INFLUENCE OF SUPERPLASTICIZERS ADMIXTURES IN THE ALKALI-SILICA REACTION

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Abstract

The alkali-silica reaction (ASR) consists of the reactive process in which aggregates containing reactive silica constituents react with alkalis and hydroxyl ions present in cement pore solution. It is suspected that some superplasticizers admixtures can contribute to the increase in concrete alkalinity. Literature presents some contradictory results about its influence on ASR. In this work the influence of superplasticizers admixtures in mortars prepared with pozzolanic admixtures was evaluated by accelerated mortar-bar tests and atomic absorption spectrophotometry. In the pozzolanic mixes the cement was replaced by 15% (weight %) of metakaolin or silica fume. Three superplasticizers admixtures (melamine, lignosulfonate and naphthalene) were utilized in three levels. The results show the mortars with the melamine based superplasticizers presented the lower content of soluble alkali and expansion. It is concluded that this admixture could be the most indicated for use with MK, or SF, to the inhibition of the ASR, considering the aggregate tested.

Keywords: superplasticizers, alkali-aggregate reaction, metakaolin, silica fume, mitigation.

1 INTRODUCTION

To originate the alkali-silica reaction in concrete is necessary the presence of reactive constituents in the aggregates, high alkalinity and sufficient moisture. The main source of alkalis in concrete is generally Portland cement, although others constituents, such as mineral admixtures and some types of aggregates can also be alkalis suppliers.

Mineral admixtures are the materials most used in AAR mitigation [1,2], which includes metakaolin, silica fume and coal fly ash [3,4]. However, the use of mineral admixtures in concrete normally causes the increase in water/cement ratio, which affects some durability properties of concrete. To overcome these losses, water-reducer and superplasticizers admixtures are used in concrete formulations to reduce the water content.

Some works found in literature dealing with water-reducer and superplasticizers admixtures in AAR [5,6,7] have shown that the admixtures content may increase or reduce the AAR expansion, and there isn't a tendency that indicate whether each type of admixture has a positive or negative behavior. This divergence motivates the necessity of more researches in this area.

Some superplasticizers admixtures have an alkali content that isn't negligible, suspecting that these alkalis may interfere in the AAR development.

Given what has been exposed here, it is observed that there are gaps in knowledge of the AAR mitigation on important issues such as negative or positive contribution of superplasticizers admixtures in this pathology, there are few researches about the superplasticizers in deleterious reaction, and even less involving these admixtures together with the mineral admixtures.

To investigate the behavior of the superplasticizers in AAR a testing campaign was implemented, including the use of accelerated mortar-bar tests and the hot-water extraction method to measure the soluble alkalis by atomic absorption spectrophotometry (AAS). The objective of this work is to evaluate the influence of superplasticizers in AAR, studying the behavior of mortars prepared with metakaolin or silica fume.

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2 MATERIALS AND METHODS

2.1 Materials

Cement

A Brazilian cement CPV ARI (0.56% of Na_2O_{eq}. and blaine fineness of 461 m^2/kg), similar to a CEM I type, was selected for the tests. This cement type has no pozzolanic materials, which allows greater identification of the influence of types of mineral admixtures in the AAR expansion/mitigation without interference of these admixtures, and due to the fact that the CPV ARI is one of the cements recommended to be use in the accelerated mortar-bar test NBR 15577-5 [8].

Pozzolans

Two commercial pozzolans were used, namely silica fume (SF) and metakaolin (MK), as partial cement replacement in 15 % (wt %). The choice of metakaolin was based on the high demand for use in the Northeast region of Brazil, and silica fume because it presents high mitigation among the existing mineral admixtures [3,9]. The silica fume is constituted of fine powder originated from steel industries.

Aggregate

The selected aggregate was a mylonite, from a quarry located in the city of Vitoria de Santo Antão - PE/Brazil. The choice of this aggregate was due to the fact that this shows greater reactivity among the various aggregate types investigated by Silva [10]. The rock was collected from a pile in the quarry for further crushing. The aggregate particle size used was specified by NBR 15577-5 [8] and it is similar to the particle size recommended in the ASTM C 1260 [11].

Chemical admixtures

The chemical admixtures selected were of superplasticizers based on melamine (ME), naphthalene (NA) and lignosulfonate (LI) for being previosuly widely used in constructions; this paper did not tested polycarboxylate admixtures that are nowadays widely used. The superplasticizer lignosulfonate and naphthalene were from only one manufacturer, and the melamine was supplied by another manufacturer.

2.2 Methods for assessment, mix designs and analysis

Methods for materials characterization

X-ray fluorescence (XRF) [12] was used for chemical analysis of cement, aggregate, mineral admixtures and superplasticizers admixtures. The petrographic analysis was used for the mineralogical characterization of the aggregate by NBR 15577-3 [13]. The specific surface (BET) was determined in the mineral admixtures and also the pozzolanic activity at 28 days [14]. The pozzolanic activity test were prepared three combination of mortars, being 1 used as reference (only cement) and 1 with metakaolin and silica fume as partial cement replacement in 35 % (wt %). The pozzolanic activity was given by the relationship between the compressive strength of the mortars with the pozzolans and of the reference mortar. The amount of water was obtained through the consistency index of the mixture should reach (225 $\pm$ 5) mm, such as recommended by the AMBT. Were prepared 6 cylindrical specimens (5x10) cm of each mixture of mortars and tested at 28 days of wet curing. The pozzolanic activity index with cement at this age should be at least 75% for the material to be considered pozzolan.

Accelerated mortar-bar tests (NBR 15577-5, 2008)

This accelerated mortar-bar test (AMBT) is employed to analyze the possible mitigation effect when mineral admixtures are used in the mortar mix. The mix proportion used was 1:2.25 (cement: aggregate) by weight, w/c ratio = 0.47. The cement was replaced by 15 % (wt %) of metakaolin or silica fume.

The superplasticizers were utilized in three dosages, referred as minimum, optimum and maximum dosage. The minimum and maximum dosages were recommended by the manufacturers, and the optimum was defined by the result obtained in the Marsh cone test. These dosages used were as follows:

- Lignosulfonate - minimum (0.6 % SF, 0.6 % MK), optimum (0.8 % SF, 0.8 % MK) and maximum (1.0 % SF, 1.0 % MK);
- Melamine - minimum (0.5 % SF, 0.5 % MK), optimum (1.0 % SF, 1.1 % MK) and maximum (1.5 % SF, 1.5 % MK);

- Naphthalene - minimum (0.6 % SF, 0.6 % MK), optimum (0.8 % SF, 0.7 % MK) and maximum (1.5 % SF, 1.5 % MK).

Thus, 21 mortar combinations were obtained, being 3 of them serving as reference (1 with cement without pozzolan and superplasticizer admixture; 1 with 15 % metakaolin without admixture; and 1 with 15 % silica fume without admixture) and 18 mortars prepared with 3 admixtures, using 3 admixtures dosages and two mineral admixture types (MK and SF). Three bars for each mortar combination of materials were prepared.

In this test, the mortar bars are immersed for 14 or 28 days in 1 M sodium hydroxide (NaOH) solution, respectively 16 and 30 days after casting, being performed regular expansion measurements during this time. According to the limits of NBR 15577-5 [8], a given mixture with mineral admixture that presents an expansion lower than 0.10 % at 16 days after casting is classified as potentially innocuous, while if the expansion value exceeds this limit the mixture is classified as potentially reactive. According to the NBR 15577-4 [15] the expansion limit at 30 days after casting is 0.19%. Since the mixtures tested present at 16 and 30 days after casting similar expansion behaviors (proportional trend), it was decided to investigate the results at 30 days.

Measurement of the Alkali Content of Concrete Using Hot-Water Extraction

Mortars were prepared with the same procedure of NBR 15577-5 [8], but in this case were stored in a plastic container without NaOH contact. The mortars were tightly sealed and wrapped in sealed plastic bags in order not to lose moisture, and stored at 80˚C. This procedure was performed to attend the same conditions of the AMBT, but without being subjected to the contact with extra alkali sources. All mortars were tested at 30 days after casting and some also at 2 days after casting.

Twelve combinations of mortars were prepared, being 3 used as reference (1 with cement without pozzolan and superplasticizer; 1 with 15 % MK and without superplasticizer, and 1 with 15 % SF without superplasticizer) and 9 mortars prepared with the maximum dosage of the three superplasticizers and with and without MK and SF.

After the required period of time in the oven at 80º C, the mortar samples were dried, finely ground and passed through a 106 µm sieve. A sub-sample of 10 g of each mortar was immersed in 100 ml of deionized boiling water for 10 minutes. The pulp was allowed to rest during 24 h at room temperature being then filtered and volume solution was adjusted with distilled water to complete two balloons of 1000 ml. The Na and K concentrations were obtained after by AAS [16].

3 RESULTS

Tables 1 to 4 show the results of characterization of cement, aggregate, pozzolan and superplasticizers admixtures. These data are to emphasize the alkali equivalent content of the three employed superplasticizers, which increases in order LI - NA - ME.

The results according to AMBT NBR 15577-5 [8], obtained at 30 days after casting, with the use of the materials mentioned in 2.1 are shown in Figures 1 and 2. These figures presents the results obtained for each type of pozzolan (MK and SF) in the reference samples and with superplasticizers.

From Figure 1 we can observe that mortar Ref, which was prepared without MK and admixture, showed the highest expansion as expected, because not contain material to mitigate the AAR, confirming the aggregate reactivity. The Ref-MK mortar, incorporating 15 % MK and 0 % of admixture, presents in comparison with the precedent one a minor expansion value, but near to the expansion limit value of 0.19 % at 30 days [8]. Regarding the effect of different superplasticizer types, it was observed that in general a dosage increase lead to an increase in expansion value. However, with the minimum dosage only the LI contributed to the increase of the expansion (15 % extra), while the ME and NA showed a mitigation effect (respectively 12.8 % and 6.4 % less). With the optimum superplasticizer dosage the expansion values increase with all superplasticizers, and particularly with LI (25.7 % extra). The ME and NA with optimum dosage presents expansion values near the limit of 0.19 % at 30 days after casting. With the maximum superplasticizer dosage, the LI and NA had a significant increase in the expansion values, and the ME remained near the limit of 0.19 %. The LI increased the expansion value in the order of 31.6 %, while the NA increased in the order of 42.8 %.

It was observed in the Figure 2 that the Ref-SF mortar, with 15 % SF and 0 % admixture, had a high-reduced expansion compared to the sample Ref-MK. This result is consistent with the greater pozzolanicity of the SF (Table 2). Regarding the results of the superplasticizers with SF, it was observed a similar trend to the observed previously with MK, i.e., expansion increases with the increase in superplasticizer dosage. Regarding the minimum dosage of admixture there are no considerable variations in expansion values at 30 days after casting. However, with the optimum dosage of admixture is observed an increase in the expansion values, which are much more evident with LI (50.0 % extra), though remaining below of the expansion limit of AMBT NBR 15577-5 [8]. With the maximum admixture dosage, the LI and the NA had a significant increase in expansion, however remaining below of the expansion limit at 30 days. The LI increased expansion in the order of 71.9 %, and the NA in 56.2 %.

Figures 3 and 4 presents the results of the water–soluble alkali contents obtained for mortar after 30 days of the test, expressed in terms of Na_2O and K_2O, respectively, and obtained for the reference samples and in the samples with the introduction of superplasticizer. In general, it was verified that the mortars with NA have the highest content of soluble alkalis, while the SF is less effective than MK in reducing the alkalis in pore solution.

The Figure 5 shows the relation obtained between expansion versus Na_2O_{eq} at 30 days after casting, for the mortars prepared with superplasticizer and with the two pozzolans. From Figure 6 is evident the good correlation obtained between these two parameters.

The Figure 6 presents the results of Na_2O_{eq} evolution from 2 to 30 days for mortar samples with MK and SF, relative to the reference mortar and with the superplasticizer ME. These results show a beneficial effect of the use of ME superplasticizer in terms of the soluble alkalis in the pore solution.

4 DISCUSSION

The expansion results obtained with MK and SF (Figures 1 and 2) show that the LI and NA superplasticizers have an negative effect in AAR expansion, which increases with the dosage increase of these two admixtures. The melamine is among the three studied superplasticizers the one that has a more innocuous behavior in relation to AAR expansion, although this is the admixture with the higher alkalis content. Moreover, in terms of AAR expansion the mortars containing LI and NA appear to be much more sensitive to the alterations in the admixture dosage.

The results of the soluble sodium content obtained (Figure 3) for the mortar samples without admixtures (Ref, Ref-MK and Ref-SF) show that the highest value was obtained for the mortar with SF (0.111 %), followed by mortar with metakaolin (0.102 %) and of the mortar with only cement (0.061 %). This behavior can be due to the consumption of alkalis to the formation of AAR products (high in Ref mortar, since is the one that show high expansion) and concurrently with the contribution in alkalis from the mineral admixtures. In this case, the SF mortars were the most unfavorable, because this pozzolan is the one that contains higher content of soluble alkalis.

The use of the different admixtures presented variations, as expected, in the Na_2O values independently of the use of SF or MK. When using the maximum dosage of ME admixture, and in comparison to the same mortars without superplasticizer admixture, we observe a decrease in Na_2O content with SF and MK, and an increase in the Ref mortar. Regarding the maximum dosage of LI admixture, the SF mortar is now the mortar that shows higher Na_2O content (0.138 %), followed by MK mortar (0.092 %) and the Ref mortar (0.080 %). Generally, mortars produced with SF, with or without superplasticizers admixtures are those which had the higher Na_2O soluble content, which is according with the higher soluble content of Na_2O in SF compositions. The mortars group with NA superplasticizer was the ones that provided the higher Na_2O content.

In terms of soluble K_2O values (Figure 4) it was observed that the incorporation of pozzolans and chemical admixtures was a tenuous effect. For example, the reference mortars (with metakaolin and silica fume and without superplasticizer) obtained values of the order of 0.088 % to 0.103 %, while with admixture ME the variation is between 0.091 % and 0.109 %. Regarding the admixture LI the range is between 0.087 % and 0.110 %, being for admixture NA 0.101% to 0.120 %. As previously mentioned with Na_2O, the group of mortars with NA is what has most soluble K_2O content.

Confronting the results of expansion and soluble alkalis obtained (Figures 1 to 5), is observed that mortars with LI and NA admixtures presented the highest alkali content, indicating that the use these superplasticizers, even with MK, are not efficient in AAR suppression. This suppression behavior seems be favored when the SF is used, being also in this case dependent of admixture type used.

These results prove that the alkalinity of the admixtures materials interferes in the AAR behavior as expected. However, it is not possible to infer from these results that there is a direct influence of the alkali content of the superplasticizer (Table 4) in the increase of the alkalinity of mortars or in expansion due to AAR.

On the other hand, it was observed an increase in the soluble alkalis content with time, namely from 2 days to 30 days (Figure 6), following the same tendency of expansion in AMBT tests. This can be explained by the increase in solubilization of the aggregate minerals over the 30 days, which release alkalis to the pore solution. This is in agreement with the concerns referred by some authors about the aggregates influence on the alkalinity increase of the cement pore solution. This is particularly important in aggregates rich in alkaline minerals such as feldspars [17]. It is important emphasize that, besides quartz, feldspar is the main mineral presented in the mylonite aggregate used in this study (Table 3), which proves the aggregate interference in the alkalinity of these mortars.

5 CONCLUSIONS

This work shows that the superplasticizers type and superplasticizers dosage can interfere in the AAR expansion, as expected. A positive trend was obtained between expansion and the increase of admixtures dosage, regardless of the type of pozzolan used.

The mortars with the superplasticizer based naphthalene showed the higher content of soluble alkalis and of expansion, indicating that the use of this admixture requires high caution in the presence of reactive aggregates.

The mortars with the superplasticizer based melamine showed the lower content of soluble alkali and of expansion, concluding that this type of admixture is the most indicated to be used with MK, or SF, for the AAR inhibition or mitigation.

The results show that there is a relation between the alkalinity of the medium and the highest expansion obtained in AMBT independently of the superplasticizers used, and in the presence of MK and SF. However, it was not established that this alkalinity increase was related to the admixtures alkali content. The interference of the dissolution of the aggregate minerals in alkalinity increase of the mortars was proved.

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TABLE 1: Chemical characteristics of the cement and pozzolans.

Chemical properties (%)	Cement	Metakaolin	Sílica fume	Aggregate
CaO	68.2	0.80	0.89	3.75
SiO_2	19.17	51.90	94.2	64.56
Al_2O_3	3.70	33.40	0.21	11.82
Fe_2O_3	4.00	9.10	0.16	6.20
MgO	-	0.20	0.31	0.60
SO_3	2.85	0.10	0.19	0.20
P_2O_5	0.30	0.12	0.16	0.34
TiO_2	0.30	-	-	0.87
Na_2O	0.10	0.10	0.30	4.45
K_2O	0.70	1.20	0.76	6.05
MnO	-	-	-	0.13
Rb_2O	-	-	-	0.08
SrO	-	-	-	0.08
Cr_2O_3	-	-	-	0.07
LOI	0.78	3.11	2.80	0.71
Total alkalis				
Na_2O	0.10	0.10	0.30	4.45
K_2O	0.70	1.20	0.76	6.05
Na_2O_{eq}	0.56	0.89	0.80	8.43
Soluble alkalis				
Na_2O	0.08	0.00	0.15	-
K_2O	0.70	0.00	0.11	-
Na_2O_{eq}	0.54	0.00	0.21	-
NOTE: The LOI was included. $Na_2Oeq = \%Na_2O + 0.658.\%K_2O$.				

TABLE 2: Physical characteristics of the pozzolans.

Pozzolans	Metakaolin	Silica fume
Pozzolanicity at 28 days (%) NBR 5752	79.0	88.0
BET (m^2/g)	17.25	20.02

TABLE 3: Mineralogical characteristics of the aggregate.

Main mineralogy	- Feldspars (plagioclase and microcline) - Quartz
Subordinate minerals	- Biotite, calcite, epidote, apatite, sericite-muscovite and opacs
Deleterious minerals	- Altered feldspars (>5%) and quartz microcrystalline (>5%)
Lithotype	- Mylonitic texture - Fine grain size with mid to large-grade porphyries - Medium altered (sericitised feldspars and some covered by pulverised opaque minerals) - Extremely deformed rock - Presence of biotite
Denomination	Mylonite

TABLE 4: Physical and chemical characteristics of the admixtures.

Physical characteristics			
Description	Naphthalene	Melamine	Lignosulfonate
Density (g/cm³)	1.21	1.12	1.20
Solid content (%)	40.90	21.60	44.80
Chemical characteristics (%)			
Description	Naphthalene	Melamine	Lignosulfonate
Al_2O_3	0.2	0.1	0.4
CaO	3.3	0.4	42.1
SO_3	90.5	93.2	50.0
SiO_2	0.8	0.6	1.5
MgO	-	-	0.3
P_2O_5	-	-	0.3
Fe_2O	-	-	0.7
MnO	-	-	0.2
ZnO	-	-	0.3
Na_2O	4.9	5.4	2.9
K_2O	0.1	0.1	1.2
Na_2O_{eq}	4.96	5.46	3.69
pH	7.84	8.20	6.70
NOTE: $Na_2Oeq = \%Na_2O + 0.658.\%K_2O$.			

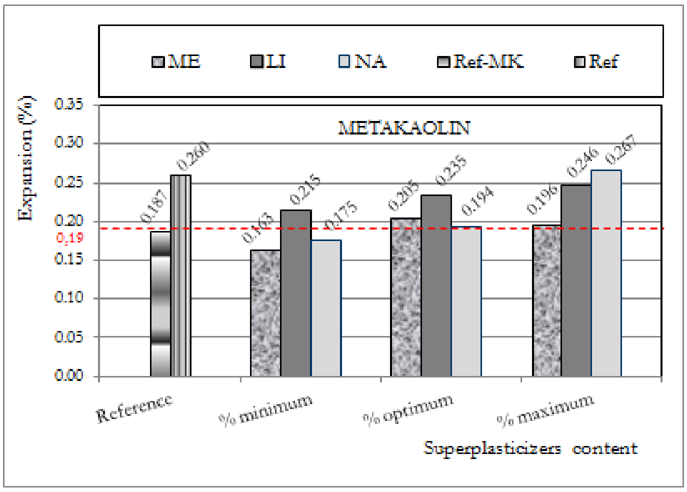

FIGURE 1: AMBT expansion results at 30 days after casting with 15% MK and the three superplasticizers admixtures.

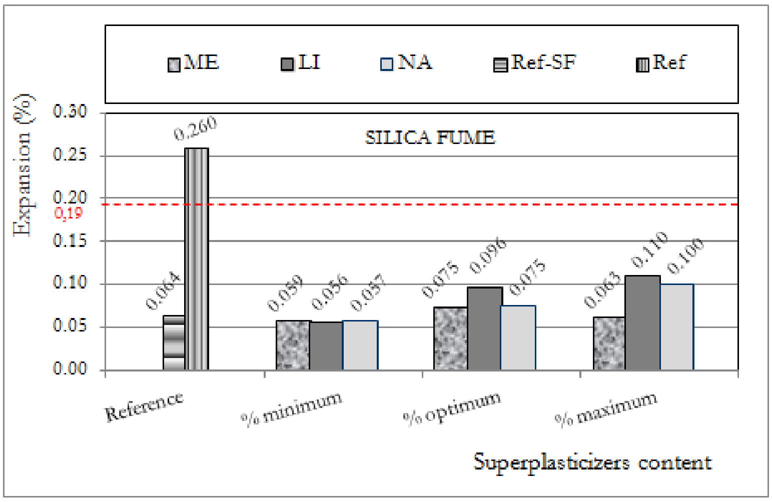

FIGURE 2: AMBT expansion results at 30 days after casting with 15% SF and the three superplasticizers admixtures.

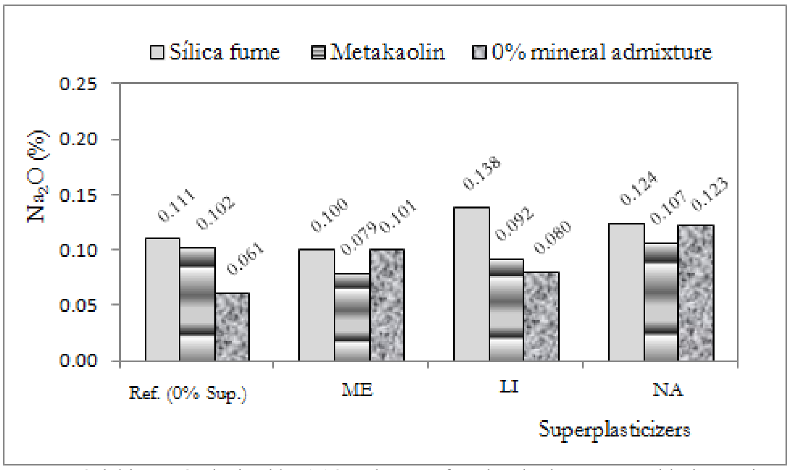

FIGURE 3: Soluble Na_2O obtained by AAS at the age of 30 days in the mortars with the maximum superplasticizers dosage.

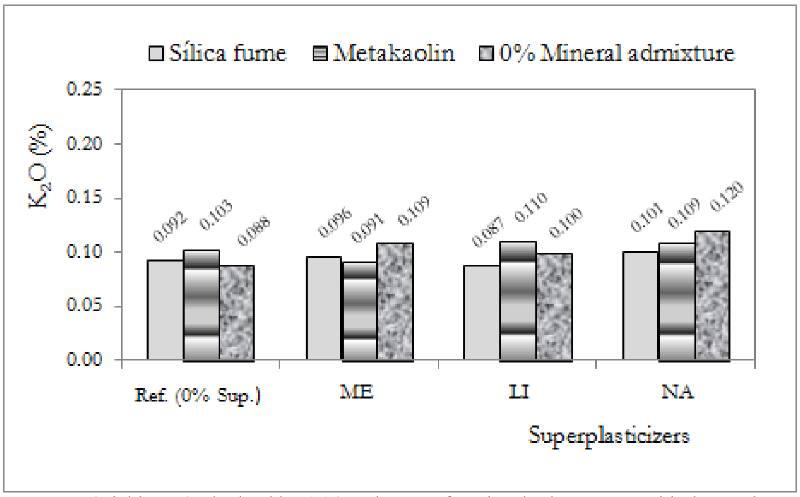

FIGURE 4: Soluble K_2O obtained by AAS at the age of 30 days in the mortars with the maximum superplasticizers dosage.

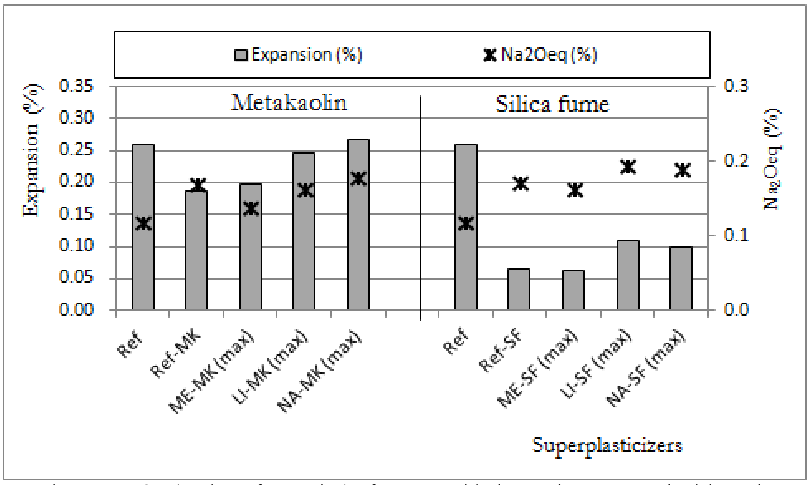

FIGURE 5: Expansion vs Na_2O_{eq} (30 days after casting) of mortars with the maximum superplasticizers dosage and with MK and SF.

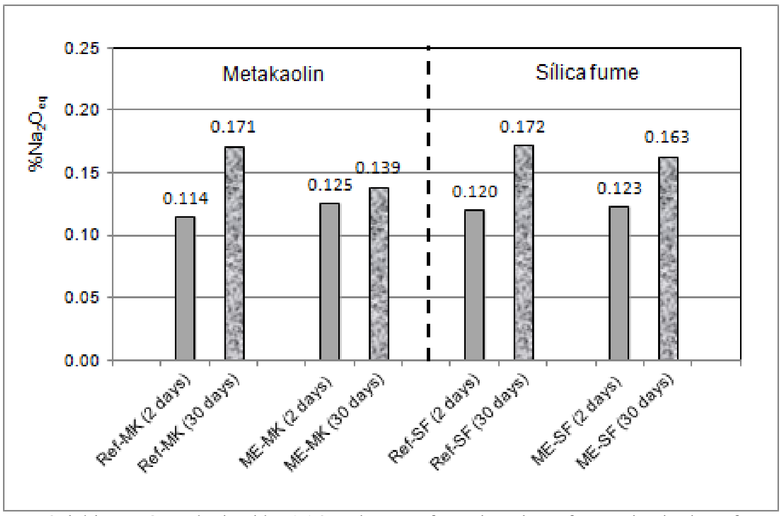

FIGURE 6: Soluble Na_2Oeq obtained by AAS at the age of 2 and 30 days after casting in the reference and melamine mortars with maximum dosage of superplasticizers.