

Effectiveness in ASR mitigation: incorporate SCM during the Portland cement manufacturing or in the concrete production?

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Abstract

The use of supplementary cementitious material (SCM) with the purpose of mitigating the expansion caused by the alkali silica reaction (ASR) in concrete of important constructions is a topic studied by several researchers and which has shown promising results. From a practical point of view, some builders ask whether it is more effective to use composites Portland cements (whose addition of SCM occurs during the manufacture of cement) or to use SCM directly in the production of concrete on site. The research analysed the ASR mitigation rates in both situations using the accelerated test on mortar bars. The test method contained in the Brazilian standard ABNT NBR 15577:2018 was used in this study, which was edited based on ASTM C 1260, ASTM C 1567 and CSA A23.2-25A. In addition to the reference mortar, two types of mortar batches were produced: a batch with different types of Brazilian composites Portland cements and a batch with partial replacement of standard cement by SCM. This SCM used in the second batch were fly ash (15%, 30% and 50%) and granulated blast furnace slag (35%, 45% and 55%), the same being used by factories whose composites Portland cements were purchased. The results showed similar efficiency for the two situations of SCM incorporation. However, the construction flow and the variability of the concrete production process can make the SCM more effective when incorporated into the industry.

Keywords: alkali silica reaction; concrete production; supplementary cementitious material; portland cement manufacturing

1. INTRODUCTION

It is already a consensus among researchers that supplementary cementitious materials (SCM) are effective in attenuating the development of the alkali silica reaction (ASR). The SCM already studied are natural pozzolans, fly ash, silica fume, metakaolin, rice husk ash, granulated blast furnace slag, among others.

Ollivier and Vichot [1] claim that this advantage comes from the SCM pozzolanicity property. For the authors, these fines modify the portlandite content in the paste; the Ca/Si ratio of the hydration product C-S-H, providing greater alkali fixation; the microstructure of the hardened paste, making it more compact; and, in addition, they can dilute alkalis when used in partial replacement to Portland cement.

For Chen, Soles and Malhotra [2], the SCM properties that guarantee the expansion reduction are the high total concentration of $\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$, the fineness of the particles and the low alkaline content.

For Hong and Glasser [3, 4], the alumina contained in the SCM contributes in some way to prevent the release of alkalis to the concrete pores solution. However, Chappex and Scrivener [5, 6] believe that this effect is extremely small and that the contribution of alumina is due to its performance directly in the reactive phases of the aggregates, in which the aluminium present in the pore solution will be able to inhibit the dissolution of amorphous silica from reactive aggregates. Leeman and colleagues [7] agree

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with this statement when they indicate that the aluminium present in the pore solution is only able to delay the dissolution of SiO_2 , but does not change the morphology, structure and composition of the reaction products.

At the level of Brazil, Ribeiro [8] points out that, since Portland clinker is the main source of alkalis and that the alkalis concentration is one of the factors necessary for the ASR occurrence, decreasing its concentration in the mixture is one of inhibition measures. Thus, by replacing part of the cement with the SCM, it is expected that there will be a reduction for alkalis, since the active SCM has in general a lower alkalis concentration in its composition compared to the concentration observed in the cement.

According to Guillante and colleagues [9], some SCM may not be effective in attenuating ASR, but they may be feasible for increasing mechanical resistance. The authors then suggest the combination of different SCMs in order to guarantee the synergistic effect and obtain better mechanical resistance combined with the ASR mitigation.

Therefore, what is seen in the literature is a range of research that addresses the possibilities of ASR attenuation using different SCMs. The incorporation of SCM is always linked to the partial replacement of Portland cement for additional sustainability purposes because it incorporates less Portland clinker in the mortar or concrete.

Specifically in Brazil, there is a variety of cements produced with SCM as a partial substitute for Portland clinker. The standardized SCM for the production of these Portland cements are pozzolanic materials and granulated blast furnace slag [10].

Understanding the dynamics involved in the construction execution stage, in which any attempt to reduce the variability in the concrete quality is viable, this research aimed to analyse if there is any difference in the effectiveness of the ASR mitigation according to the moment of SCM insertion: during the concrete production or during the Portland cement manufacture?

To obtain a more reliable analysis of the results, the pozzolanic material (fly ash) and granulated blast furnace slag used in the study come from the industries that supply their by-products to the cement industry to produce the different types of Portland cement. These same cements were also the subject of the research.

2. METHODOLOGICAL PROCEDURES

The research consisted of physical, chemical, mineralogical and microstructural analyses of the SCM and the mortars produced in order to obtain a more detailed understanding of the results. The materials used, the defined sampling and the tests performed are explained below.

2.1 Materials

The basic raw material used in the mortars production were:

- Standard-cement defined by the Brazilian standard ABNT NBR 15577-4 [11];
- Portland cements CP II-Z-32-RS and CP IV-32-RS containing fly ash; CP II-E-32-RS and CP III-40-RS containing granulated blast furnace slag;
- Fly ash supplied by Thermal Power Plant in Northeast Brazil;
- Granulated blast furnace slag supplied by Steel Plant in Northeast Brazil;
- Fine recycled glass aggregate.

2.1.1 Standard-cement

For the assessment of the reactivity degree of the aggregate and ASR expansion, ABNT NBR 15577-4 [11] recommends the production of mortars containing cement considered standard because it has the following characteristics:

- specific area - Blaine - of (4900 ± 200) cm^2/g ;
- total alkaline equivalent expressed in $\text{Na}_2\text{O}_{\text{eq}}$ of $(0.90 \pm 0.10)\%$;
- expansion in an autoclave below 0.20%.

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2.1.2 Brazilian Portland Cements

ABNT NBR 15577-1 [12] recommends the use of Brazilian Portland cements of the types CP II-E, CP II-Z, CP III and CP IV, which already have SCM in their constitution, as measures to mitigate the ASR expansion.

These four types of cement produced by a single cement industry were analysed. Table 2.1 contains the technical characteristics of the cements, such as the type and content of SCM incorporated, and the composition limits established by the Brazilian standard ABNT NBR 16697 [10], which addresses the requirements of Portland cements.

Table 2.1: Technical characteristics of Portland cements and composition limits established by ABNT NBR 16697 [10].

Portland cement type	Alkaline equivalent (%)	Specific Area - Blaine (cm ² /g)	Fineness - residue on the 0.075mm sieve (%)	Type of supplementary cementitious material	Content added to cement by industry	Composition limit established by ABNT NBR 16697 [10]
CP II-Z-32-RS	0.83	4109	2.90	fly ash	14 %	6 % - 14 %
CP II-E-32-RS	0.60	3604	0.90	granulated blast furnace slag	34 %	6 % - 34 %
CP IV-32-RS	1.80	3571	0.90	fly ash	30 %	15 % - 50 %
CP III-40-RS	0.56	4178	0.50	granulated blast furnace slag	50 %	35 % - 75 %

2.1.3 Fly ash – FA

The fly ash processing consisted of drying at (105 ± 5) °C until dough consistency and sifting through the 0.075 mm mesh sieve to obtain the fineness closest to that of the binders.

The average particle diameter was 33.18 µm, with values of D10%, D50% and D90% equal to 2.77 µm, 18.311 µm and 78.47 µm, respectively. The specific mass obtained was 2.23 g/cm³. The fineness by the air permeability method (Blaine method) was 1020 cm²/g.

The chemical composition analysed by X-ray fluorescence is shown in Table 2.2. Fly ash has the sum of silicon dioxide (SiO₂), aluminium oxide (Al₂O₃) and iron oxide (Fe₂O₃) greater than 70 % (80.19 %), as recommended by ABNT NBR 12653 [13] for a pozzolan Class C. ASTM C618 [14] requires that this sum present a minimum value of 50 % and a maximum CaO content equal to 18 % for fly ash Class F4. The test did not identify the presence of Na₂O, so the alkaline equivalent obtained was 2 % in Na₂Oeq.

Table 2.2: Chemical composition of fly ash by X-ray fluorescence.

Oxides	SiO ₂	Fe ₂ O ₃	Al ₂ O ₃	CaO	TiO ₂	K ₂ O	P ₂ O ₅	SrO	ZrO ₂	ThO ₂	Rb ₂ O
Concentration (%)	48.81	16.72	14.66	9.13	3.66	3.05	3.00	0.51	0.28	0.12	0.06

Note: The test did not identify the presence of Na₂O.

X-ray diffraction resulted in the diffractogram shown in Figure 2.1. The main crystalline compounds found were quartz (SiO₂) and mullite (Al₆Si₂O₁₃), consistent with the results achieved in X-ray fluorescence (Table 2.2). Mullite is a ceramic phase obtained by the reaction between alumina (Al₂O₃) and silica (SiO₂) at elevated temperatures, resulting from the reactions during the combustion of mineral coal. Quartz was supposed to be present in the coal and did not melt in the burning conditions of the thermal power plant.

It was also possible to observe a broad band (halo) up to around 42° due to the presence of amorphous aluminosilicates.

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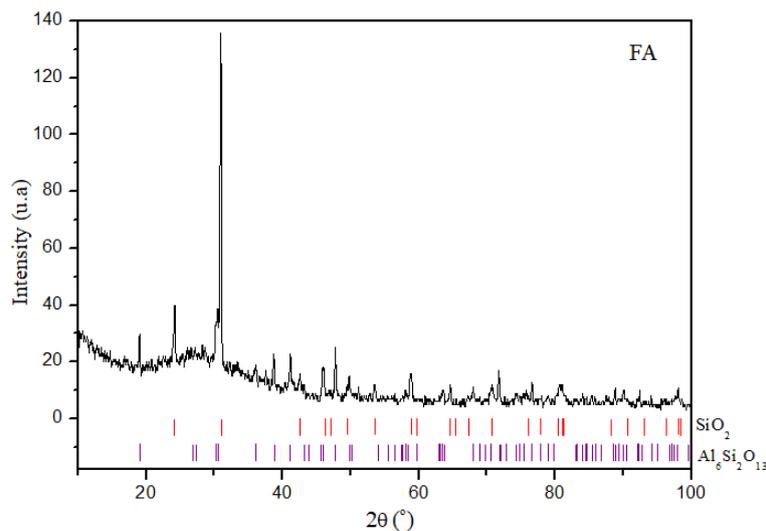


Figure 2.1: Fly ash diffractogram.

2.1.4 Granulated blast furnace slag – GBFS

GBFS was obtained by rapid cooling with controlled water jets, combined with mechanical forces for crushing. The processing in the laboratory consisted of drying at (105 ± 5) °C until dough consistency, crushing in the Los Angeles equipment and sieving in the 0.075 mm mesh sieve to obtain the fineness closest to that of the binders.

The laser granulometry test revealed an average diameter of 48.74 μm , with values of D10%, D50% and D90% equal to 15.56 μm , 46.03 μm and 84.62 μm , respectively. The specific mass obtained was 3.36 g/cm^3 .

X-ray fluorescence gave the chemical composition of GBFS shown in Table 2.3. The slag had a high content of Fe_2O_3 (46.04 %), and CaO (39.92 %), as expected, since iron ore and lime (calcitic and dolomitic) are, respectively, the basic raw material and the fondant used in the pig iron production. In addition, SiO_2 (6 %) and MnO (5.70 %) were also found among the most significant concentrations; these are neutralized by the slag during the production process ensuring the protection of the refractory lining against premature wear.

Table 2.3: Chemical composition of granulated blast furnace slag by X-ray fluorescence.

Oxides	Fe_2O_3	CaO	SiO_2	MnO	P_2O_5	Al_2O_3	TiO_2	CoO	K_2O	SO_3
Concentration (%)	46.04	39.92	6.00	5.70	0.73	0.72	0.60	0.13	0.09	0.07

Note: The test did not identify the presence of Na_2O .

Although the relationship between the slag composition and its reactivity is not perfectly clear, there is a certain pattern in adopting the CaO/SiO_2 ratio: if greater than or equal to 1, there is a basic and reactive slag; if less than 1, the slag is acidic and with low reactivity [15]. CaO/SiO_2 ratio of 6.65 was obtained (Table 2.3), indicating that GBFS is basic, so it can be used as a cementitious material.

X-ray diffraction resulted in the diffractogram in Figure 2.2.

Figure 2.2 reveals that the main crystalline phases of GBFS are dicalcium ferrite with brownmillerite structure ($\text{Ca}_2\text{Fe}_2\text{O}_5$) and iron and calcium silicate with hedenbergite structure ($\text{CaFeSi}_2\text{O}_6$).

The brownmillerite structure is the main constituent of the ferrite phase of Portland cement and can represent several series with variation in the cation that will bind to oxygen. For this GBFS it was verified that the brownmillerite structure can be represented by $\text{Ca}_2\text{Fe}_{1,40}\text{Al}_{0,60}\text{O}_5$ (low aluminum content already identified in Table 2.3) and have a secondary wustite phase ($\text{Fe}_{0,909}\text{O}$).

The hedenbergite crystalline structure makes up the group of pyroxenes that are part of the silicate minerals class. Its structure is of the monoclinic type, with simple chain polymerization [16]. The greater reactivity of the glassy slag depends on the lower polymerization, as the silicate structure will be less stable.

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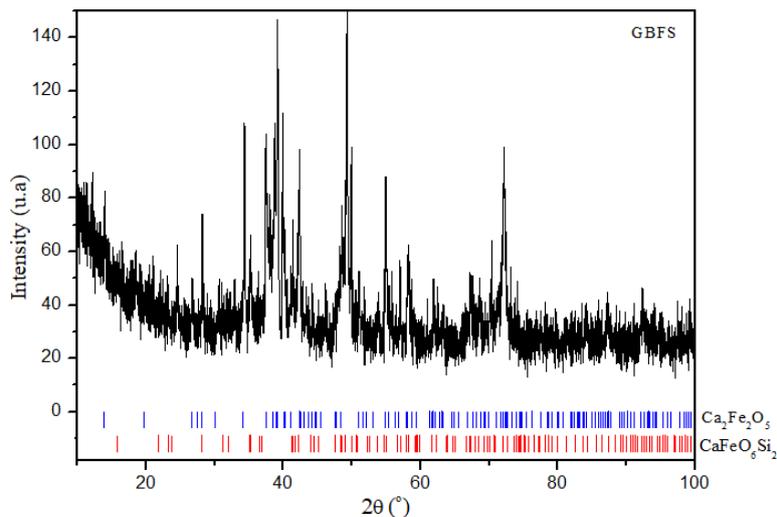


Figure 2.2: Granulated blast furnace slag diffractogram.

2.1.5 Fine recycled glass aggregate – FRGA

The fine aggregate used in the production of mortars came from colorless long neck glass bottles in order to obtain high potential for ASR reactivity. They were previously washed, dried and subjected to manual crushing by applying 300 strokes with a 5 kg sledgehammer, keeping the impact height fixed.

After beneficiation, the FRGA was sieved to obtain a maximum characteristic diameter of 2.36 mm. The specific mass was 2.46 g/cm³.

The chemical composition of FRGA analysed by X-ray fluorescence showed a concentration of 56.76 % SiO₂, 38.37 % CaO and 1.18 % Na₂O (Table 2.4). These concentrations classify glass as sodium-calcium, where sodium and calcium oxides act as network modifiers. These oxides tend to break the continuity of the silica polyhedron chain network, not forming polyhedra in the glassy structure [17]. The total alkaline equivalent obtained from the contents of Na₂O and K₂O was 1.59 % in Na₂Oeq.

Table 2.4: Chemical composition of fine recycled glass aggregate by X-ray fluorescence.

Oxides	SiO ₂	CaO	Fe ₂ O ₃	Na ₂ O	Al ₂ O ₃	K ₂ O	Rb ₂ O	SrO
Concentration (%)	56.76	38.37	1.33	1.18	1.07	0.63	0.34	0.32

To classify the reactivity degree of FRGA according to ABNT NBR 15577-1 [12], a mortar composed only of standard-cement and FRGA was produced and submitted to the expansion test in mortar bars by the accelerated method [11]. This is the reference mortar (REF).

2.2 Sampling

The research addressed two situations: (a) SCM incorporated during the mortar production from the partial replacement of standard cement and (b) SCM constituting the four types of Portland cements. The SCM of the two situations came from the same industries.

The replacement contents of standard-cement were 15 %, 30 % and 50 % for FA and 35 %, 55 % and 75 % for GBFS, in volume, initially. Such portions were defined based on the composition limit of Portland cements established by ABNT NBR 16697 [10] (Table 2.1). However, the mortar produced with 75 % GBFS was very dry, requiring the use of a chemical additive to correct the fluidity, but it was decided not to use it since it was not used in the other mortars. Thus, the replacement contents of standard-cement with GBFS were 35 %, 45 % and 55 %. Figure 2.3 shows the production chart of the mortars.

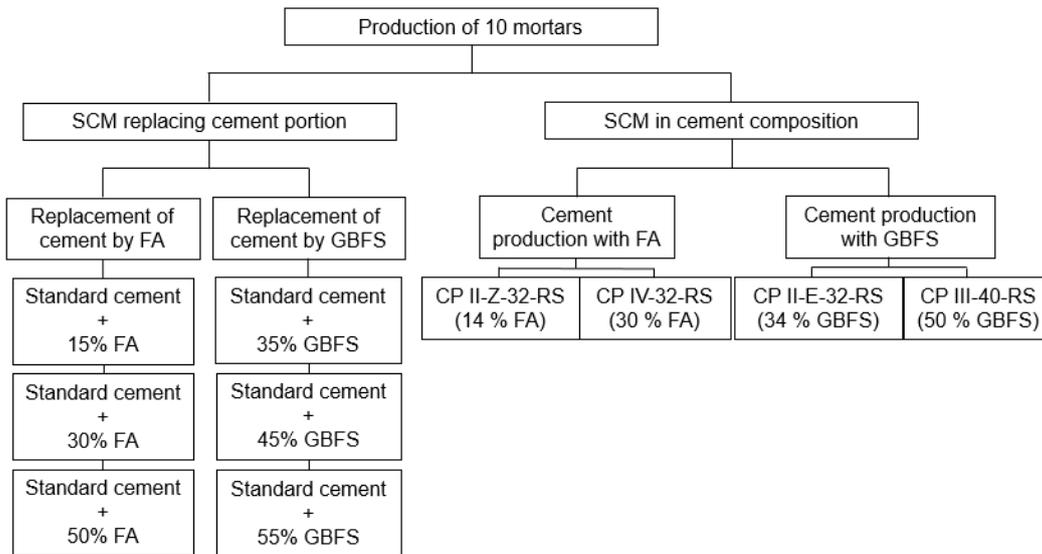


Figure 2.3: Mortar production organization chart.

2.3 Test methods

For each mortar in Figure 2.3, three prismatic bars were molded with a square section and dimensions (25.0 ± 0.7) mm on the side and 285 mm in length to determine the expansion mitigation by the accelerated method following ABNT NBR 15577-5 [18]. This Brazilian standard was based mainly on the ASTM C1260 [19] and ASTM C1778 [20] standards.

At the end of the test, the average expansion of the three bars for each mortar was performed and the values obtained were compared with the limits prescribed by ABNT NBR 15577-1 [12] to verify the mitigation of the reaction.

The reduction (R) of the average expansion due to the use of SCM was calculated according to Equation 1 of ABNT NBR 15577-5 [18]. This equation relates the values of the average expansions (E_5) with the values obtained by the method with standard-cement (E_4) to verify the extent of mitigation.

$$R = \frac{100 \times (E_4 - E_5)}{E_4} \quad (1)$$

Afterwards, the mortars were subjected to X-ray fluorescence and scanning electron microscopy tests to analyse the chemical composition and microstructural characteristics.

3. RESULTS AND DISCUSSIONS

3.1 Accelerated expansion in mortar bars

Figure 3.1 shows the evolution of the reference mortar expansion. An average expansion of 0.632 % was obtained at 30 days classifying the FRGA as a potentially reactive aggregate degree R3. There was already an expectation of obtaining high expansion values through the choice made for the type of recycled aggregate (glass), consisting basically of amorphous silica, with a strong tendency to react to the attack of alkaline hydroxides.

Figures 3.2 and 3.3 show the evolution of the modified mortar expansion. It appears that all modified mortars showed an average expansion at 30 days less than 0.19 % indicating that the reactivity in those conditions is not harmful and that the mitigation with the materials used was proven [12].

Figure 3.2(a) reveals that the mortar 50%FA did not show a linear behavior: up to the 16th day there was an upward expansion, with a peak of 0.033 %; between the 20th and 28th days there was a drop; and new growth on the 30th day. Mortars 15%FA and 30%FA presented similar behaviors, especially after the 20th day. These factors lead to the understanding that there is a maximum limit between 30 % and 50 % of FA incorporation that guarantees control in the ASR expansion process. If, on the one hand,

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the FA had an alkali content greater than 1.5 % in $\text{Na}_2\text{O}_{\text{eq}}$ (2 %), on the other hand it had a low CaO content (9.13 %), which may have contributed to such low expansion values for mortar with lower FA content (15%FA), compared to the reference mortar.

Figure 3.2(b) shows that at 35%GBFS there is no reliability in the results since there was practically no evolution in the expansion over the days, keeping a short interval between 0.004 % and 0.011 %. In view of the reactive potential of the aggregate used and noting that this mortar with the lowest GBFS content presented such low expansion values among all studied (including mortars with FA), it is understood that low GBFS contents can generate a false negative result. Mortars 45%GBFS and 55%GBFS showed a relatively similar behavior until the 16th day. After that, the 45%GBFS mortar expanded more sharply, the difference being greater on the 24th day (81.82 % higher than the 55%GBFS mortar). It is understood that the content of 55 % of this GBFS is subject to greater control over ASR expansion. Possibly, the effectiveness of ASR attenuation with a higher GBFS content is influenced by the high CaO content of GBFS.

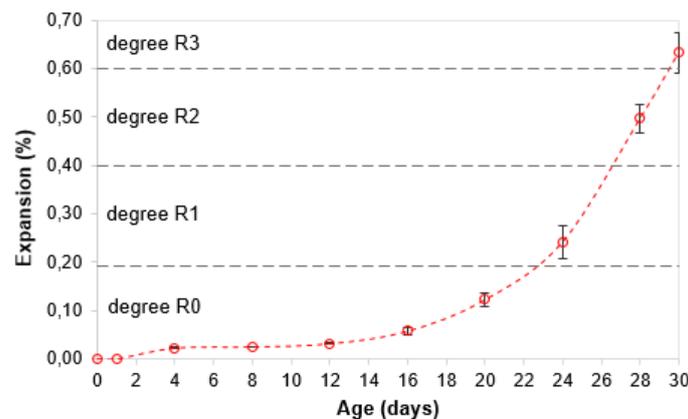


Figure 3.1: Reactivity degree of FRGA due to expansion at 30 days.

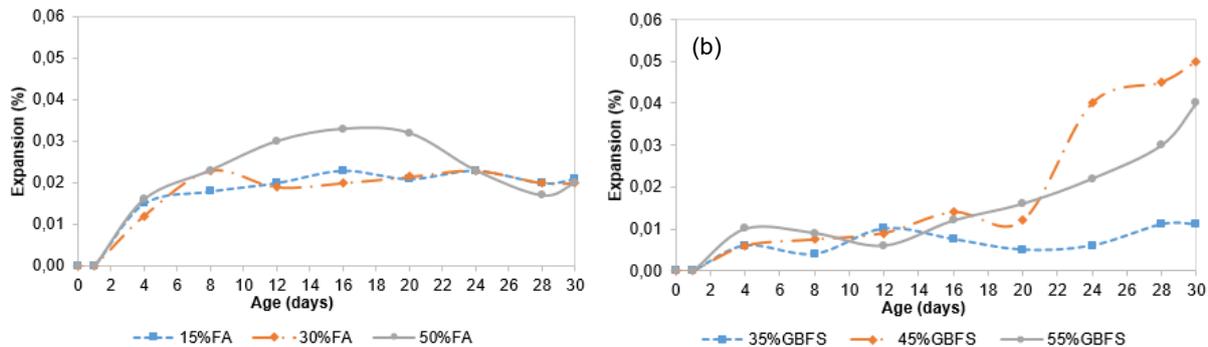


Figure 3.2: Expansion of mortars containing (a) fly ash and (b) granulated blast furnace slag.

Figure 3.3 shows that the CP-III mortar showed a different behavior from the others. It maintained a low expansion between 0.002 % and 0.006 % until the 20th day, with a significant increase around 7 times higher after the 24th day. The CP-IV mortar showed the lowest average expansion on the 30th day among all analysed in Figure 3.3, with a smooth evolution on each test day, although until the 20th day it had the greatest expansion.

The relative reduction in expansion (R) due to the use of SCM was calculated considering the ages of 16 and 30 days to verify the real extent of mitigation, obtaining the percentages shown in Table 3.1.

Analysing only the mortars composed by FA in Table 3.1, we have that, although the relative reduction in expansion at 30 days was the same for the three mortars, the age of 16 days reveals that the best mitigation evolution was achieved by 30%FA. For mortars composed by GBFS, it is reaffirmed that 35%GBFS had anomalous behavior, which cannot be evaluated, and that the mortar 55%GBFS showed

a slightly greater percentage reduction compared to 45%GBFS in both ages, indicating the content more favorable when only the expansion mitigation capacity is analysed.

Analysing only the mortars composed by inhibiting Portland cements in Table 3.1 and comparing with Table 2.1, it appears that the cement company incorporates the maximum limit of SCM established by ABNT NBR 16697 [10] for composite Portland cements (CPII-Z and CPII-E) and this approach guarantees good mitigation of ASR expansion. For types CP-III and CP-IV, the cement plant incorporates an average value between the minimum and maximum limits allowed. However, ABNT NBR 15577-1 [12] establishes that cement type CP-III must have a minimum content of 60 % slag and type CP-IV must have at least 30 % pozzolan when used to mitigate the ASR expansion. It can be seen from Table 3.1 that although CP-III does not comply with the requirement, in case of using it for this purpose, it presented low values of expansion in the short term even with the use of potentially reactive aggregate degree R3.

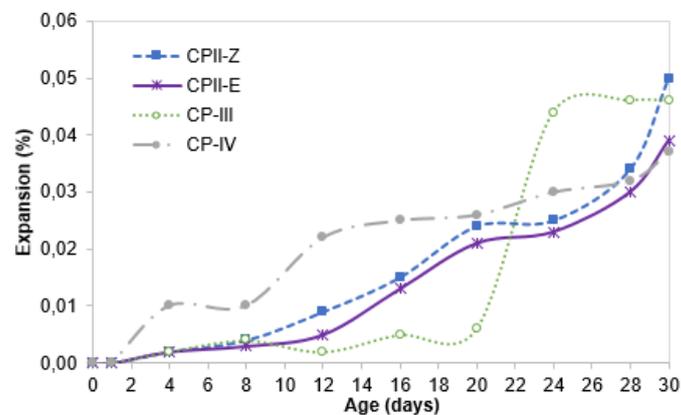


Figure 3.3: Expansion of mortars containing inhibiting Portland cements.

Table 3.1: Expansion reduction of modified mortars in relation to the reference mortar.

Mortar	15% FA	30% FA	50% FA	35% GBFS	45% GBFS	55% GBFS	CPII-Z**	CPII-E**	CP-III**	CP-IV**
Reduction at 16 days (%)	60	65	42	*	75	79	74	77	91	56
Reduction at 30 days (%)	97	97	97	98	92	94	92	94	93	94

* Reduction not calculated. The average expansion value at 16 days was discarded due to the discrepancy between the values of each bar.

**The content of FA and GBFS from Portland cements is described in Table 2.1.

3.2 X-ray fluorescence

The analysis of the chemical composition of mortars with the greatest relative reduction in expansion (R) at the ages of 16 and 30 days and of the reference mortar (REF) is shown in Table 3.2.

The REF mortar in Table 3.2 suggests that the high concentration of Ca^{2+} ions in the composite may have promoted the formation of additional C-S-H that acted as a semipermeable membrane surrounding the reactive aggregate. This membrane allowed the entry of alkaline ions and OH^- into the aggregate pores formed by amorphous silica and favoured the formation of hydrated alkaline silicate gel (A-S-H). In addition, this C-S-H makes it difficult for the A-S-H gel to escape from the interior of the aggregate pores, generating a pressure that can exceed the tensile stress and cause cracking. In fact, the REF mortar bars showed white spots indicative of gel and cracking along the entire length, denoting that such a mechanism may have occurred.

55%GBFS mortar stands out in Table 3.2 by the concentration of Fe_2O_3 , being almost four times higher than the REF mortar, and presented the lowest concentration of CaO. The chemical composition of GBFS showed a high concentration of Fe_2O_3 (46.04 %) and it replaced the standard cement in high content (55 %). This caused the amount of $Ca(OH)_2$ produced in the initial hydration reactions to be

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reduced and later consumed by GBFS. Thus, less OH⁻ ion was available to react with the aggregate silica.

Regarding alumina, there is a higher concentration in 30%FA mortar, although it is not expressive (Table 3.2). The fly ash of the study showed a relevant concentration of 14.66 % of Al₂O₃. There is no convergence among researchers on the role of alumina present in SCM for the ASR mitigation. Some claim that Al₂O₃ contributes to alkalis fixation in C-S-H [3, 4]; others believe that the role lies in inhibiting the amorphous silica dissolution from reactive aggregates [5, 6]. The fact is that mortars containing FA showed the greatest relative reductions in expansion (R) on the 30th day.

Table 3.2: Chemical composition of mortars by X-ray fluorescence.

Mortar	CaO	SiO ₂	Fe ₂ O ₃	Al ₂ O ₃	K ₂ O	SO ₃	MnO	Na ₂ O	Trace elements*
REF	68.68	22.09	4.69	1.72	0.75	0.85	-	-	1.24
30%FA	63.64	23.49	6.22	3.15	1.22	1.00	-	-	1.28
55%GBFS	50.38	24.84	18.36	1.71	0.91	0.54	2.27	-	0.99
CPII-Z	65.72	23.14	5.50	2.87	1.06	0.81	0.25	-	0.66
CPII-E	67.04	24.01	4.24	1.73	0.70	1.29	0.34	-	0.64
CP-III	64.17	21.84	3.13	2.31	0.89	0.96	0.45	5.30	0.94
CP-IV	58.55	26.89	8.54	2.34	1.36	0.90	0.24	-	1.19

* Trace elements: Sr, Rb, Ag, Cd, Zn, P, Cl, Rh.

The mortars CaO/SiO₂ ratios were analysed and the difference (Δ) between the value obtained for the modified mortars and the value of the reference mortar was calculated, obtaining the results shown in Table 3.3.

Table 3.3: Mortar CaO/SiO₂ ratio and difference (Δ) between modified mortars and the reference mortar.

Mortar	REF	30%FA	55%GBFS	CPII-Z	CPII-E	CP-III	CP-IV
CaO/SiO ₂	3.11	2.71	2.03	2.84	2.79	2.94	2.18
Δ	-	-12.86 %	-34.73 %	-8.68 %	-10.29 %	-5.47 %	-29.90 %

Considering that all mortars had a relatively close SiO₂ concentration, the high value of the CaO/SiO₂ ratio for the REF mortar in Table 3.3 is due to the high CaO concentration already observed in Table 3.2. Similarly, the largest delta obtained for 55%GBFS mortar comes from the lowest concentration of CaO.

Although there are variations in delta (Δ), in general, it appears that the SCM introduction, either by replacing cement during the concrete production or during the manufacture of cement, contributes to the reduction of the CaO/SiO₂ ratio of the C-S-H. This reduction allows the alkalis fixation in crystalline network of C-S-H, leaving less alkalis in the pore interstitial solution, which would contribute to the dissolution of amorphous silica. Additionally, authors such as Ollivier and Vichot [1] report that the C-S-H produced by the SCM tends to extract greater amounts of alkalis from the interstitial solution, decreasing its alkalinity and reducing its aggressiveness towards reactive aggregates.

As for alkalis in mortars, Table 3.2 shows that all mortars had K₂O, consistent with the literature that claims to be the most common alkali metal founded in the clinker composition [21]. Only CP-III mortar showed Na₂O, leading to believe that this concentration is not specifically due to the reactive aggregate (which presented 1.18 % Na₂O). In addition, the technical characteristics shown in Table 2.1 reveal that this cement presented the lowest alkaline equivalent among all the analysed cements. Thus, it is understood that Na₂O concentration may result from the fact that the bars of this mortar have presented a significant number of surface voids that may have contributed the access of sodium hydroxide solution (NaOH) of the test more easily to pores solution. In fact, CP-III mortar bars showed more voids after demoulding and cracks at the test end than the others analyzed. As a result, CP-III mortar showed a high total alkalis concentration in Na₂Oeq (5.89 %). The medium in which the bars were inserted may

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have influenced performance of expansion over time. As already discussed in Figure 3.3, the expansion evolution of this mortar was significantly upward from the 24th day of the test. Table 3.3 also found that this mortar had the smallest delta (Δ), which implies a high CaO/SiO₂ ratio.

3.3 Scanning electron microscopy

The scanning electron microscopy test was carried out for mortars that had a higher SCM content after 1 year of bars production and their photomicrographs are shown in Figures 3.4 and 3.5.

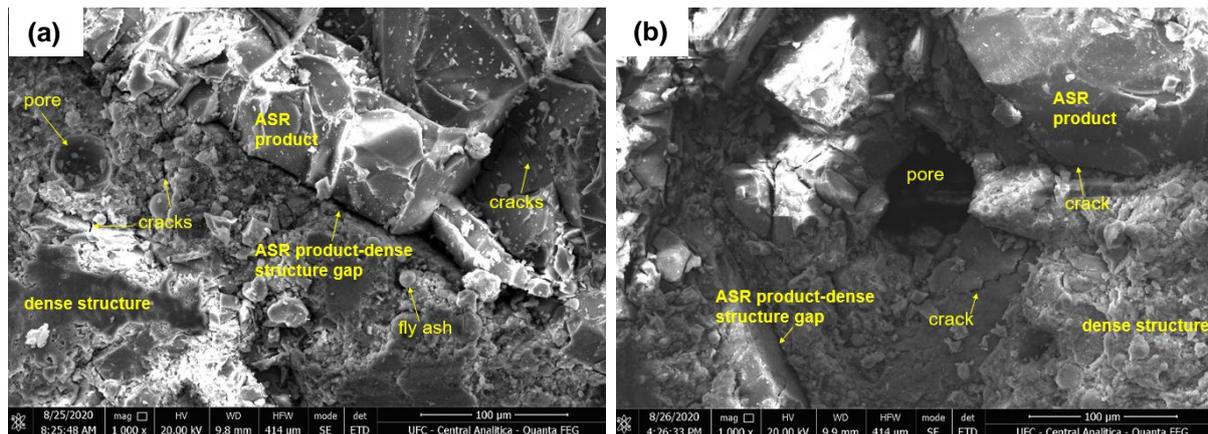


Figure 3.4: Photomicrography of mortars (a) 50%FA and (b) CP-IV.

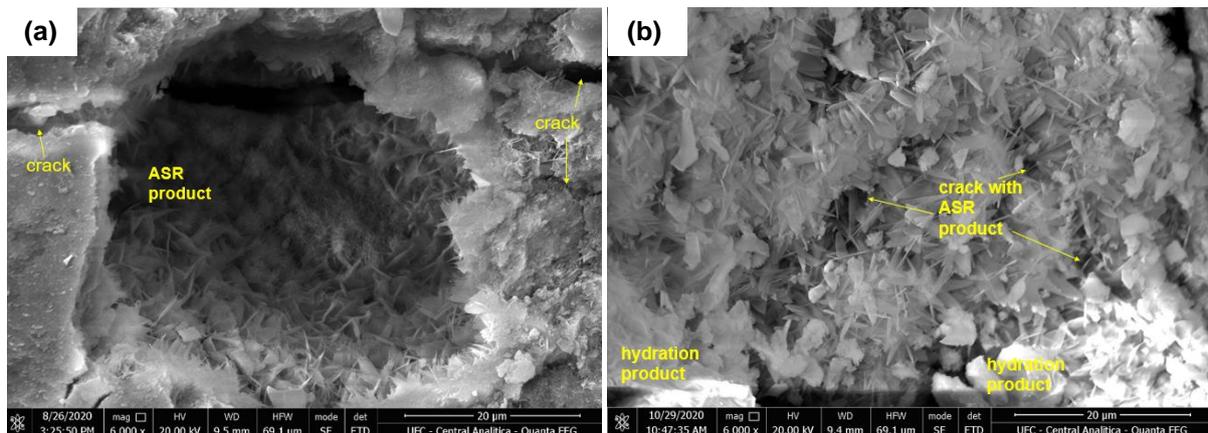


Figure 3.5: Photomicrography of mortars (a) 55%GBFS and (b) CP-III.

Figure 3.4 shows the photomicrographs of 50%FA and CP-IV mortars. There is a clear formation of reaction product as a thick amorphous deposit, with a gap between it and the dense matrix structure. Still in the matrix, it is possible to see points of fly ash not hydrated in Figure 3.4(a) even after 1 year of mortar production, reinforcing the understanding of the maximum limit content of 30 % by fly ash. Both the reaction product and the matrix showed micro cracking throughout.

Figure 3.5 shows the photomicrographs of 55%GBFS and CP-III mortars. It is noticed the formation of reaction product with more crystalline morphology. The photomicrograph of Figure 3.5(a) shows a pore filled with ASR product with a rosettes-type morphology in the center and rod-type morphology on the sides. The cement matrix was dense and with micro cracks. Figure 3.5(b) shows the ASR product with lamellar crystal morphology occupying the micro cracks and a large part of the cement matrix, overlapping the hydration products C-S-H and Ca(OH)₂. This CP-III mortar was the only one that showed Na²⁺ in its composition, with the suspicion that this ion came from the NaOH solution of the test. Probably, this alkali contribution is responsible for distributing the ASR product throughout practically the entire cement matrix and for the expansion evolution results already discussed.

It is known that the ASR product can be presented in several microstructural ways. For mortars composed by fly ash, the product looked like a thick cracked gel, with considerable gaps in the interface

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with the cement matrix. Mortars composed of granulated blast furnace slag showed the reaction product with more crystallized texture, where the morphology varied between rods and rosettes. For 55%GBFS, the ASR product was located more in the pores and in some larger cracks; for CP-III the product was practically well distributed by the cement matrix.

4. CONCLUSIONS

The results obtained in the study allowed us to conclude that SCM are good alternatives for mitigating the harmful effects of ASR, even when the aggregate has a high reactivity potential. However, there is a minimum and maximum limit for effectiveness SCM actions, regardless of when SCM is incorporated: during the manufacture of cement or during the concrete production. The main conclusions of this study are listed below:

- a) Fly ash was more efficient in mitigating the reaction than granulated blast furnace slag.
- b) There is a certain maximum limit of this fly ash to be incorporated between 30 % and 50 % that guarantees effectiveness in reducing ASR. The evolution of the expansion for the mortar with 50% fly ash did not show a linear behavior, showing that a lower concentration than this is the limit for a better control of the expansion reduction.
- c) Slags needs to be incorporated in higher concentrations than ashes to achieve similar ASR mitigation rates. The mortar with 35 % GBFS showed a very small expansion evolution when compared to mortars with 45 % and 55 % GBFS, whose expansions evolved in an increasing way over the days. As the aggregate used presented high reactive potential, it is understood that low GBFS concentrations can generate a false negative result.
- d) Low slag content generated a false negative result, which may lead to mistakes in deciding the content to be adopted.
- e) All modified mortars showed a reduction in the CaO/SiO₂ ratio of C-S-H, compared to the reference mortar. This reduction allows the alkalis fixation in C-S-H crystalline network, leaving less alkalis in the pore interstitial solution, which would contribute to amorphous silica dissolution.
- f) The minimum limit of SCM to be incorporated in Portland cements for ASR mitigating indicated by Brazilian standard ABNT NBR 15577-1 [12] are feasible, however the results of this study revealed that there is a need to define a maximum limit so as not to get the bad effect.

Considering the materials used in this study, the conclusions led the researchers to understand that the incorporation of SCM during the Portland cements manufacture and in concentrations indicated by technical standards has an efficiency similar to the incorporation of SCM in replacement of cement during the concrete production. Nevertheless, if the variability of concrete production process is considered, such as the possibility of nucleation point formation due to conditions of mixture homogenization, it can be said that the efficiency will be greater for SCM incorporated in the cement industry.

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