EFFECT OF MINERAL ADMIXTURES ON TO THE MITIGATION OF ALKALI-SILICA REACTION IN CONCRETE

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Abstract

Alkali-aggregate reaction (AAR) requires the action of water, reactive aggregate and alkalis altogether. Prevention means eliminating one of these factors. Otherwise, when reactive aggregates are used, other preventive measures must be taken. One solution is to use mitigating admixtures to composite cements, which is the object of the present research. Experimental work included two reactive aggregates, basalt and granite. Basalt carries deleterious glass and chloropheite while granite carries microgranular, recrystallized quartz and deformed feldspar, both give rise to alkali-silica reaction, though differing in the speed of reaction, basalt are rapid-reacting and granite, slow-reacting aggregates. The aggregates were mixed with 15 experimental composite cements, following composition of Brazilian industrial cements (blast-furnace slag at 15%, 30%, 45%, 60%, and fly ash at 10%, 15%, 25%, 35%) and the amounts generally added to concrete (metakaolin at 5%, 10%, 15%, 20%, and silica fume at 5%, 10%, 15%).

Keywords: alkali-aggregate reaction, alkali-silica reaction, reactive aggregate, admixtures

1. INTRODUCTION

Alkali-aggregate reaction has become one of the most challenging problems in concrete technology today. Due to environmental concerns, changes in the manufacturing process of portland cement have led to increases in its alkali content. In addition, sources of non-alkali reactive aggregates are being depleted around the world. This combination of factors has set favourable scenarios for alkali-agreggate AAR to occur more frequently.

The interaction of cement, fine and coarse aggregates, water and additives will determine the concrete properties and influence its durability. The service useful life of concrete structures will be determined by the quality of these materials and also by the construction processes, physical properties, exposure conditions and the kind of solicitation for which it is designed.

Durability of concrete means its resistance to chemical, physical, mechanical and biological aggressions from the environment and to the mechanisms occurring within the concrete itself. Among the chemical aggressions, the attack by chloride and sulphate ions, carbon dioxide, acids and alkali-aggregate reactions stand out.

The reaction between alkali hydroxides within the liquid phase of concrete pores and reactive aggregates is slow and results in a gel. By accumulating in the voids and on the interface paste-aggregate the gel, in presence of water, expands and exherts internal pressure in to the concrete. When it exceeds the tensile strength, the internal pressure may promote fissures.

The fissures increase permeability and allow more water/moisture into the concrete, accelerate the alkali-aggregate reaction and make the concrete more vulnerable to pathological phenomena, endangering the quality of the structure.

Three conditions are necessary to start up the alkali-aggregate reaction in concrete: 1) presence of reactive phases in the aggregate, 2) moisture, 3) concentration of alkali hydroxides (K^+, Na^+, OH^-) in the concrete pore solution to react with the reactive phases of the aggregates. When one of these factors lacks, the reaction will not occur [1-2].

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The most efficient measure to prevent the AAR is to use non-reactive aggregates, which is often neither practical nor economically viable. Mineral admixtures such as blast-furnace slag, fly ash, metakaolin and silica fume have been recommended and used for the mitigation of the deleterious effects of AAR in concrete. Pozzolanic admixtures are believed to improve the resistance of concrete to AAR by reducing the diffusivity of ions into concrete and through the consumption of $Ca(OH)_2$. However, a complete understanding of how these mineral admixtures influence the chemistry of AAR is still needed. Minimum amounts of these additions to portland cement may vary according to the aggregate reactivity, alkali content in cement, quality of these materials as well as mechanisms for expansion decrease [3].

In Brazil, blast-furnace slag and pozzolans from fly ash and calcined clay are constituents of blend portland cement, while metakaolin and sílica fume may be added to concrete (NBR 12655/2006). Seven types of cement are produced, which, besides clinker and calcium sulphate, may contain limestone filler, blast-furnace slag and pozzolanic materials (fly ash or calcined clay) in different amounts. The most efficient types of cement to AAR mitigation are the blast-furnace (CP III) and pozzolanic (CP IV) ones, representing 18% and 7% of national production in 2005, respectively. The other types, less efficient to this purpose, represent 75% of national production [4].

The presence of blast-furnace slag and pozzolanic materials in certain types of cement does not guarantee AAR mitigation, as it will depend also on the amount of addition, reactivity degree of aggregate and total amount of alkali in concrete. On the other hand, these cements with additions are not available nationwide, because its production depends on availability of blast-furnace slag and pozzolanic materials.

Deleterious expansion and cracks in concrete coming from the AAR may also be significantly reduced and even prevented by the use of low-alkali cements or by limiting the total alkali in concrete to a specific value, $3 kg/m^3$ Na_2O_e being the most recommended [5].

This limit applies to the majority of aggregates and may vary from 1.8 to 3 kg/m^3 Na_2O_e, but in practice, it depends on the reactivity degree of the aggregate, the total alkali in cement, cement consumption in concrete (kg/m^3), exposure conditions of the structure, the structure design and the risk analysis of potential occurrence of the reaction [5].

The aggregate reactivity may be determined by the accelerated method of mortar bars ASTM C 1260 or by the long-term method with concrete prisms - ASTM C 1293. The petrographic analysis allows evaluating the reactivity of the aggregate based on the identification of reactive phases present in the material.

When the aggregate is reactive and there is availability of cements with slag or pozzolan, the question is to know whether the present amount is enough to mitigate the AAR. Otherwise, what would this amount be?

If the cement available in the region is not AAR mitigating and in case it is not possible to bring it from somewhere else, metakaolin and silica fume are technically and economically viable options. In this case, for the cement type and aggregate available, what would the adequate amount be to mitigate the aggregate reactivity?

The best way to prevent the pathology related to the AAR is to determine the aggregate reactivity before its use in concrete, and, upon this evaluation, select the most adequate portland cement.

2 MATERIALS AND METHODS

2.1 General

Potentially reactive milonitic granite from the Metropolitan Area of Recife (PE) and basalt from Marilia (SP) were used in all the mixes [6].

Slow-reacting aggregates - The Recife milonitic granite (alkali-feldspar protomilonitic granite) went through tectonic processes that led to textural deformation and shearing, thus increasing entropy and modifying the silicates crystal structures. The occurrence of frequently recrystalized microcrysts of quartz associated to deformed feldspar and quartz showing undulatory-extinction indicate susceptibility to reaction with the concrete alkali. Due to the crystalline state of silica, those aggregates that bear these phases will slowly react with the alkalies [7].

Rapid-reacting aggregates - Basalt rocks from Brazil's South and Southeast regions have been largely used in concrete on both current (e.g. residential) and infrastructure (e.g. dams) building works. Volcanic glass, calcedony and chloropheite, poorly crystallized mineral substances with uncoherent, desordinate, flawed crystal structures, are phases susceptible to contribute alkali to concrete pore solution. These phases in aggregates will enhance their reaction with the alkali [7].

The blast furnace slag produced by CSN - Companhia Siderurgica Nacional (RJ) and fly ash, by COPESUL - Companhia Petroquimica do Sul (RS), used were equivalent to those generally added to the Brazilian blast-furnace and pozzolan composite cements. Metakaolin from Caulim do Nordeste S/A, Ipojuca (PE) and silica fume from Camargo Correa Cimentos S/A, Sao Paulo (SP) were similar to those added directly to concrete in Brazil. They are the only admixtures allowed to concrete according to Brazilian Standard NBR 12655.

2.2 Materials and mix designs

The granite contained mainly microcline K-feldspar and plagioclase feldspar (61%) and quartz (22%), with smaller amounts of muscovite and biotite (13%), ore minerals (1%), epidote (1%), and others (allanite, titanite, zircon, carbonates, chlorite, Fe-hydroxides). The basalt contained plagioclase (An_{45-50}) feldspar (29%), augite (39%), ore minerals (10%), Fe-rich dark glass (18%), Fe-hydroxides (2%), chloropheite (2%) and calcedony (<1%).

The blast-furnace slag was made up by glassy (90% vitrification degree), irregular-shaped grains, that in XRD shows an amorphous halo within $2\theta=20^{\circ}$-40° and crystallized melilite ($Ca_2Al_2SiO_7$), merwinite ($Ca_3Mg(SiO_4)_2$) and quartz (SiO_2). The fly ash shows in XRD crystallized quartz (SiO_2) and mullite ($3Al_2O_3.2SiO_2$), and an amorphous halo within $2\theta=15^{\circ}$-30° corresponding to the glassy phase.

Metakaolin is composed mainly by metakaolinite that corresponds to the amorphous halo within $2\theta=15^{\circ}$-30° shown in XRD, indicating the efficacy of calcination. Quartz (SiO_2) and hematite (Fe_2O_3) are present in trace amounts. Silica fume is almost completely amorphous, with a halo within $2\theta=15^{\circ}$-30°, bearing only minor quartz (SiO_2).

A high-alkali (0.26% Na_2O, 0.90% K_2O, 0.85% Na_2O eq.), high early-strength, AAR-non-mitigating, 0.10% autoclave expansion, 2.8% carbonate filler, cement (ASTM C 150 Specification for Type III) was used.

Mortar bars were prepared and tested in accordance with the Accelerated Mortar Bar Test Method ASTM C 1567 [8] for assessing the ability of blast furnace, fly ash, metakaolin and silica fume to control expansion due to AAR. It is thought that this standard is the first to include the accelerated mortar bar method for evaluating preventive measures.

The standard requires that mineral admixtures be tested for a range of replacement levels to determine the minimum "safe level" required to limit expansion in the presence of an alkali-silica reactive aggregate to <0.10% at the end of the test period. The standard further requires that the reactive aggregate used in the test produce expansions of at least 0.30% when tested without mineral admixtures.

The control bars were cast using Recife milonitic granite and Marilia basalt aggregates with the OPC. The reactive coarse aggregates were crushed and graded according to the standard test procedure. Mortar mixes were proportionated to have an aggregate/cementitious material ratio of 2.25 and water/cementitious material ratio equal to 0.47. Samples were cured at room temperature, in their moulds, for 24 h. Then, they were stripped, immersed in water and maintained at 80°C for another 24 h. After that, samples were taken out, their initial lengths were measured and they were soaked in 1 M NaOH solution at 80°C throughout the testing period. Length changes were measured periodically until 28 days.

The 14-day expansion results are taken as reference for the reactivity of the aggregate with alkali. Combinations that yield a mortar bar expansion value higher than 0.20% indicate that the aggregate is reactive. Within 0.10% and 0.20%, it is potentially reactive and complementary tests should be carried out to assess its reactivity. Values less than 0.10% indicate the aggregate is inocuous [9].

A total of 15 mixes were cast using various replacement levels of blast-furnace slag, fly ash, metakaolin and silica fume for the high early-strength cement. The amounts of slag and fly ash in the mixes followed those of Brazilian industrialized composite cements. Metakaolin and silica fume contents followed the range usually added directly to concrete. Figure 1 illustrates the composition of the mixes.

3 RESULTS

The chemical compositions of the OPC, admixtures and aggregates and the physical properties of the high early-strength cement and admixtures are shown in Tables 1 and 2, respectively.

The determination of the aggregate reactivity (ASTM C 1260) through the development of expansion with time of the control samples with Recife milonitic granite and Marilia basalt aggregate is shown in Figure 2. Also shown in the graph are the 14-day expansion reference and classification according to ASTM C 1260/05. Average expansion values yielded by the granite and the basalt control samples were 0.25% and 0.49%, respectively.

Figures 3 and 4 show the expansion evolution at 14 and 28 days of mortar bars containing milonitic granite and basalt aggregates, respectively, stored at 80°C in 1 M NaOH solution (ASTM C 1567), with increasing replacement levels of blast furnace, fly ash, metakaolin and silica fume admixtures.

Figure 5 shows the expansion at the end of the 14-day immersion period of Recife milonitic granite and Marilia basalt aggregates in mixes with high early-strength cement and increasing replacement levels of blast-furnace slag, fly ash, metakaolin and silica fume admixtures.

4 DISCUSSION

At the end of the 14-day immersion period, the granite control specimens had expanded to average 0.25% and the basalt control specimens had expanded to average 0.49%. The basalt aggregate expanded more rapidly and to a greater extent than those made with the granite aggregate. Their reactivity confirmed previous results from petrographic analysis of the rocks.

The results of the expansion tests show that the efficacy of admixtures in controlling expansion due to AAR varies within a wide range. However, all types of admixtures at all replacement levels reduced expansion compared to the control samples containing the Recife milonitic granite and Marilia basalt aggregates but no mineral admixture. Therefore, expansion of mortar bars decreased - and so did the difference in expansion at 14 and 28 days - as the amount of admixtures in experimental cements increased. Moreover, the rate of expansion was systematically reduced with increasing level of replacement for all admixtures.

The pozzolanic materials showed similar trends probably due to the analogous reaction mechanisms. The pozzolanic reaction is likely to respond for the more rapid decrease in expansion.

The safe levels of cement replacement required to control the alkali-silica reaction in the granite mortar bars for 14-day expansion to less than 0.10% were 60% blast-furnace slag, 16% fly ash, 15% metakaolin and 10% silica fume. On the other hand, the safe levels of admixtures to mitigate the 14-day expansion caused by the alkali-silica reaction in the basalt mortar bars to less than 0.10% were 45% blast-furnace slag, 20% fly ash, 13% metakaolin and 9% silica fume.

Although early expansion of the basalt was twofold the expansion of the granite at 14 days, the efficacy of admixtures in mitigating the reaction caused by the basalt was higher than that caused by the granite.

Based on expansion values obtained with experimental cements with 15% admixtures, the silica fume seemed to be the most efficient in minimizing the alkali-silica reactions in both cases, followed by metakaolin and fly ash. The same order was observed from determining calcium hydroxide content in the bars, suggesting that $Ca(OH)_2$ plays an important role on the ASR expansion.

Comparatively, blast-furnace slag was the least efficient among the admixtures investigated, as the amounts to reach the same degree of efficacy were sixfold that for silica fume. Metakaolin and fly ash showed similar performance in mitigating the granite reaction, however metakaolin showed better efficacy upon the basalt's. Silica fume was the best one as a low 10% amount was enough to mitigate expansions to acceptable levels.

The blast-furnace slag poorer performance was probably related to its chemical composition, whose calcium amount was higher among the admixtures. More amounts were necessary to reduce the CaO/SiO_2 ratio of the experimental composite cements and the $Ca(OH)_2$ amount in mortar after the hydration reactions.

Tests carried out with 60%-blast-furnace slag mortar bars with both the aggregates showed the highest strength and the lowest total porosity values comparatively to the other admixtures, as comproved in a former study [6], which suggests the slag thermal and chemical activation released higher quantities of hydrated products to the system [10-11]. This in consequence filled in the mortar voids, thus reducing the pores, and also contributing to the slag's poorer performance in mitigating the ASR. As total porosity was reduced, the reaction products could exhert higher pressure on the paste, increasing expansion, which is the parameter used to evaluate the efficacy of mineral admixtures.

5 CONCLUSIONS

Both basalt and milonitic granite aggregates analysed were potentially reactive with alkaline hydroxides. Glass, chloropheite and calcedony (criptocrystalline silica) present in the basalt and microgranular, recrystallized, undulatory-extinction quartz and deformed feldspar crystals in the granite gave rise to alkali-silica reactions, which depending on the thermodynamic state of silica, showed different kinetics to the accelerated tests on mortar bars.

Scanning electronic microscopy showed corroded feldspar crystals that suggest attack from hydroxil ions, thus providind both silica and alkali to the system (Photo 1). This confirms the contribution of feldspars to the reaction, as mentioned by other authors [12-13]. Basalt preferentially vitreous and amorphous reactive phases react rapidly with alkali hydroxides thanks to their high internal energy. Granite milonite reactive phases are crystalline though, quartz and feldspar crystal structures are unstable as a result of tectonic stresses, which enhanced their reactivity with alkali hydroxides from pore solutions. Basalt showed double the expansion of granite at 14-day curing.

All the admixtures tested contributed to mitigate the alkali-aggregate reaction, but the efficacy varied according to the chemical and mineralogical composition and their proportion in cement, and also with the reactivity degree of the aggregate. Silica fume was the most efficient in minimizing the alkali-silica reaction, followed by metakaolin, flys ash and blast-furnace slag. The results agree with those found in literature [14-16].

Minimum amounts to mitigate the expansion of the aggregate analysed were 10% and 15% of silica fume and metakaolin, respectively. This performance is probably related to the chemical composition of materials and to the diameter of particules that provides high pozzolanic reactivity, reduces strongly the amount of calcium hydroxide in mortar and favours the mitigation of AAR [17-19].

In the case of blast-furnace slag, higher amounts were necessary to reduce the CaO/SiO_2 ratio of experimental composite cements and the $Ca(OH)_2$ amount in mortar after the hydration reactions. The less efficacy of this admixture is related to its chemical composition whose calcium amount is higher than that of the other admixtures.

The efficacy varies according to the admixtures' composition and proportioning in cement, and to the aggregate reactivity.

6 REFERENCES

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TABLE 1: Chemical composition of the cement, admixtures and aggregates (mass %).

Composition	Cement	Admixtures				Aggregates	
		Slag	Fly ash	Metakaolin	Silica fume	Granite	Basalt
LOI	2.45	0.00	1.31	1.99	3.15	0.94	1.60
SiO_2	19.21	35.03	66.39	49.92	91.56	69.37	50.03
Al_2O_3	4.97	11.07	18.68	41.39	0.09	10.38	11.74
Fe_2O_3	2,89	1.96	5.87	3.83	0.30	2.73	15.39
CaO	64.52	44.70	2.64	0.69	0.85	3,45	11.47
MgO	0.50	4.84	2.89	1.85	0.25	5.16	5.99
SO_3	2.92	-	0.12	0.09	0.26	0.13	0.02
Na_2O	0.26	0.10	0.15	0.03	0.05	3.92	1.90
K_2O	0.90	0.31	1.85	0.20	2.40	3.65	0.80
CO_2	1.22	-	-	-	-	-	-
IR	0.86	-	-	-	-	-	-
Free CaO	1.71	-	-	-	-	-	-
Na_2O_{eq}	0.85	0.30	1.34	0.16	1.63	-	-

TABLE 2: Physical properties of the cement and admixtures.

Property	Cement	Admixtures			
		Slag	Fly ash	Metakaolin	Silica fume
Fineness - > 75µm (dry), %	0.2	0.2	1.2	0.2	0.0
Density, g/cm^3	3.10	2.94	2.21	2.56	2.69
Surface area – Blaine, cm^2/g	4400	4160	4680	23430	-
Autoclave expansion, %	0.10	-	-	-	-

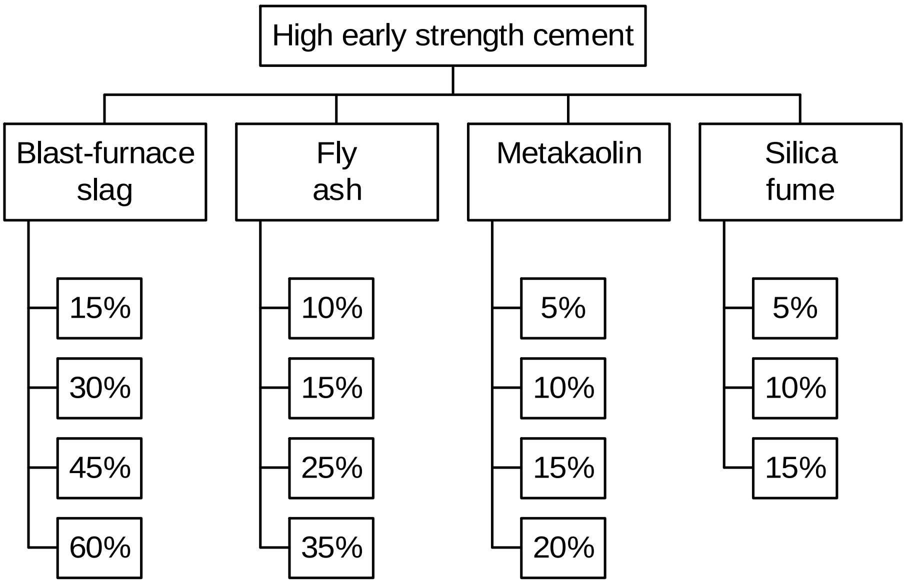

Figure 1: Chart of the 15 experimental composite cements prepared for tests.

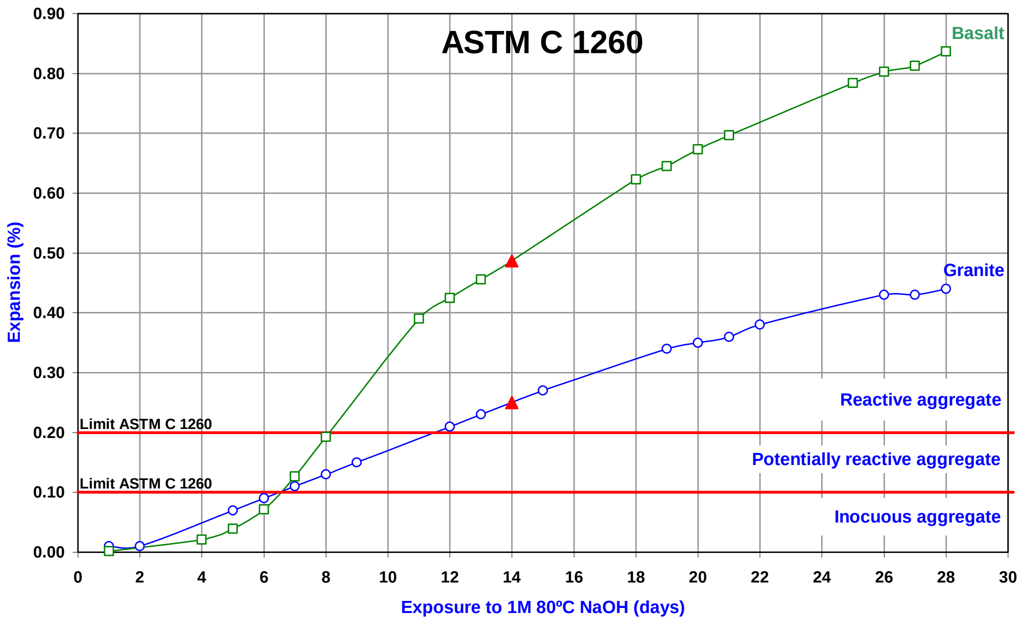

Figure 2: Development of expansion with time of control bars with milonitic granite and basalt.

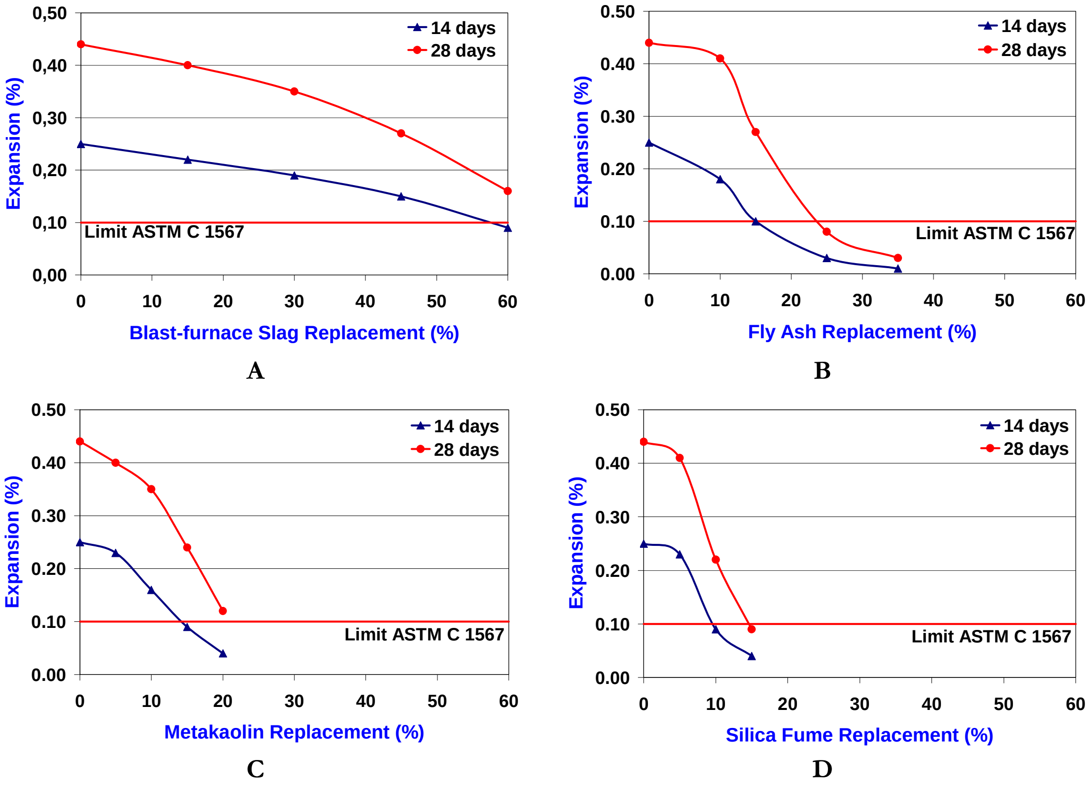

Figure 3: Expansion evolution of mortar bars containing milonitic granite aggregate and different replacement levels of blast-furnace slag (A), fly ash (B), metakaolin (C) and silica fume (D) admixtures.

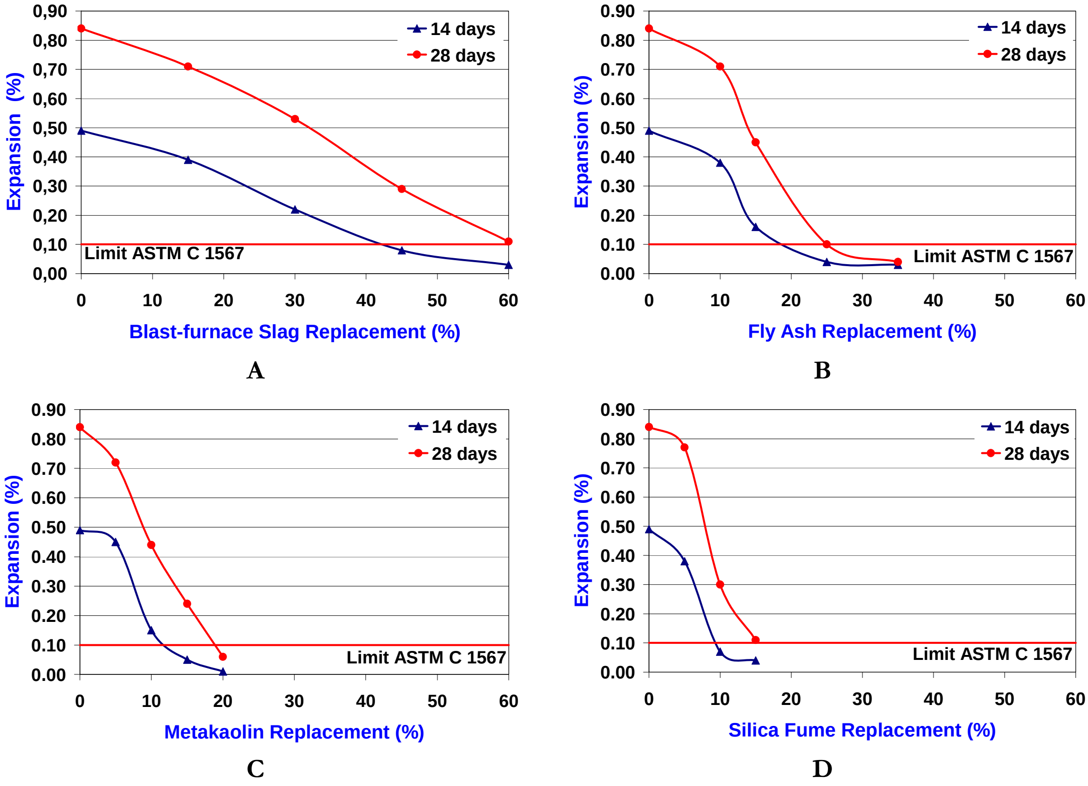

Figure 4: Expansion evolution of mortar bars containing basalt aggregate and different replacement levels of blast-furnace slag (A), fly ash (B), metakaolin (C) and silica fume (D) admixtures.

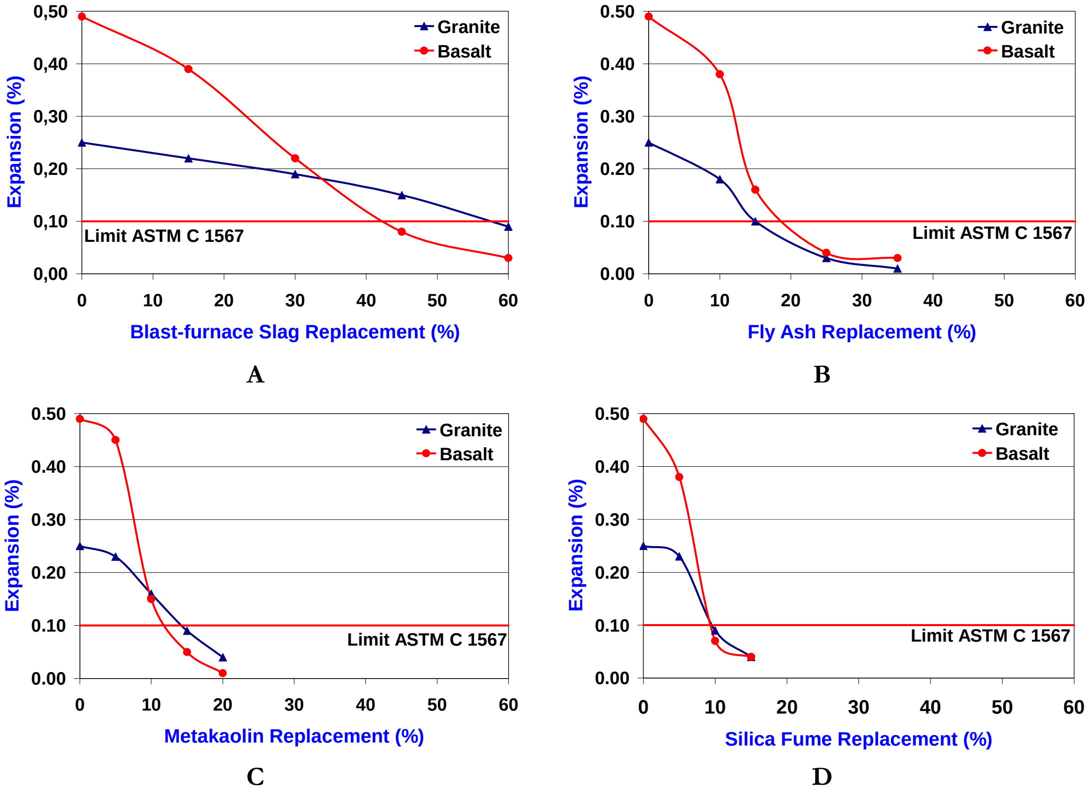

Figure 5: Efficacy of replacement levels of blast-furnace slag (A), fly ash (B), metakaolin (C) and silica fume (D) admixtures in controlling expansion of Recife milonitic granite and Marilia basalt reactive aggregates.

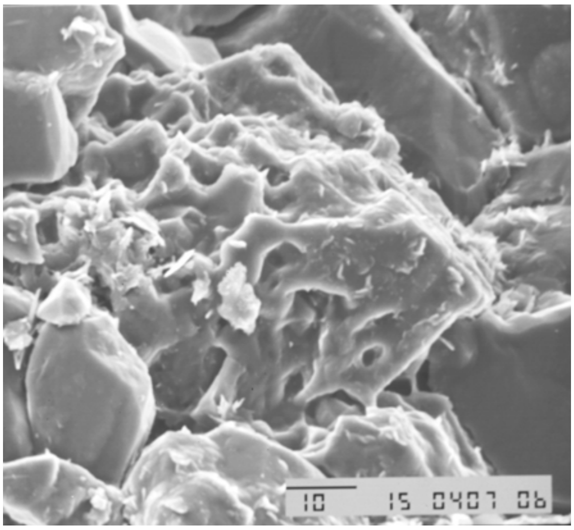

Photo 1: Felspar crystal with deep corrosion probably due to ASR. SEM 1500x.

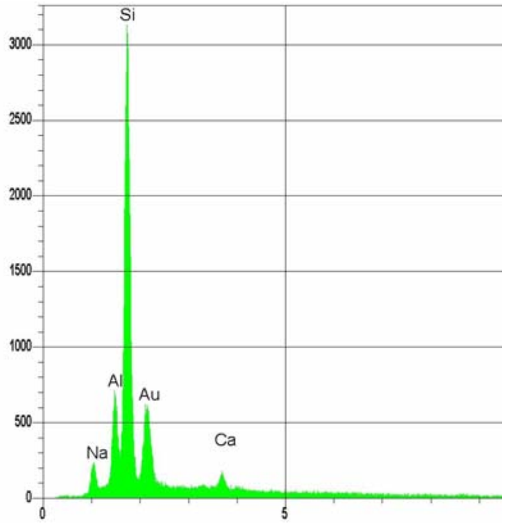

Figure 6: EDS spectrum confirming the PHOTO 1 crystal is actually feldspar.