cement porosity at early ages that influences the alkali leaching, namely during drying-humidification cycles.

The results also indicate that the higher the cement replacement, the higher is the soluble alkali content of the concrete. This behavior, with the exception of LF compositions, follows the trend of decreasing expansion with the increase of the additions content.

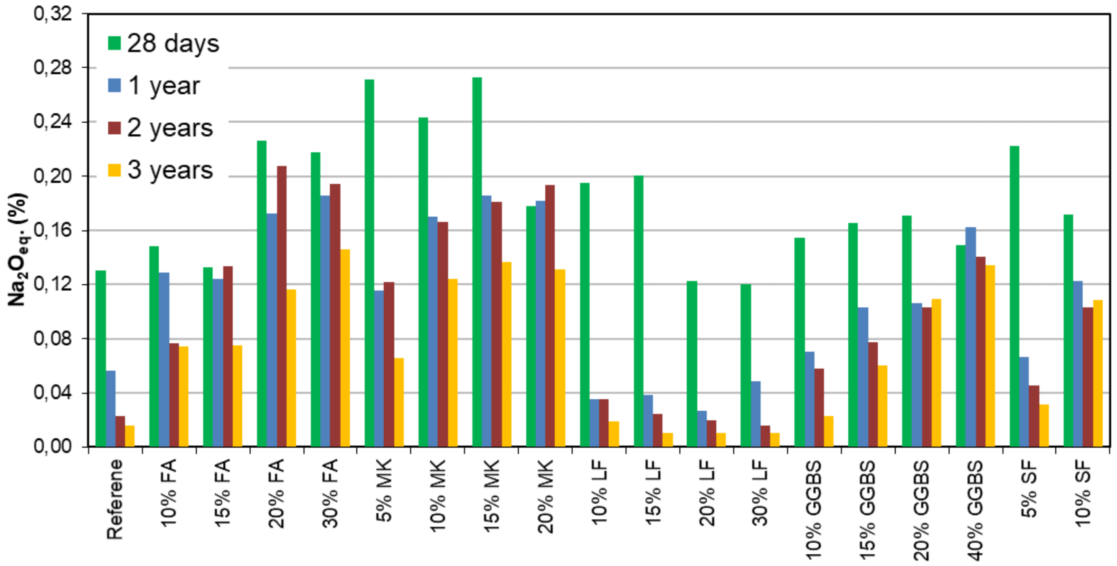

Figure 3.4: Evolution of the water-soluble alkalis content in the concrete compositions tested

It is also shown that for FA, MK, GGBS and SF the alkalis content decreases when the addition content increases. So, the results are consistent with the existence of a critical threshold for the alkalis content that allows absence of deleterious expansion. After 3 years of testing the soluble alkalis content measured, expressed as Na_2O_{eq}, are: 0.02 % (reference), 0.15 % (30% FA), 0.14 % (15% MK), 0.14 % (40% GGBS) and 0.11 % (10% SF). However, it is well known that the leaching of alkalis promotes the precipitation of ettringite which then leads to expansion of the concrete [20]. The quantities of soluble alkalis for 30% FA, 15% MK, 40% GGBS and 10% SF would then allow a sufficiently content of soluble alkalis to be maintained to avoid this precipitation of ettringite. This could partly explain the beneficial effect of these additions. This phenomenon is seen very well for GGBS because the content of soluble alkali varies significantly at 3 years with the amount of GGBS (10, 15, 20 and 40 %).

These results thus point to a beneficial effect of mineral additions, namely with the increase in the alkalinity of concrete at early ages, which delays the formation of ettringite [31] and increases its solubility [14].

3.3 Evolution of calcium hydroxide content with ageing

Figure 3.5 presents the results of the evolution of the portlandite content for some of the analyzed concrete mixtures (FA, MK, LF, GGBS and SF) with ageing.

With the exception of LF mixtures, it was confirmed that the greater the replacement of cement, the lower the value of free portlandite in concrete.

It is also verified that the MK and FA mixtures, which had the lowest expansion values, are the ones that had a higher consumption of portlandite through the pozzolanic reaction. In contrast, mixtures with LF and GGBS (exception to 40 % GGBS composition), which showed the greatest expansions, are those that show the least reduction in the portlandite content. The SF mixtures do not follow the typical behavior of increasing effectiveness with increasing portlandite consumption. However, the earliest portlandite consumption provided by the silica fume (high silica content and high fineness), when compared with other additions, may be one of the reasons for obtaining equivalent efficiency with higher portlandite content.

Based on these results, it can be inferred that there is a good correlation between the expansion reduction due to DEF and the consumption of portlandite [22, 23]. These observations suggests that the effectiveness of mineral additions in mitigating expansion by DEF will depend, among other parameters, on the reduction of the portlandite content [17, 20].

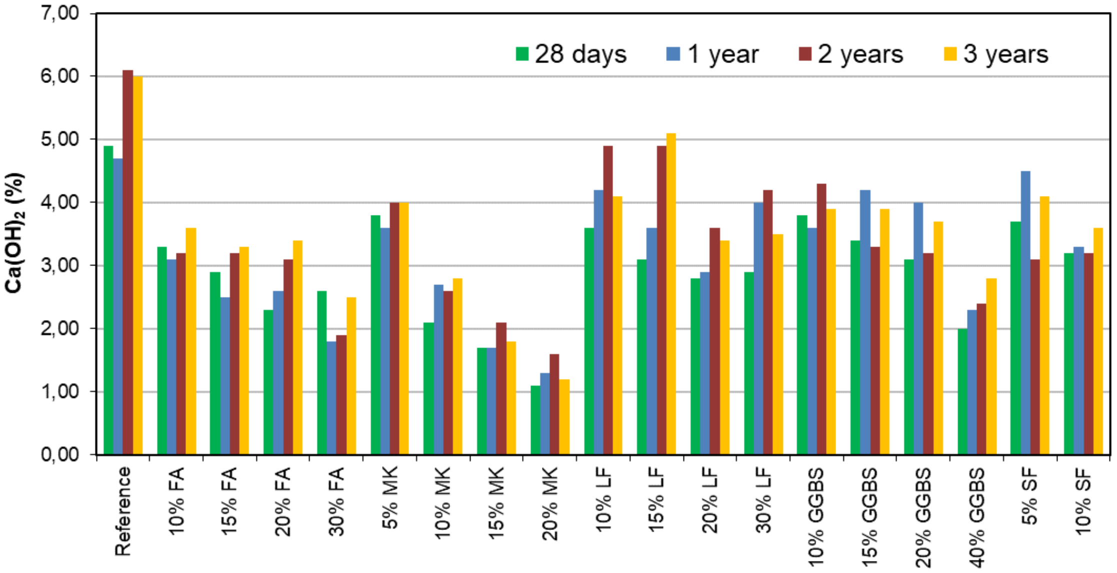

Figure 3.5: Evolution of the portlandite content in the concrete compositions tested

4. CONCLUSIONS

In this paper, the results of concrete specimens prepared with different mineral additions (coal fly ash, metakaolin, blast furnace slag, silica fume, tungsten mine sludge, biomass fly ash and limestone filer) for about 8 years of monitoring were presented.

The results obtained show that mineral additions can be efficient in inhibiting expansion by DEF, depending on the effectiveness of the type and content of mineral addition. The pozzolanic and hydraulic additions have mitigating and inhibiting capacity, which is not the case of non-pozzolanic and inert additions (biomass fly ash and limestone filer).

For concretes subject to curing temperature in the order of 80 °C (expected maximum temperature reached by a solid piece of concrete with dimensions of 14 x 3.5 x 1.5 m^3), the content of additions required to reduce the DEF expansion to a level similar to a reference concrete without heat treatment is: 30% FA, 15% MK, 40% GGBS, 10% SF and 30% TMS.

The mechanism for suppressing the expansion due to DEF by mineral additions is complex, however, it has been found that the alkalinity of the concrete as well as the portlandite reduction have beneficial effects in this process. It is observed that there may be a critical threshold value for soluble alkalis content of concrete which would inhibit the expansion due to DEF.

5. ACKNOWLEDGEMENTS

The authors acknowledge the support of Laboratório Nacional de Engenharia Civil (LNEC), Portugal, for funding the research project RE-IMPROVE: Expansive reactions in concrete - Prevention and mitigation of its effects.

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