

USE OF MINERAL ADDITIONS FOR THE INHIBITION OF INTERNAL EXPANSIVE REACTIONS IN CONCRETE STRUCTURES: GOOD AND BAD SYNERGIES

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Abstract

Several studies have been performed along the last few years related with the use of fly ash in the suppression of expansion due to alkali-silica reaction (ASR). However, relatively little attention has been focused in its effectiveness to control the delayed ettringite formation (DEF) in hardened concrete, and the use of metakaolin to control the ASR and DEF.

The research work presented in this paper deals with the influence of fly ash (FA) and metakaolin (MK) in the inhibition of ASR and DEF in concrete. The influence of other additions like ground granulated blast furnace slag (GGBS), silica fume (SF) and limestone filler (LF) was also investigated in the DEF suppression.

The mechanisms of mineral additions or supplementary cementitious materials (SCM) in the suppression of ASR and DEF are discussed. Results obtained indicated that the reduction of the calcium hydroxide content is the most beneficial effect of SCM in ASR and DEF inhibition mechanism. Furthermore, the results obtained indicate that the use of limestone filler is ineffective in the inhibition of expansion by DEF.

Keywords: ASR, DEF, mechanism, mineral additions, supplementary cementing materials.

1. Introduction

Over the last years several studies have shown that the use of supplementary cementitious materials (SCM), like fly ash (FA) and metakaolin (MK), can be used for the prevention of expansion due to alkali-silica reaction (ASR) and delayed ettringite formation (DEF) in concrete [Thomas, 1996; Ramlochan *et al*, 2003]. However, these studies with MK have been conducted using mortars and the existing ones are mainly devoted to ASR.

The work presented in this paper is part of an extensive experimental program conducted by The Portuguese National Laboratory of Civil Engineering (Laboratório Nacional de Engenharia Civil -LNEC), a public institution of the Portuguese Ministry for Public Works, Transports and Housing, aimed at elucidating the role that mineral additions have in the mechanism of inhibition of ASR and DEF in concrete. The results were obtained in concretes made with two portland cements CEM I 42.5R (OPC) and with additions as partial replacement by volume or mass of cement. Concretes were cured at normal (20 °C) and elevated temperatures (up to 80°C) and then stored in saturated air environment or in water at ambient temperature for as long as 4 years.

2. EXPERIMENTAL PROGRAM

2.1 Materials

The chemical compositions obtained by WD-XRF of cement, fly ash (FA), metakaolin (MK), ground granulated blast furnace slag (GGBS), silica fume (SF) and limestone filler (LF) used in this research work are detailed in *Table 1*.

Table 1. Chemical composition of cement and mineral additions (% mass)

| Oxide | OPC 1 | OPC 2 | FA | MK | GGBS | SF | LF |
|----------------------------------|-------|-------|-------|-------|-------|------|-------|
| 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 |

Two control concrete compositions were produced: the first one using the OPC 1, a reactive siliceous limestone (0.22 % at 14 days according to RILEM AAR-2 method [Recommendations 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 OPC 2 using a non reactive alluvial quartzitic as coarse and fine aggregate.

2.2 Expansion testing

Concrete prisms and cylinders were cast and tested in accordance with the RILEM AAR-3 test method for ASR [RILEM, 2000] (equivalent to ASTM C 1293) using 440 kg/m³ of cementitious material, water/binder of 0.45, and with an alkali content of 5.50 kg/m³ Na₂O_{eq.}, calculated on the basis of available alkalis from the cement, additions and added NaOH. This formulation was also used for casting specimens for the study of DEF. Mix compositions are reported in Table 2.

Table 2. Concrete mixtures

| Cement, aggregate and replacement type | Control | FA (%) | MK (%) | GGBS (%) | SF (%) | LF (%) |
|--|---------|--------|--------|----------|--------|--------|
| OPC 1, siliceous limestone, % volume | 1 | 20 | 20 | - | - | - |
| | | 40 | - | - | - | - |
| | | 60 | - | - | - | - |
| OPC 2, quartzitic aggregate, % mass | 2 | - | 5 | - | 5 | - |
| | | 10 | 10 | 10 | 10 | 10 |
| | | 15 | 15 | 15 | - | 15 |
| | | 20 | 20 | 20 | - | 20 |
| | | 30 | - | - | - | 30 |
| | | - | - | 40 | - | - |

In order to promote the occurrence of DEF immediately after casting some of the concrete mixtures, prepared as described before, were sealed and placed in a climatic chamber with controlled temperature and humidity, and heat cured. The heat-curing cycle that was used 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 it was maintained at temperatures above 70° C during 3 days. This cycle was computed by the TEXO program part of the CÉSAR-LCPC finite element design code [Divet *et al.*, 1998]. Following the heat-curing cycle, the concrete specimens were demolded and subsequently 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].

2.3 Determination of water-soluble alkali content

The reduction of alkalinity in the cement paste by the formation of calcium silicate hydrates (C-S-H) with a low C/S ratio is one of the mechanisms proposed to explain the effectiveness of the use of mineral additions in suppressing expansion due to ASR. The effectiveness of this mechanism is related with the capacity of these hydrates to entrap more alkalis, thus reducing the amount of alkali ions available in the pore solution for reaction with potentially reactive aggregates [Shehata and Thomas, 2000, 2002]. The alkalinity reduction of the pore solution can prevent also the solubility of ettringite, thus reducing the risk of DEF in concrete [Divet, 2001].

In order to evaluate the consumption of alkalis by the mineral additions the water-soluble alkali content of concrete was determined at various ages by the hot-water extraction method [Bérubé *et al.*, 2000]. The sodium and potassium contents of the extracted solutions were determined by atomic absorption spectrometry (AAS).

2.4 Determination of calcium hydroxide content

The consumption of calcium hydroxide (portlandite) by pozzolanic reaction is, according many authors [Chatterji and Thaulow, 1983; Shehata and Thomas, 2000], the principal mechanism of expansion control by ASR. With respect to DEF inhibition, recent results [Ramlochan *et al.*, 2003] have shown that the portlandite consumption can be also benefit.

The portlandite content of the concrete samples was determined by thermogravimetry in an argon environment using a heating rate of 10° C/min. The portlandite content was determined from the mass loss in the range of 400 °C to 500 °C.

3. RESULTS

3.1 Expansion results

Figure 1a and 1b present the expansion curves according, respectively, ASR and DEF test methods, for concrete mixtures with limestone aggregates with 440 kg/m³ of cementitious material and a water/binder = 0.45.

As shown in figure 1a, at one year, the expansion of control specimens is lower than 0.05 %, 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 the expansion mortar-bar AAR-2 method. Petrographic analysis of coarse aggregate has also indicated potential risk of ASR on coarse aggregate. From figure 1a 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 0.04% at 2 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.

Figure 1b summarizes the 4-year expansion results of heat-cured concrete, tested accordingly LPC method [LCPC, 2007]. As shown in the figure, 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 0.46% at 4 years, while mixtures with FA or MK present no appreciable expansion (not more than 0.05% with 20% MK). These results are in agreement with the results of Ramlochan [Ramlochan *et al.*, 2003] obtained for mortar samples.

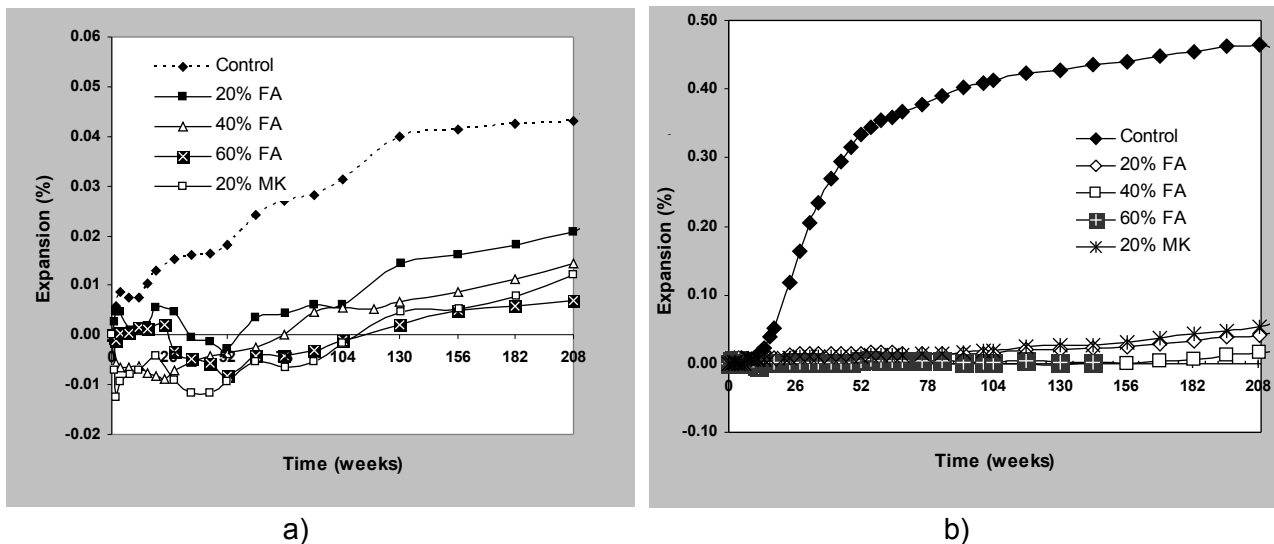


Fig. 1 - Effect of various levels of replacement (% volume) of FA or MK on expansion of concrete with limestone aggregates with 440 kg/m^3 of cementitious material and a water/binder = 0.45. Expansion due to (a) ASR and (b) DEF.

Figure 2a to 2e 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 and 440 kg/m^3 of cementitious material (water/binder=0,45). Each value on these curves represents the average of 3 measurements on three specimens.

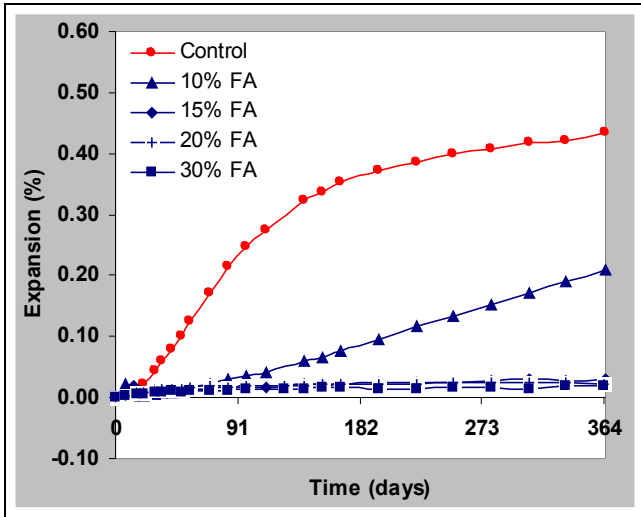
The tests are still ongoing, but the results obtained until now show that 15% replacement of cement by FA (% mass) is enough for inhibition of expansion due to DEF. With MK or SF, the same effect is obtained with 10 % replacement. Using GGBS 40% replacement is needed to achieve inhibition. These different behaviors of minerals additions, concerning the percentage of cement replacement needed to inhibit DEF, could be related with their pozzolanic activity, which is more intense for SF and MK.

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 than the control concrete and the expansion increase with the amount of cement replacement.

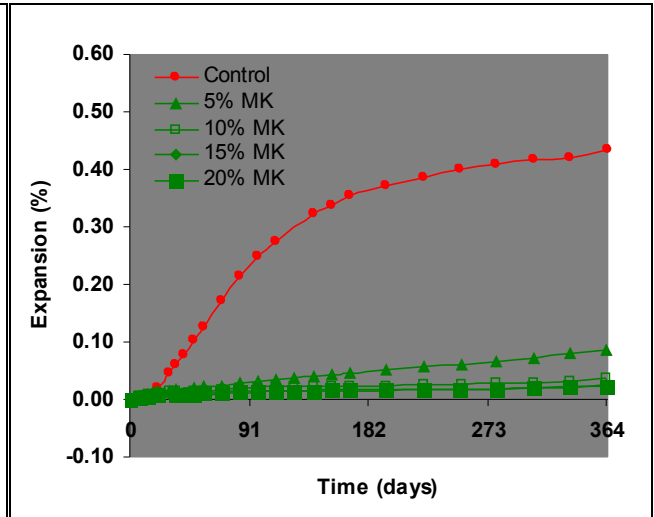
3.2 Water-soluble alkali content

The evolution of water-soluble alkali content of concrete samples tested in accordance with the RILEM AAR-3 method, expressed in % $\text{Na}_2\text{O}_{\text{eq}}$, at ages of 28, 90 and 365 days are presented in figure 3a. A clear reduction of alkalinity with time of control concrete is observed, which is more pronounced after one year. This can be attributed to the formation of ASR gels, which consumes alkalis. On the contrary, alkalinity of blended mixtures with FA or MK has not decreased significantly during the same period. The consumption of alkalis during the pozzolanic reaction is suggested to explain the mechanism of supplementary cementing materials in ASR suppression. [Diamond, 1983; Duchesne and Bérubé, 1994]. The alkalis consumed in the pozzolanic reactions are not available to the formation of ASR. It is admitted that the alkalis extraction process removes alkalis from pozzolanic products but not from ASR gels.

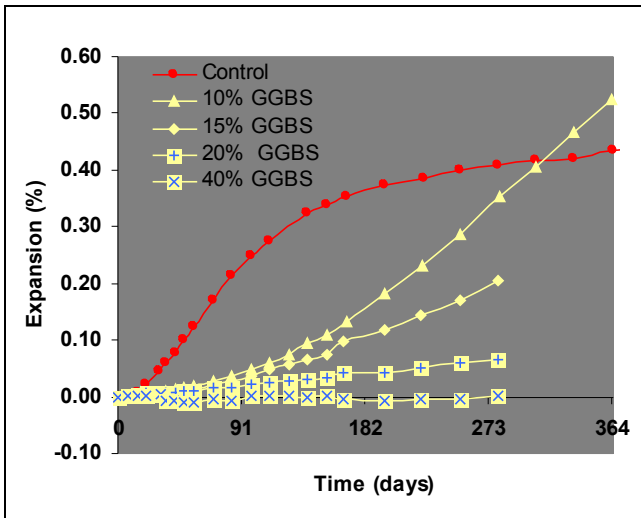
Figure 3a also indicates an increase in the alkalinity of concrete pore solution with the increase in the FA replacement. Furthermore, the mixture with 60% of FA shows that, along the time, more alkalis are released to the solution than entrapped into the reaction products. This suggests that the mechanism of controlling ASR expansion by FA is not mainly dependent on the alkalis entrapped in pozzolanic hydrates [Santos Silva *et al*, 2007].



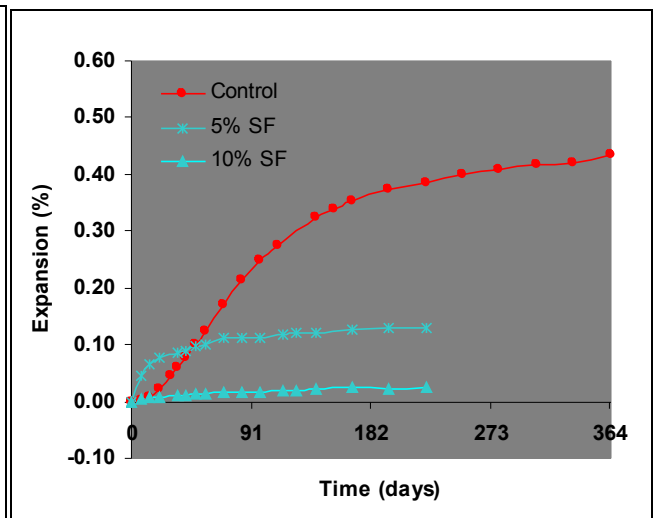
a)



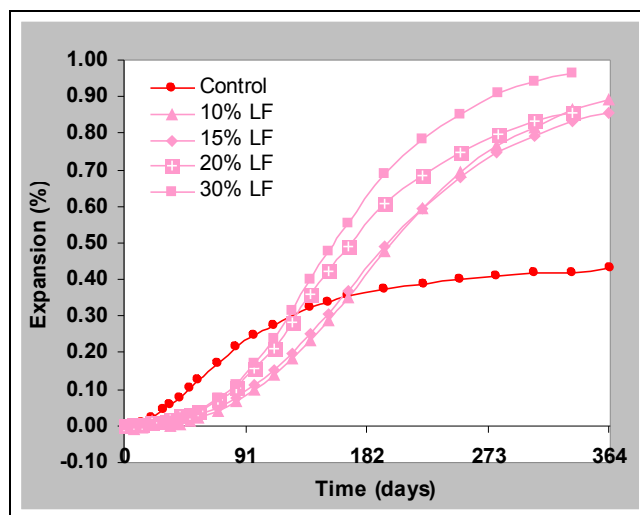
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c)



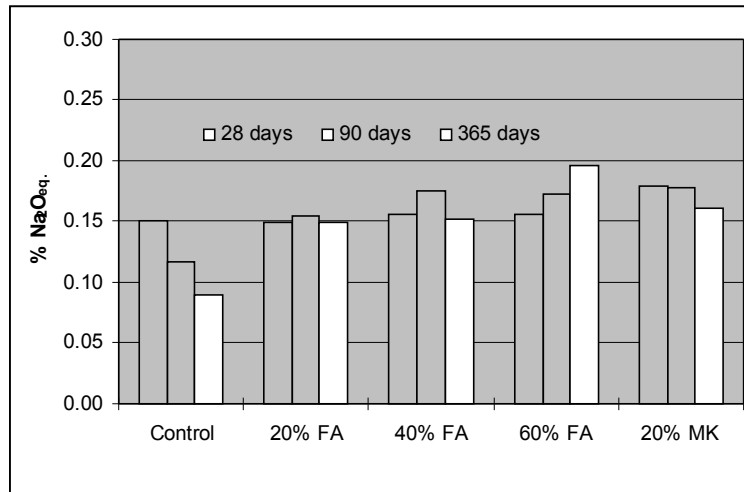
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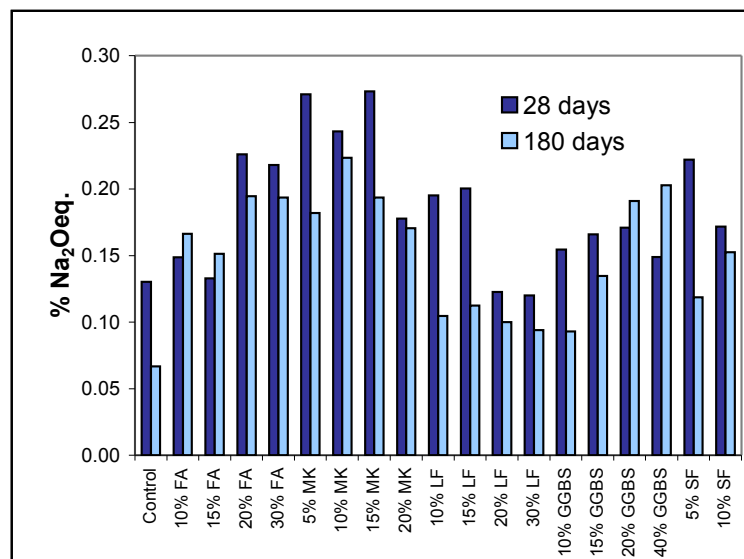
e)

Fig. 2 – 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.

The water-soluble alkali content results obtained in specimens tested according to the DEF test method (figure 3b) were similar to those obtained with the ASR test method. In this case, it is interesting to observe that the mixtures with lower alkalinity were the ones that expanded more, and the mixtures where more alkalis are released showed lower expansions.



a)



b)

Fig. 3 – a) Effect of FA and MK (substitution in volume) on the alkalinity of pore solution for concrete mixtures with limestone aggregates and tested with the RILEM AAR-3 method; b) Effect of mineral additions (substitution in mass) on the alkalinity of pore solution for concrete mixtures with quartzitic aggregates and tested according the DEF method.

3.3 Portlandite content

The evolution of portlandite content for the concrete mixtures tested according the AAR-3 test method is illustrated in figure 4. As expected, all concrete mixtures with blended binder contain less portlandite than control concrete. In fact, the increase in the cement replacement produces a significant reduction in portlandite content not only due to the dilution effect but also due to the pozzolanic reaction. Figure 4 also shows that MK have consumed more portlandite than FA, which is consistent with the lower ASR expansion obtained for the MK mixture when compared with the mixture with FA, for the same level of cement replacement (% volume). This behaviour is attributed

to the higher fineness and amorphous silica content of the MK. These results indicate that the portlandite consumption is the major role of FA and MK in suppressing ASR.

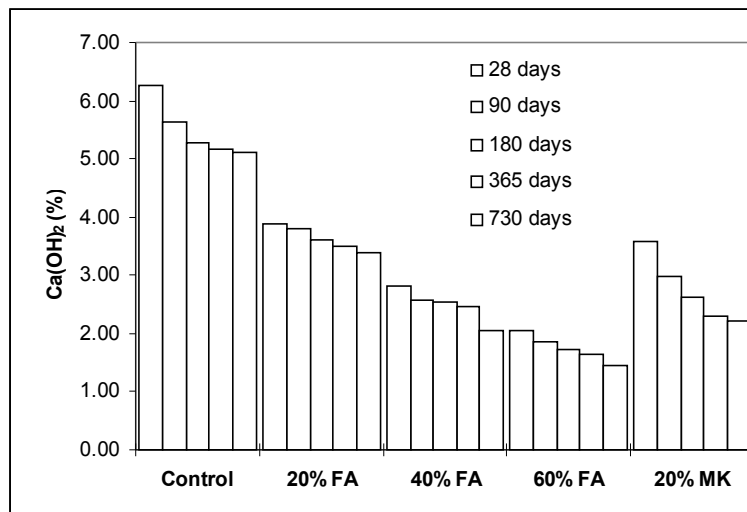


Fig. 4 – Effect of FA and MK on the portlandite content evolution for concrete mixtures tested with the RILEM AAR-3 method.

Analysing now the portlandite content of the specimens used for the DEF test, figure 5, we observe that, contrarily to the ASR expansion, it is not clear the existence of a correlation between portlandite consumption and reduction in concrete expansion by DEF. However, the mixtures that have presented more expansion are those that show less reduction in the portlandite content. This tendency is particularly evident for the blended mixtures with LF and GGBS. This observation suggests that the effectiveness of mineral additions in suppressing expansion due to DEF, besides the reduction in portlandite content, depends on other parameters, namely the Al_2O_3 content of supplementary cementing materials [Ramlochan *et al*, 2004].

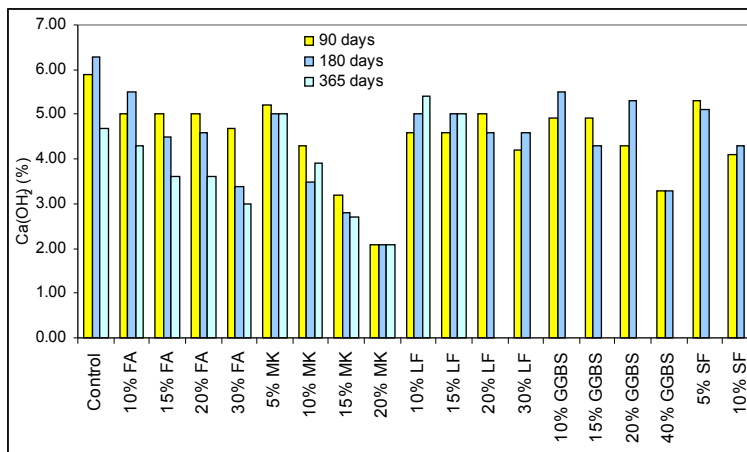


Fig. 5 – Effect of mineral additions on the portlandite content evolution for concrete mixtures tested with the DEF test method.

4. Conclusions

The research work presented in this paper deals with the influence of mineral additions: fly ash (FA), metakaolin (MK), ground granulated blast furnace slag (GGBS), silica fume (SF) and limestone filler (LF) in the inhibition of ASR and DEF in normal and heat-cured concretes. After 4 years of tests the use of 20% of FA or 20% of MK (% volume) has proved to be efficient in eliminating the expansion by ASR or DEF in normal and heat-cured concretes. Expansion test results, obtained for DEF analysis, suggest that the efficiency of blended binders is dependent on

the mineral addition type, being only the pozzolanic additions effective in this respect. Moreover, the efficiency of the pozzolanic additions depends also on the content of the mineral admixture.

Results obtained indicate that the reduction of the calcium hydroxide content is the most beneficial effect of FA and MK in the ASR inhibition mechanism. The mechanism of DEF suppression by FA, MK, GGBS and SF is not completely understood so far and no well correlation was obtained with respect to portlandite consumption by pozzolanic reaction. However, the use of these additions has a positive double effect in the inhibition of DEF. Besides the reduction in expansion, they also reduce the heat of hydration, particularly for massive cast-in-place concrete.

References

- Bérubé, M.A., Frenette, J., Rivest, M. and Vézina, D., Measurement of the alkali content of concrete using hot-water extraction, *Proceedings of 11th International Conference on Alkali-Aggregate Reaction in Concrete*, Québec City, Canada, 2000, 159-168.
- Bleszynsky, R., Thomas, M. and Hooton, D., The efficacy of ternary cementitious systems for controlling expansion due to alkali-silica reaction in concrete, *Proceedings of 11th International Conference on AAR in Concrete*, Québec City, Canada, 2000, 583-592.
- Chatterji, S. and Thaulow, N., Studies of alkali-silica reaction with special reference to prevention of damage to concrete. A preliminary study, *Proceedings of 6th International Conference on Alkali-Aggregate Reaction in Concrete*, Copenhagen, Denmark, 1983, 253-260.
- Diamond, S., Alkali reaction in concrete-pore solution effects, *Proceedings of 6th International Conference on AAR in Concrete*, Copenhagen, Denmark, 1983, 155-166.
- Divet, L., Les réactions sulfatiques internes au béton: contribution à l'étude des mécanismes de la formation différée de l'ettringite., *Études et Recherches des laboratoires des Ponts et Chaussées, Ouvrages d'Art*, vol. 40, Paris, 2001, p. 227.
- Divet, L., Guerrier, F. and Le Mestre, G., Existe-t-il un risqué de développement d'une activité sulfatique d'origine endogène dans les pièces en béton de grande masse ? Le cas du pont d'Ondes (Haute-Garonne), *Bulletin des Laboratoires des Ponts et Chaussées*, **213**, 1998, 59-72.
- Duchesne, J. and Bérubé, M.A., The effectiveness of supplementary cementing materials in suppressing expansion due to ASR: Another look at the reaction mechanisms Part 2: pore solution chemistry, *Cement and Concrete Research* **24** (2), 1994, 221-230.
- LCPC, Méthode d'essai des LPC n° 66, Réactivité d'une formule de béton vis-à-vis d'une réaction sulfatique interne. Essai de performance, LCPC, Paris, 2007, p. 24.
- Ramlochan, T., Zacarais, P., Thomas, M.D.A. and Hooton, R.D., The effect of pozzolans and slag on the expansion of mortars cured at elevated temperature. Part I: Expansive behaviour, *Cement and Concrete Research* **33** (6), 2003, 807-814.
- Ramlochan, T., Thomas, M.D.A. and Hooton, R.D., The effect of pozzolans and slag on the expansion of mortars cured at elevated temperature. Part II: Microstructural and microchemical investigations', *Cement and Concrete Research* **34** (8), 2004, 1341-1356.
- RILEM Recommendations : A-TC 106-2-Detection of potential alkali-reactivity of aggregates – The ultra-accelerated mortar-bar test; B-TC-106-3-Detection of potential alkali-reactivity of aggregates – Method for aggregate combinations using concrete prisms', *Materials and Structures*, **33**, 2000, 283-293.
- Shehata, M.H. and Thomas, M.D.A., The effect of fly ash composition on the expansion of concrete due to alkali-silica reaction, *Cement and Concrete Research* **30** (7), 2000, 1063-1072.
- Shehata, M.H. and Thomas, M.D.A., Use of ternary blends containing silica fume and fly ash to suppress alkali silica reaction in concrete, *Cement and Concrete Research* **32** (3), 2002, 341-349.
- Thomas, M.D.A., Review of the effect of fly ash and slag on alkali-aggregate reaction in concrete, Building Research Establishment, Ltd., Watford, 1996.
- Santos Silva, A., Ribeiro, A.B., Jalali, S., Divet, L., "The use of fly ash and metakaolin for the prevention of alkali-silica reaction and delayed ettringite formation in concrete", *Proceedings of the International RILEM Workshop on Performance Based Evaluation and Indicators for Concrete Durability*, Ed. V. Baroghel-Bouny, C. Andrade, R. Torrent and K. Scrivener, RILEM, 2007, p. 335-342.