THE USE OF FLY ASH AND METAKAOLIN FOR THE PREVENTION OF ALKALI-SILICA REACTION AND DELAYED ETTRINGITE FORMATION IN CONCRETE

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Abstract

One of the most popular preventive measures to minimize the occurrence of chemical expansive reactions, namely the alkali-silica reaction (ASR) and delayed ettringite formation (DEF) in hardened concrete is the use of supplementary cementing materials (SCMs). Several studies have been performed along the last few years related with the use of fly ashes in the suppression of expansion due to ASR. However, relatively little attention are been focused in its effectiveness to control the DEF in 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 ashes (FA) and metakaolin (MK) in the inhibition of ASR and DEF in concrete. The mechanisms of FA and MK in the suppression of ASR are discussed. Results obtained indicated that the reduction of the calcium hydroxide content is the most beneficial effect of FA and MK in ASR inhibition mechanism. Furthermore, the results obtained indicate that the use of FA and MK, for partial replacement of cement in concrete, is effective in the inhibition of expansion by DEF.

1. INTRODUCTION

The use of supplementary cementing materials, like fly ash (FA) and metakaolin (MK), is one of the measures proposed to prevent expansion due to alkali-silica reaction (ASR) and delayed ettringite formation (DEF) in concrete [1,2]. However, relatively few studies have been conducted using concretes with MK and the existing ones are mainly devoted to ASR.

The work presented in this paper is part of an extensive study aimed at elucidating the role that FA and MK have in the mechanism of inhibition of ASR and DEF in concrete. The results are obtained for concretes made with a high alkali portland cement CEM I 42,5R with FA or MK as partial replacement by volume of cement, which were cured at normal and elevated temperatures (up to 80ºC) and then stored in saturated humidity ambient or in water at ambient temperature for as long as 2 years.

2. EXPERIMENTAL PROGRAM

2.1 Materials

The chemical compositions of the cement, FA and MK used in this research work are given in Table 1.

Table 1: Chemical composition of cement, fly ash and metakaolin used in this study

Oxide (mass %)	Cement	Fly Ash	Metakaolin
SiO_2	18.81	53.22	54.66
Al_2O_3	5.15	23.20	37.98
Fe_2O_3	3.18	5.85	1.22
CaO	63.70	5.36	0.01
MgO	1.50	1.63	0.46
SO_3	2.69	1.00	0.01
K_2O	1.02	1.42	3.09
Na_2O	0.19	0.44	0.00
$Na_2O_{eq.}$	0.86	1.37	2.03
TiO2 + P_2O_5	0.34	1.87	0.49
LOI	3.18	5.16	0.94

As shown in Table 1 the FA is a type F in accordance with ASTM C 618. The MK used was obtained from a Portuguese kaolin by calcinations at about 750º C during 24h. A reactive siliceous limestone (0.22 % at 14 days according to RILEM AAR-2 method [3]) was used as the coarse aggregate together with non reactive limestone sand (0.00 % at 14 days according AAR-2) in all the mixes.

2.2 Expansion testing

Concrete prisms and cylinders were cast and tested in accordance with the RILEM AAR-3 test method for ASR [3] (equivalent to ASTM C 1293) using 440 kg/m^3 of cementitious materials, with a water to cementing material ratio of 0.45 and with an alkali content of 5.50 kg/m^3 $Na_2O_{eq.}$ calculated on the basis of available alkalis from the cement, FA, MK and added NaOH. This formulation was also used for casting specimens for the study of mechanism of inhibition of DEF in concrete. This procedure avoided the possibility of the simultaneous variation of several parameters that are likely to interact on the development of the DEF.

The FA (20, 40 and 60 %) and MK (20 %) were incorporated as a partial cement replacement maintaining a constant (in volume) water/cementing ratio.

In order to promote the occurrence of DEF immediately after casting some of the moulds prepared as described before described were sealed and placed in a climatic chamber with controlled temperature and humidity, and the concretes were heat cured. The heat-curing cycle that was 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.

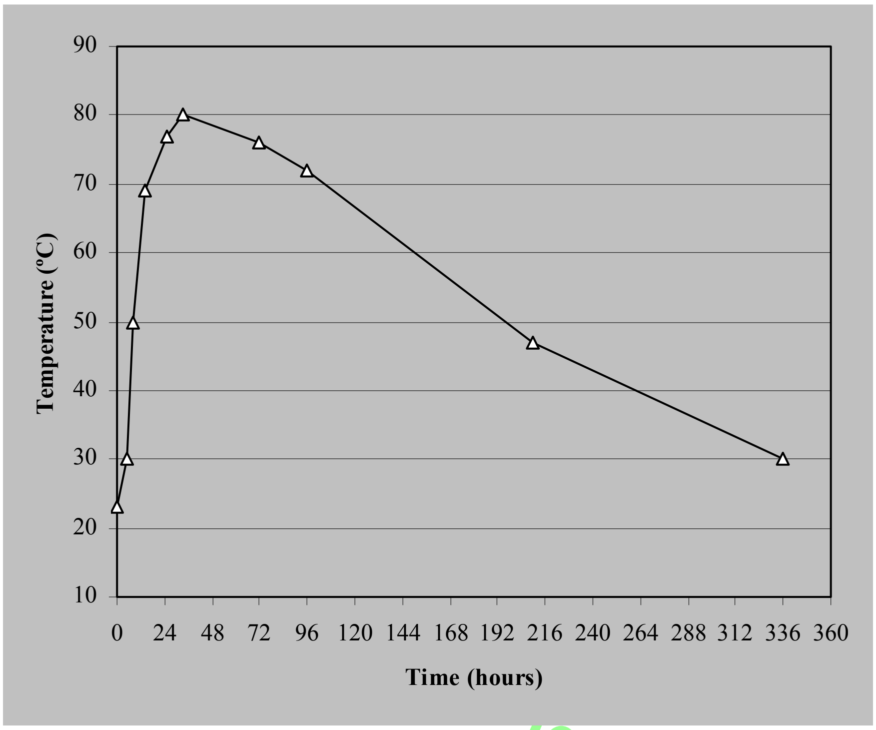

Figure 1 - Heat-curing cycle used for concrete to promote the occurrence of DEF.

The concrete reached a maximum temperature of 80ºC after 15 hours, and it was maintained at temperatures above 70º C during 3 days. This cycle was computed by the TEXO program part of the CÉSAR-LCPC finite element design code [4]. Following the heat-curing cycle, the concrete specimens were demolded and subsequently immersed in water for long-term storage at 20 ± 2ºC. Length and mass measurements were taken periodically in accordance to the accelerated concrete performance French test LPC nº 59 [5].

2.3 Determination of water-soluble alkali content

One of the mechanisms proposed to explain the effectiveness of supplementary cementing materials in suppressing expansion due to ASR is the reduction of alkalinity in the cement paste by the formation of low calcium silicate hydrates (C-S-H). These hydrates can entrap more alkalis, thus reducing the amount of alkali ions available in the pore solution for reaction with potentially reactive aggregates.

In order to evaluate the consumption of alkalis by the FA and MK the water-soluble alkali content of concrete was determined at various ages by the hot-water extraction method as suggested by Bérubé et al. [6]. 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 plays according some authors [7, 8] an important role in controlling the expansion by ASR.

According to some studies [2] the portlandite consumption can be also beneficial with respect to inhibition of DEF.

The portlandite content of the concrete samples was determined by thermogravimetry in an argon environment using an Setaram TGA92 Thermal Analysis System at a heating rate of 10º C/min. The portlandite content was determined from the loss mass in the range 400º to 500º C.

2.5 Microstructural and microanalytical investigations

Microstructural and microanalytical examination of concretes was performed in a JEOL JSM 6400 scanning electron microscope fitted with an Oxford INCA 400 energy dispersive X-ray analyser. Polished and freshly fractured surfaces from concrete samples tested for ASR and DEF were observed with different ages.

3. RESULTS

3.1 Expansion results

Figure 2 shows the expansion of concretes that were investigated in this study according the RILEM AAR-3 test method.

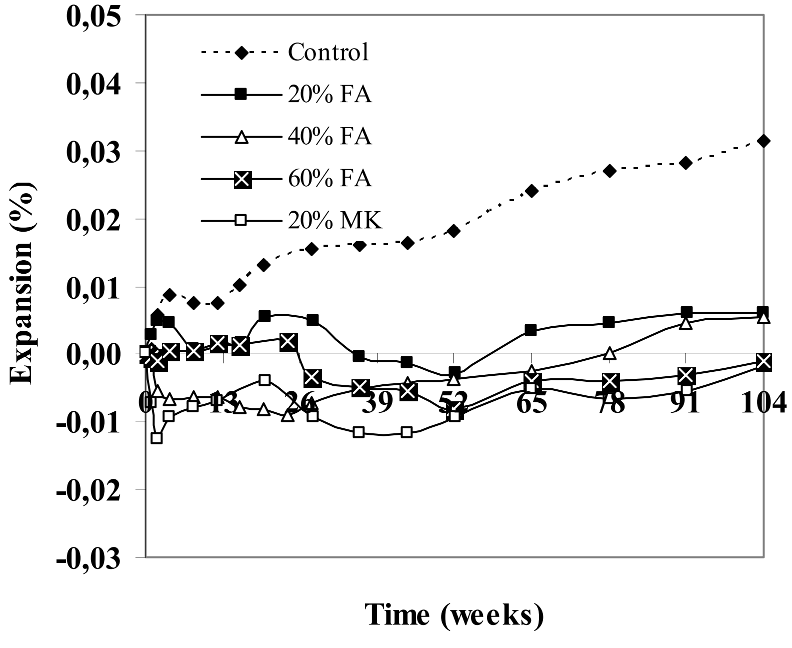

Figure 2 – Effect of FA and MK on expansion of concrete due to ASR.

As shown in figure 2, the 2-year expansion criterion of the RILEM AAR-3 was not reached for the control composition. This result could be explained by a possible marginally reactive composition as predicted in the AAR-3 method. However the results obtained after 2 years of exposition have shown an increase in the expansion that confirms the reactive behaviour obtained in the expansion mortar-bar AAR-2 method for the coarse aggregate and that was also confirmed by the petrographic analysis.

From figure 2 it can also be observed that 20% of FA or MK were effective in inhibiting the expansion by ASR, also the 20% of MK was significantly more effective than the 20% FA.

Figure 3 summarizes the 2-year expansion of concretes heat-cured and tested according to LPC method [5].

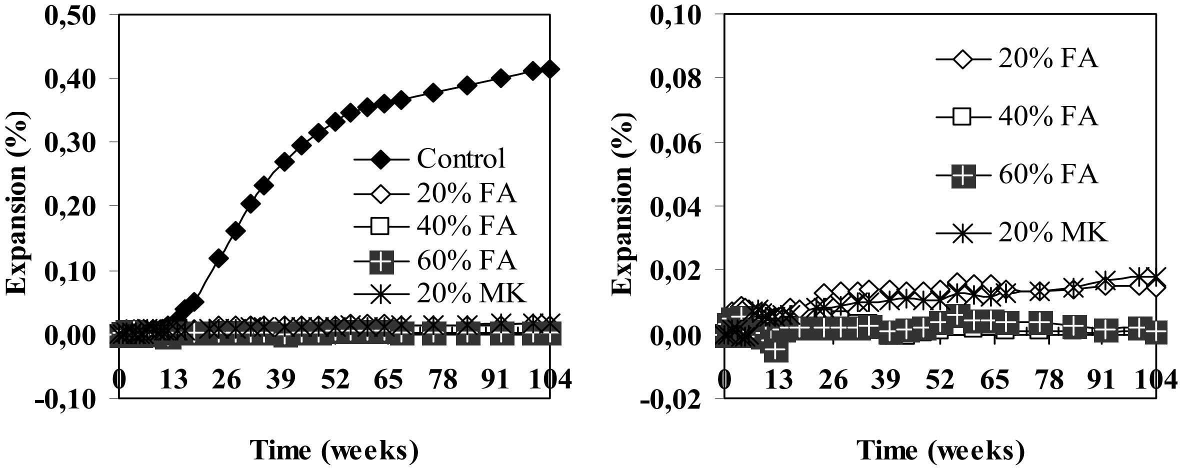

Figure 3 – Effect of FA and MK on expansion of concrete due to DEF.

As shown in the figure 3, 20% of FA or 20% of MK were effective in reducing the expansion by DEF compared with the control concrete. The control concrete expanded by more than 0,40% at 2 years, while no appreciable expansion was observed (not greater than 0,02%) with mixtures with FA or MK. These results are in agreement with the results of Ramlochan et al. [2] obtained for mortar samples.

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 % $Na_2O_{eq.}$, at ages of 28, 90 and 365 days are presented in figure 4. A clear reduction of alkalinity with time for the control concrete which is more pronounced at one year is noted. This observation can be attributed to the formation of ASR gels that consumed the alkalis during this period. On the other hand, the mixtures with FA, as well as MK, didn't show a markedly decrease in alkalinity during testing time as a result of its consummation during the pozzolanic reaction, as suggested by many authors [9, 10] to explain the mechanism of supplementary cementing materials in ASR suppression.

Figure 4 also indicates an increase in the alkalinity of concrete pore solution with the increase in the FA replacement. Besides this result, the mixture with 60% of FA shows more alkalis are released than entrapped with time. This suggests that the low expansion observed for concrete mixtures with FA is not dependent mainly on alkalis entrapped in pozzolanic hydrates.

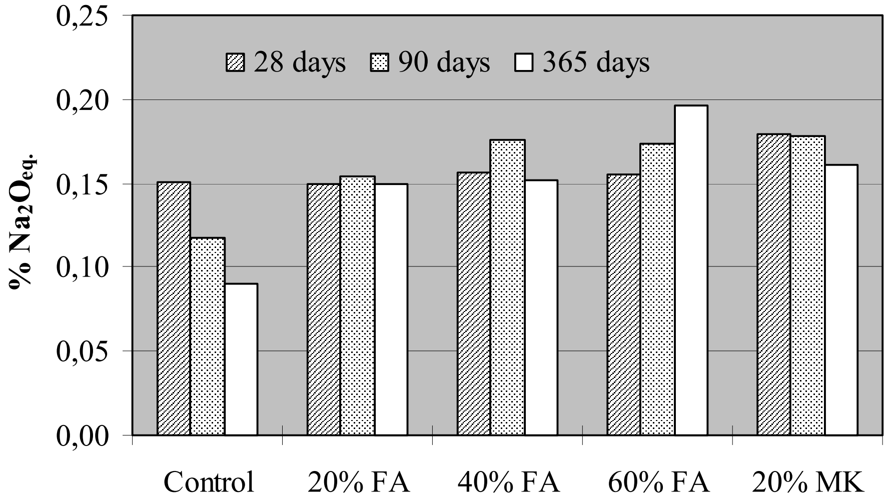

Figure 4 – Effect of FA and MK on the alkalinity of pore solution for concrete mixtures tested with the RILEM AAR-3 method.

3.3 Portlandite content

Figure 5 shows the evolution of portlandite content of concretes in the AAR-3 method with time. As expected all blended concrete mixtures contain less portlandite than the control concrete. Moreover, the increment in the cement replacement produces a significant reduction in portlandite content that is attributed to a dilution effect and also to the pozzolanic reaction.

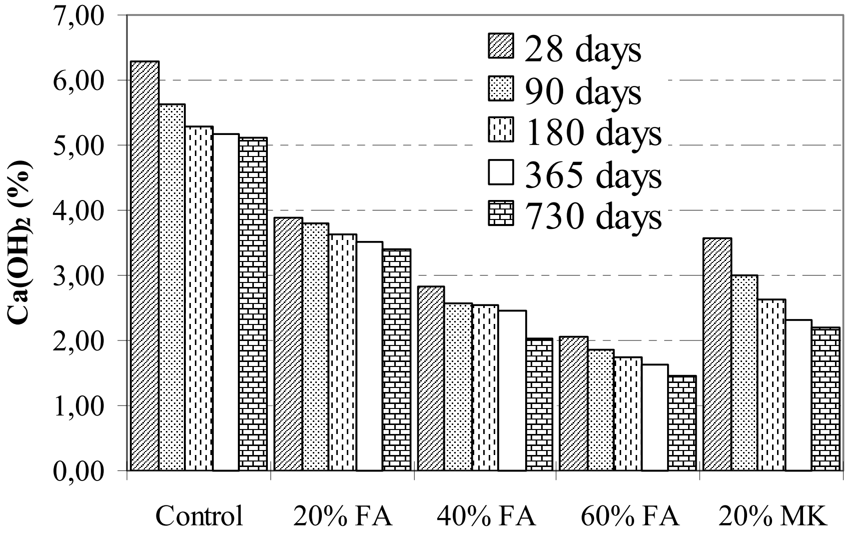

Figure 5 – Effect of FA and MK on the portlandite consumption for concrete mixtures tested with the RILEM AAR-3 method.

The MK consumed more portlandite than FA, which is consistent with the lower ASR expansion obtained for the MK mixture when compared with the same level of cement replacement using FA. This behaviour is attributed to the fineness and amorphous silica content of the MK. This indicates that the portlandite consumption in these tests is the major role of FA and MK in suppressing ASR.

Contrarily to the ASR expansion, no correlation was obtained between portlandite consumption and reduction in concrete expansion by DEF. This observation suggests that the effectiveness of FA and MK in suppressing expansion due to DEF depends on other parameters being the Al_2O_3 content of supplementary cementing materials one of the most important parameters in the suppression of DEF expansion [11].

3.4 Microstructural and microanalytical results

The SEM observations have confirmed the presence of ASR gels in the control concretes, heat-cured or not, which was more pronounced after 180 days of exposure. Moreover, in the FA mixtures, even with 60% of cement replacement, the presence of ASR gels near FA particles was detected (figure 6). This, as noted by other authors using silica fume blended-concretes, can explain some doubts about the long-term effectiveness of FA against ASR. Further studies are required to evaluate fully the effectiveness of FA in controlling ASR.

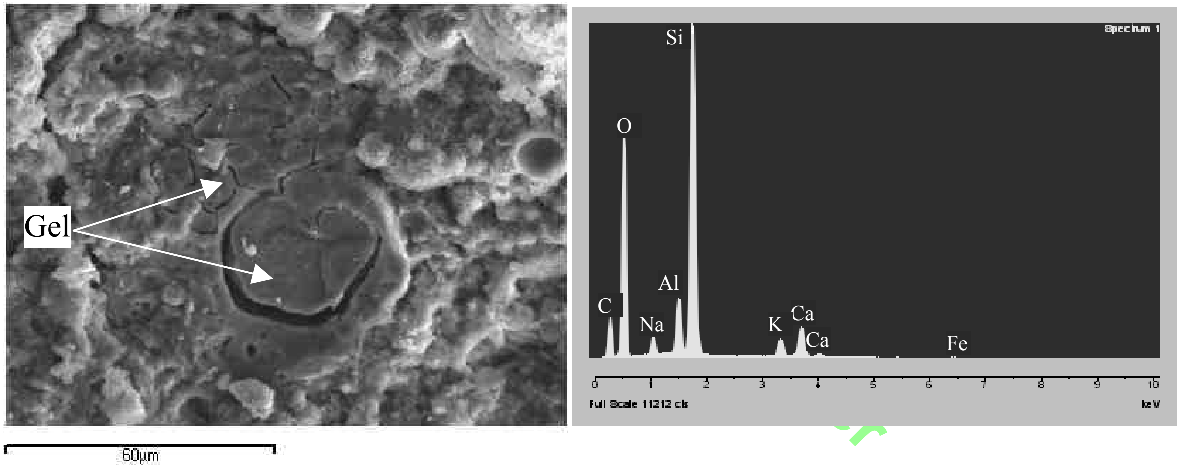

Figure 6 – SEM image of the 60% FA concrete after 180 days of storage, showing the presence of ASR gel near FA particles.

Only in the heat-cured concretes the presence of ettringite was observed. In the concrete without FA or MK the presence of great amounts of massive ettringite are found mainly filling voids and surrounding aggregate particles in the interfacial transition zone. With the FA and MK concretes these interfacial gaps were almost empty of massive ettringite. These observations combined can explain the much less expansion behaviour of these concretes when compared with the control concrete.

4. CONCLUSIONS

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 normal and heat-cured concretes. After

2 years of tests the use of 20% of FA or 20% of MK has proved to be efficient in eliminating the expansion by ASR or DEF.

Results obtained indicate that the reduction of the calcium hydroxide content is the most beneficial effect of FA and MK in ASR inhibition mechanism. The mechanism of DEF suppression by FA and MK is not completely understood so far and no 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 expansive DEF behaviour when FA and MK are used in sufficient quantity, they also reduce the heat hydration particularly for massive cast-in-place concrete.

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