



ORIGINAL ARTICLE

Evaluation of external sulfate attack (Na_2SO_4 and MgSO_4): Portland cement mortars containing siliceous supplementary cementitious materials

Avaliação do ataque externo por sulfato (Na_2SO_4 e MgSO_4): argamassas de cimento Portland contendo adições minerais silicosas

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Received 27 June 2019

Accepted 24 January 2020

Abstract: Sulfate attack is a term used to describe a series of chemical reactions between sulfate ions and hydrated compounds of the hardened cement paste. The present study aims to evaluate the physical (linear expansion, flexural and compressive strength) and mineralogical properties (X-ray diffraction) of three different mortar compositions (Portland Cement CPV-ARI containing silica fume and rice husk ash, in both cases with 10% replacement of the cement by weight) against sodium and magnesium sulfate attack (concentration of SO_4^{2-} equal to 0.7 molar). The data collected indicate that the replacing the cement by the two siliceous supplementary cementitious materials (SCMs) generate similar results, both SCMs were able to mitigate the effects of the sodium sulfate attack in both physical and chemical characteristics, however, both materials increase the deterioration (i.e. compressive strength) when exposed to MgSO_4 solution.

Keywords: durability, sulfate attack, sodium sulfate, magnesium sulfate.

Resumo: Ataque por sulfato é um termo utilizado para descrever uma série de reações químicas que ocorrem entre os íons de sulfato com os produtos da hidratação do cimento Portland. O presente estudo tem por objetivo avaliar de maneira física (expansão linear, resistência à compressão e tração na flexão) e mineralógica (DRX), três diferentes composições de argamassa, alterando a composição dos finos (CPV – ARI, CPV – ARI com substituição parcial do cimento por 10%, em massa, de sílica ativa, e, CPV – ARI com substituição parcial por sílica de casca de arroz) frente ao ataque por sulfato de sódio, bem como, por sulfato de magnésio (concentração da solução de 0.7 molar). Os resultados obtidos indicam que a substituição parcial do cimento Portland pelas duas diferentes adições, geraram, resultados similares, ambas as adições foram capazes de mitigar os efeitos causados pelo ataque por sulfato de sódio, todavia, frente ao ataque por sulfato de magnésio, ambas as adições apresentaram uma maior degradação quando em comparação com as séries de referência.

Palavras-chave: durabilidade do concreto, ataque por sulfato, sulfato de sódio, sulfato de magnésio.

How to cite: D. J. Souza, M. H. F. Medeiros, and J. Hoppe Filho, “Evaluation of external sulfate attack (Na_2SO_4 and MgSO_4): Portland cement mortars containing siliceous supplementary cementitious materials,” *Rev. IBRACON Estrut. Mater.*, vol. 13, no. 4, e13403, 2020, <https://doi.org/10.1590/S1983-41952020000400003>

1 INTRODUCTION

The deterioration of concrete due to sulfate attack is a complex process that has been widely investigated over several decades. Various damage mechanisms including expansion, cracking, spalling, and loss of strength can manifest in concrete exposed sulfate attack. Sulfate attack is a term used to describe a series of chemical reactions between sulfate ions and hydrated compounds of the hardened cement paste [1], [2]. The complex set

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Financial support: Coordenação de Aperfeiçoamento de Pessoal de Nível Superior – CAPES.

Conflicts of interest: Nothing to Declare.



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of reactions occurs between sulfate ions SO_4^{2-} (coming from the external environment or released by the cement paste after high heating) and the hydrated Portland cement products, such as portlandite $[\text{Ca}(\text{OH})_2]$, calcium monosulphoaluminate hydrate (AFm) present in the cement paste [1], [3], [4]. The interaction between SO_4^{2-} ions and hydrated Portland cement products, such as calcium hydroxide, to form gypsum; and, with aluminates, to form ettringite, which can increase the volume in about 1.2 to 2.2 times more than the initial products. Moreover, causing internal stresses in the bulk cement paste, which can form crack resulting in distress of the hydrated cement matrix [2], [5], [6].

An important aspect in studies related to external sulfate attack (ESA) is regarding to the associated cation to SO_4^{2-} (i. e., Na^+ , K^+ , Mg^{2+} , Ca^{2+} , etc.) since the physical and chemical behaviour of the matter depends on the way in which the atoms interact, all the components in pores solution should be considered in the reaction, some of them can act as a catalyst or actively on the damage [3]–[6]. Several studies indicate that MgSO_4 solutions are more aggressive than Na_2SO_4 at the same concentration level [1], [3], [4], [7]–[12]. In sodium sulfate solution the main reaction is between SO_4^{2-} ions and $\text{Ca}(\text{OH})_2$, forming gypsum, and then between gypsum and calcium monosulfoaluminate hydrate (AFm) to form secondary ettringite [3], [4], [8], [13], [14]. Magnesium sulfate solutions, besides the formation of gypsum and ettringite, also develop brucite $[\text{Mg}(\text{OH})_2]$ (from the reaction between Mg^{2+} and Portlandite) and Magnesium Silicate Hydrate (MSH) due to the decalcification of the C-S-H. MSH has negligible binding capacity and no cementitious properties [9], [12], [15].

The technical importance binder composition with supplementary cementitious materials (SCMs) derives mainly from three aspects: first, the reaction is slow, therefore, the release of heat due to the hydration reactions is also slow. Second, the reactions caused by these materials consume calcium hydroxide, rather than producing them, contributing to the paste resistance to aggressive sulfate solutions. Third, the interaction between amorphous silica, portlandite and water present in the concrete pores leads to the formation of C-S-H [16]–[18].

Siliceous pozzolans, such as Silica Fume (SF) and Rice Husk Ash (RHA), etc. consists nearly exclusively of SiO_2 of fine particle size and a relatively high pozzolanic activity. These materials, especially SF, are widely used to improve the compressive strength, abrasion resistance and durability of concrete [17], [19]–[21]. Besides of these advantages, SF presents some disadvantages, such as cost, may largely increase the drying shrinkage (by self-desiccation and also autogenous shrinkage) and cracking if curing conditions are improper [17], [21]. Although SF improves the rheology of concrete, the high specific surface area of its particles results in an increased water demand. RHA has a similar behaviour in concrete, when compared with SF, according to the literature [22]–[24]. However, RHA can show higher specific surface area due to multilatered, angular, microporous surface and honeycombed structure [25]. However, depending of the amount of carbon on composition of RHA, some particle are able to present some hydrophilic behaviour leading to lack of available water for cement hydration reaction increasing rheological properties of the concrete [25].

As chemical effect on cement hydration, blending of PC higher than 20 wt.% siliceous pozzolans can resulted after longer hydration times in the entire consumption of portlandite with ettringite and C–S–H with a reduced Ca/Si ratio as the only hydrate phase observed [26], [27]. In other words, the use of these materials as cement replacement are beneficial to reduce the sulfate attack [28], [29]. SF as part of the composition of the binder have shown very good results regarding sodium sulfate attack, SF can reduces the penetration rate of sulfate ions, as well as decrease the formation of gypsum and ettringite [30]–[33], however, when exposed to magnesium sulfate solutions the decalcification of C-S-H are more intense, resulting in a loss in strength also higher [11], [29]. This behaviour became even worse when the amount of SF is higher in the composition of the binder, showing losses in strength up to 50% [28].

Some studies [9], [34], [35] have evaluated the resistance to sulfate attack of mortar bars containing the rice husk ash, and, as SF, the durability of the mortars exposed to the Na_2SO_4 solutions was increased, reducing the expansion to very low levels and also, reducing the loss on compressive strength. Which means that RHA has high durability against sodium sulfate attack. For exposure to the MgSO_4 solution, RHA also had positive effects on expansion, however, evaluating strength loss, RHA was harmful as the replacement content increased.

The present paper is the third part of a research project to evaluate the sulfate attack on the physical-chemical properties of Portland cement composites, developed at the Federal University of Paraná (Figure 1). Part one and two can be seen in Souza et al. [36] and [37].

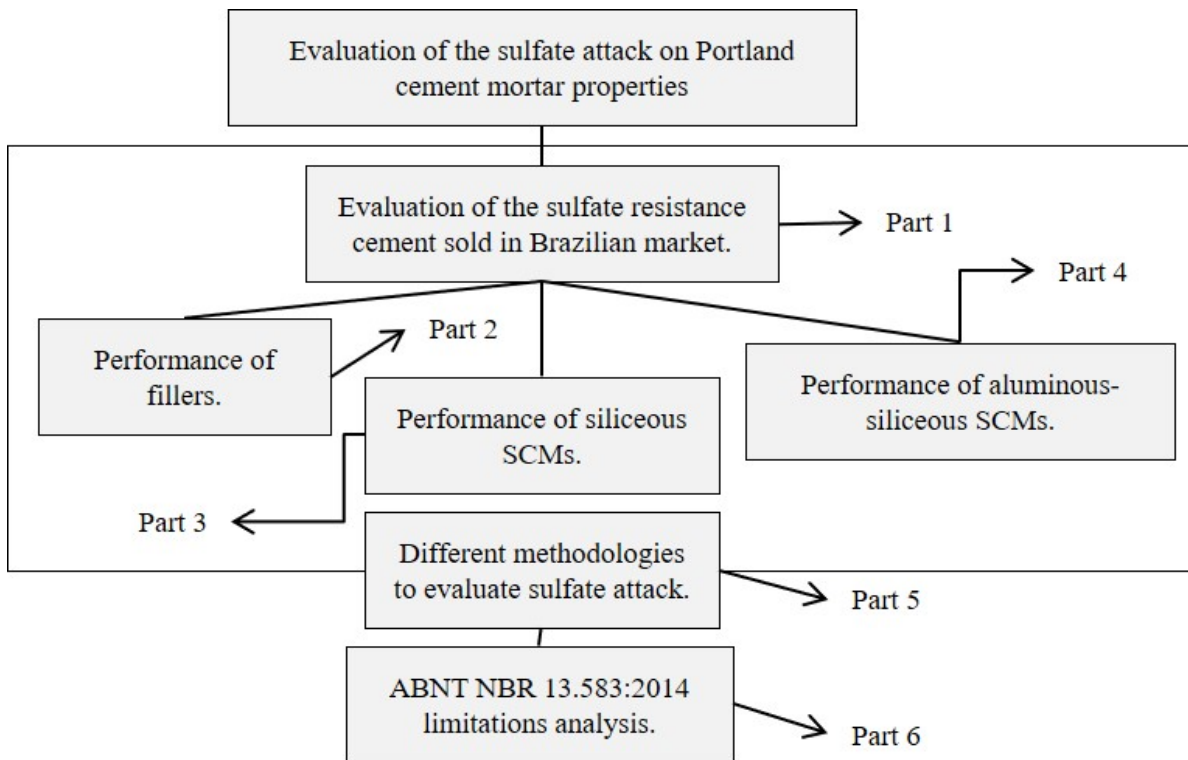


Figure 1: Division of the research project to evaluate sulfate attack on the properties of Portland cement mortars.

2 RESEARCH SIGNIFICANCE

The use of different types of siliceous SCMs with different chemical compositions could also produce different concrete behaviours when exposed to different sulfate salts, affecting cement paste properties differently, which require different remedial actions and mix design depending on the exposure conditions. The present study aims to evaluate the performance of physical and mineralogical properties of three different mortar compositions (PC, with silica fume and rice husk ash) exposed to sodium and magnesium sulfate attack. The approach of the problem will involve the manipulation of two independent variables, the type of binder material used and the aggressive solution of exposure of the mortars.

3 MATERIALS AND METHODS

In order to detect the influence of the cement type on sulfate attack damage degree, the present research has as a main concern, the evaluation of the interference of the sulfate ions in the physical properties intrinsic to the proposed objective.

3.1 Materials

Portland cement with high early age strength CPV - ARI (PC) was used as a control group and replaced partially (10% by weight) by the silica fume and rice husk ash.

The PC alone has no influence of any supplementary cementitious materials (SCM) or even addition of fillers (just clinker + gypsum) on the reference system to be evaluated; however, should be mentioned that the PC has just a small amount of carbonaceous material as allowed by Brazilian's standards (maximum of 10%, according to ABNT NBR 16697 [38]). The Portland cement was characterized by performing loss on ignition; specific gravity and BET tests. Chemical analyses were also performed, using X-ray Fluorescence; and, particle size distribution was measured using laser diffraction in a measurement range of 0.04-500 μm . Table 1 shows the chemical, mineralogical and physical composition of the PC according to the results obtained from the X-ray fluorescence and the physical characteristics of the cement.

Table 1: Chemical composition of the cement

Chemical Composition (%)		Clinker Composition (%)	
CaO	60.97	C ₃ S	52.00
SiO ₂	18.77	C ₂ S	14.60
Al ₂ O ₃	4.36	C ₃ A	6.60
Fe ₂ O ₃	2.93	C ₄ AF	8.91
MgO	3.50	Gypsum	6.71
SO ₃	3.12	CaCO ₃	4.9
Na ₂ O _{eq}	0.68	Physical Properties	
Free Lime	0.90	BET (m ² /kg)	1,070
Insoluble Res.	0.77	Specific Gravity	3.13
Loss on Ignition	3.55		

In this study, two different types of siliceous SCMs were selected, silica fume (SF) and rice husk ash (RHA). Both materials were characterized for loss on ignition, specific gravity, BET and particle size distribution. The mineralogical properties of the SCMs were also characterized using XRD tests. The analysis was performed from 5° to 75° 2θ, with an angular pitch of 0.02° 2θ and time per step of 1 second. It was used copper anode tube, 40 kV / 30 mA and divergent slit of 1°. Minerals were identified by comparison with the standards of the International Centre for Diffraction Data, ICDD. Finally, the chemical characterization of the samples was performed using X-Ray Fluorescence (XRF) method.

The fine aggregate used for the design of the mortar bars was natural quartz sand with SiO₂ content of 96% and free of contaminants, which means that it is negligible the chemical influence of this material on final results. Finally, the fine aggregate was sieved, and the particle size distribution was fixed as 25% of the total mass of sand between each of the following ranges 0.15-0.30 mm, 0.30-0.60 mm, 0.6-1.2 mm and 1.2-2.4 mm.

3.2 Methods to evaluate sulfate attack

In this section will present the procedures used to evaluate the sulfate attack in different prismatic mortars bars, such as preparing procedure of the samples; solutions; conditions of exposure; length variation test and compressive strength test.

a) Preparing of the sample for mortar bar tests

The degree of sulfate attack on mortars was analyzed in general by two main groups samples:

- Group 1: composed of 36 specimens measuring 25 mm x 25 mm x 285 mm (to evaluate induced expansion), divided into 3 different mix-designs (PC, PC + SF and PC + RHA) and 3 final exposure solutions: Control (water + calcium hydroxide), Na₂SO₄ and MgSO₄ solutions;
- Group 2: composed of 108 specimens with dimensions of 40 mm x 40 mm x 160 mm (to evaluate compressive and flexural tensile strength) and divided into 3 compositions and 3 final exposure solutions.

The mortars bars were designed based on Brazilian standard ABNT NBR 13.583/2014 with binder-to-sand ratio of 1.0/3.2, by mass, and water to binder ratio of 0.60 [39]. After casting and moulding, all bars were subject to 48 h in the mold in moist cabinet, later the samples were cured for 12 days in lime water at 23±2 °C before, finally, immersed in sulfate solutions at 40 °C, in accordance with ABNT NBR 13.853/2014, for a period of 140 days [40].

b) Exposure solutions

The concentration of anhydrous sodium sulfate, in accordance with ABNT NBR 13.853/2014, was 100g of Na₂SO₄/L of solution (0.704 mol/L); which means that the concentration of SO₄²⁻ (also 0.704 mol/L) can be defined as 67,630 ppm (67.63 g/L). Fixing the total amount of sulfate ions, the magnesium sulfate solution was prepared as 0.704 mol/L as well, (84.74g of MgSO₄/L of solution). Finally, the solution volume-to-samples volume ratio was fixed as 4.0/1.0 [13], [14], [36], [41], along the whole exposure period.

c) Length variation

The evaluation of the induced expansion followed NBR 13.583/2014, after the first and second curing procedures (48 h and 12 days, respectively), the samples had their initial lengths measured just before the exposure to the final solutions.

The measurements were performed after 2, 4, 6, 8, 10, 15 and 20 weeks of exposure. For this purpose, the samples were placed at the micrometre, always with the same face upwards, and the measurements were taken always referring to the smaller length indication identified by the apparatus after 360° rotation of the bar. The individual expansion or shrinkage of the samples are given by the difference between the value measured at the corresponding exposure time and the initial reading minus the difference of the same group of samples exposed to the lime-water solution, divided by its initial length and multiplied by 100.

d) Compressive and flexural tensile strength.

The tests of flexural tensile and compression strength were made at times of exposure of 0; 2; 6; 10; and, 20 weeks. ABNT NBR 13.279 recommendations were followed, and the tests were carried out in an equipment with a load capacity of 100 kN, and the tensile strength tests were performed in the bars before the compression.

For the flexural tensile strength test the load application rate was 50 ± 10 N/sec until failure, thus, the strength was calculated according to ABNT NBR 13.279 [42].

In compressive strength test, 6 specimens were obtained after tensile tests of 3 samples and the load application rate was 505 ± 5 N/sec until failure, thus, the strength was calculated.

4 RESULTS AND DISCUSSIONS

4.1 Physical and chemical characterization of the silica fume and rice husk ash

Table 2 reports the chemical compositions measured by XRF and the results of BET specific surface area, LOI and the specific gravity of the mineral additions.

Table 2. Chemical and physical properties of the Silica Fume and Rice Husk Ash

	Silica Fume	Rice Husk Ash
CaO	0.19	0.43
SiO ₂	92.35	88.47
Al ₂ O ₃	2.21	2.72
Fe ₂ O ₃	0.05	0.05
MgO	-	-
SO ₃	1.52	1.55
K ₂ O	0.94	1.46
Insoluble Residue	0.04	0.49
Loss on Ignition	2.7	4.84
BET (m ² /g)	20.24	14.69
Specific Gravity	2.18	2.12

Both SCMs have higher surface specific area and lower specific gravity than PC, the surface specific area of the SF is 18.9 times higher than the cement and the RHA, 13.7 times. In general, the SF and RHA have very similar chemical composition, the major differences between the SCMs are the total amount of SiO₂, 4% bigger in the SF samples, for the RHA the content of K₂O and Loss on Ignition (LOI) are higher in comparison with SF. Both values can be explained by the fabrication processes of the rice and RHA, the soil treatment to enhance quality and rice production can it be the major indicator that increases the potassium content. On the other hand, the burning process during RHA fabrication can induce to high contamination of carbon in the RHA. An example of that is the differences in the coloration of the sample before and after the LOI test, correlated to the loss of CO₂, as indicated in Figure 2.

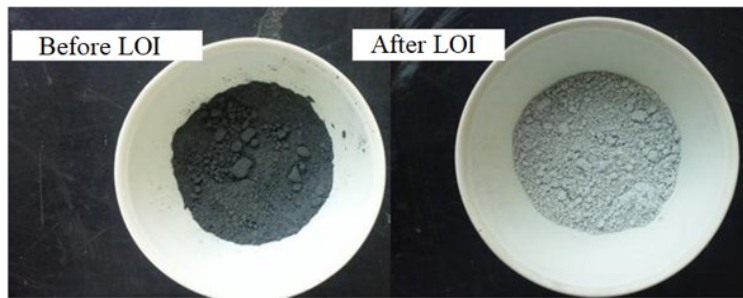


Figure 2: RHA samples before and after loss on ignition test

The XRD patterns of the SF and RHA, respectively, are shown in Figure 3. As indicated, silica fume has distinguishing amorphous halo, characteristic of its high pozzolanic reactivity, with almost any crystallinity. Moreover, RHA also presented partial amorphous minerals, the patterns resulting from the X-ray diffraction indicates crystallinity of its predominant phase, cristobalite. The distinguished molecular amorphous arrangement of the SF, indicating almost any crystallinity, in summation with the considerably higher specific surface area and lower particle size distribution (Figure 4) than the RHA, suggest that this material also present higher pozzolanic reactivity [13], [14], [36], [43].

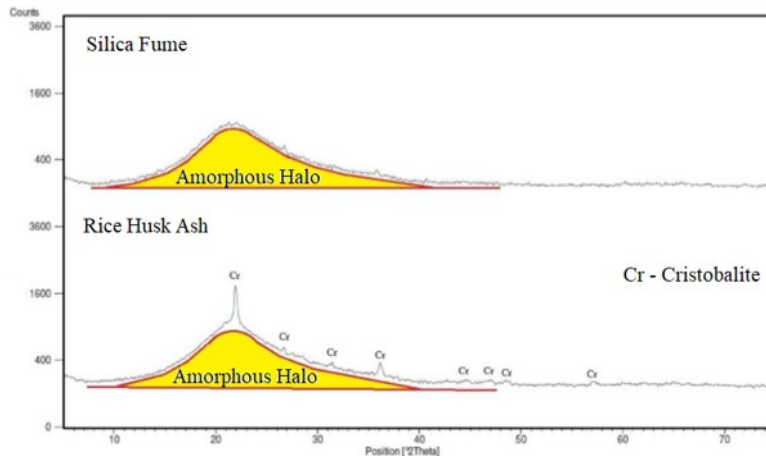


Figure 3: X-ray diffractograms of the silica fume and rice husk ash.

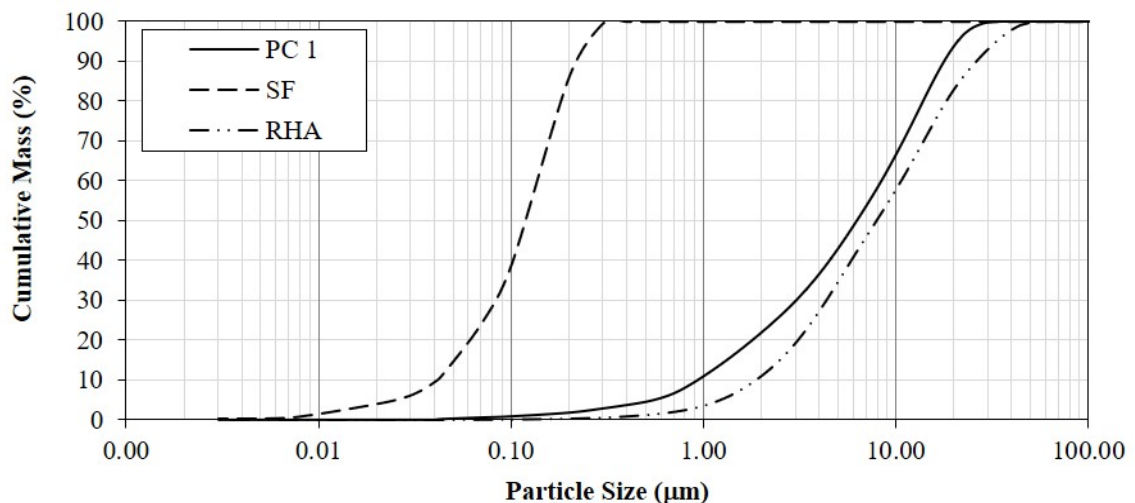


Figure 4: Particle size distribution of the CPV - ARI, silica fume and rice husk ash

In Figure 4, the particle size distributions of the cement and the SCMs are presented. The RHA has D50 equal to 8 μm , higher than the cement average, around 6 μm . However, SF showed an average particle size of 0.12 μm (52 times smaller than Portland cement). Indicating that the SF can also influence, significantly, the nucleation and hydration of the cement particles, changing the hydration kinetics of the cement [44]–[46].

4.2 Length variation analysis

The results of the analysis of length variation of the samples over the 20 weeks of exposure (140 days) in both aggressive solutions are presented in Figure 5.

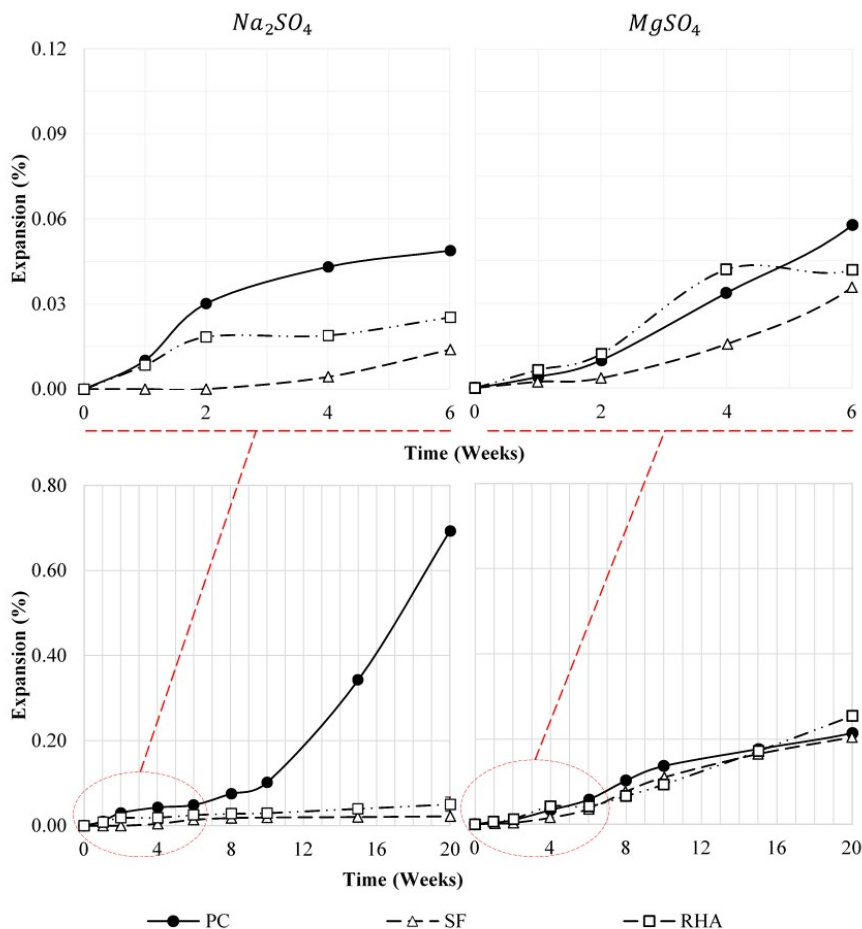


Figure 5: Expansion of the mortar bars ARI, SF and RHA exposed to solutions of Na₂SO₄ and MgSO₄ (0.7 mol/L) for 42 and 140 days (6 and 20 weeks).

It should be noted that NBR 13.583 does not specify a value to which a composition can be considered resistant or not to sulfate attack since it is only a comparative analysis. However, according to Marciano [47], compositions with expansion equal to or less than 0.030% at the 42 days of exposure (6 weeks) may be considered resistant to sodium sulfate. However, considering that SO₄²⁻ content in solution was kept constant at 0.704 M, it was observed that all groups of samples had expansion higher than 0.03% when exposed to MgSO₄, on the other hand, at sodium sulfate solution both siliceous SCMs had induced expansion lower than the maximum determined by Marciano [47], leading to conclude that, at least for short periods of exposure, both supplementary cementitious materials are the best options for both Na₂SO₄ and MgSO₄ exposure.

The comparative analysis between the averages results, Tukey's test, for 6 weeks of exposure, can be seen in Figure 6. Due to the exposure to MgSO₄ at the 42nd day, all samples can be considered as statically equal, independent

of the composition of the binder material, the behaviour of the sample were similar, regarding the induced expansion. Therefore, the decision-making should be based on the economic and non-technical benefits for these cases (when the analysis is based on NBR 13.583, at 42 days of exposure). On the other hand, when soaked in Na_2SO_4 solution, both SCMs mitigated, significantly, the sulfate attack, in about 48% for SF and 80% for RHA in comparison with CPV – ARI samples. As above mentioned, the expansion of mortars bars exposed to magnesium sulfate was more intense until the 42nd day. This behaviour is associated with the higher solubility of MgSO_4 when compared to Na_2SO_4 , which results in a higher sulfate ions content in the solution.

Along the 140 days of exposure, the excessive formation of brucite and gypsum, the *pH* of the mortar pores solution begins to decrease, since such materials have much lower solubility than the portlandite, therefore, releasing less OH^- . Consequently, the *pH* of the solution tends to decrease until levels where it can destabilize the *C - S - H*, which starts to release calcium ions to elevate *pH*. However, besides this process, the decalcification of hydrated calcium silicate, forming *M - S - H* that does not have any binder capacity. Moreover, the release of calcium ions by the *C-S-H* can react with the sulfate ions and precipitate as gypsum, decreasing more the *pH* and increasing the damage in the mortar bars. The groups of mortar SF and RHA with lower portlandite contents due to its highly pozzolanic reactivity [13] initially also presented gel formation on the surface of the samples, however, with a noticeably smaller amount, but, during 140 days of exposure, the formation of the gel was almost interrupted. Then, it was noted the occurrence of dissolution of the surface layers of the samples in the solution (Figure 7a and b).

The excessive formation of gel observed on the surface of the CPV – ARI samples exposed to MgSO_4 (Figure 7c). According to the literature [3], [8], [11], [28], [48], [49], is the first product of the interaction between magnesium sulfate and Portland cement hydration products is brucite (magnesium hydroxide), in which the electron affinity of the magnesium ion replaces the calcium ions in the portlandite particles. According to the authors, such material is presented as a gel filling the voids of the mortar and it can precipitate on the surface along with the gypsum and compositions of hydrated magnesium sulfate. Therefore, such visual indication of the interaction between the cementitious material and the aggressive solution could indicate higher expansion of the bars, but this did not occur. Such gel formation has an influence on delaying the expansion process, since it decreases the diffusivity of sulfate ions in the mortar samples. To analyze such statement, for the present study, *pH* measurements were carried out along the analyzed periods of exposure, and Figure 8 presents the comparative *pH* along the evaluation between three studied solutions (i.e. control, sodium sulfate and magnesium sulfate).

On the other hand, both highly reactive pozzolans presented, in general, considerably resistance to linear expansion due to the sodium sulfate attack at 140 days of exposure, being considered statistically equivalent as seen in Figure 9. Both SCMs obtained, on average, 94% less expansion than CPV – ARI. Therefore, it is evaluated that the morphological characteristics as the fineness of the particles, besides, of course, its amorphous structure, contributed to the good performance, favoring the packing of particles and the consumption of more portlandite, which favors the formation of new CSH particles. Likewise, making available less $\text{Ca}(\text{OH})_2$ to react with SO_4^{2-} ions, in which, as above mentioned, enhance the surface deterioration of the samples due to the exposure to MgSO_4 .

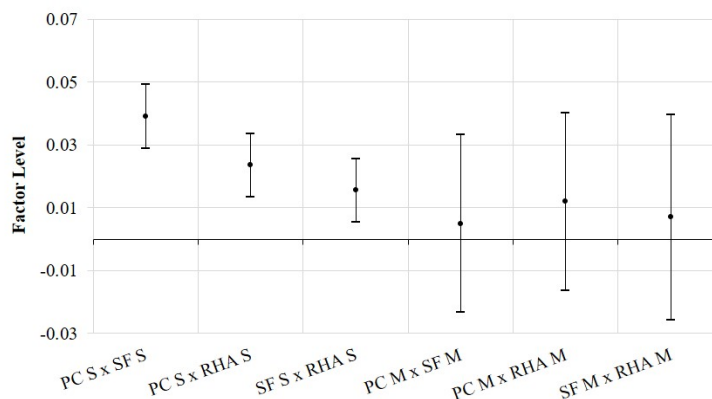


Figure 6: Comparative analysis of the averages, Tukey's test, for 6 weeks of exposure among the series studied, for a significance level of 5% (S-sodium sulfate and M-Magnesium sulfate).

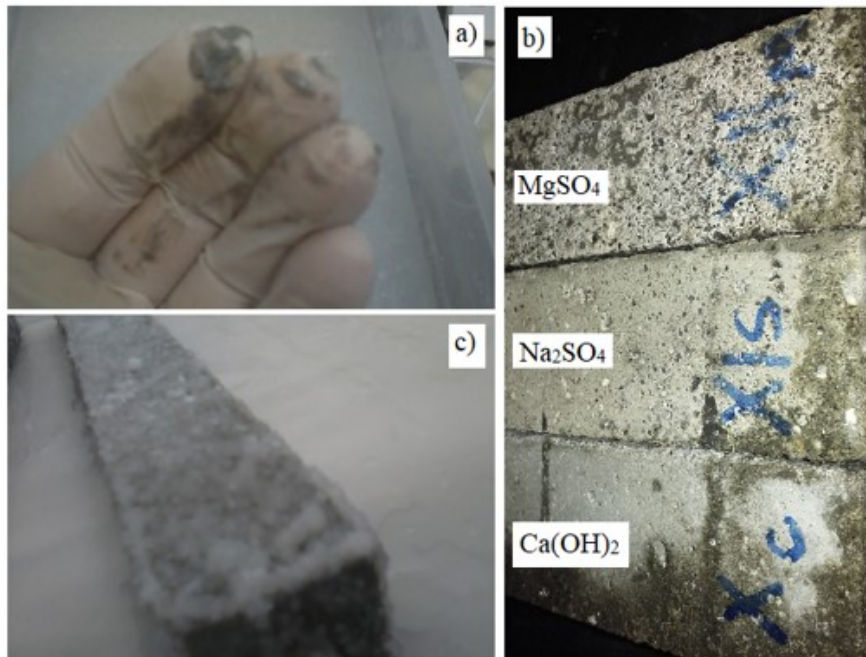


Figure 7: Samples of mortar bars after 140 days of exposures to sulfate solutions, a) indication of the disaggregated material from the SF and RHA samples due to the exposure to MgSO₄, b) surface degradation of the SF mortars due to MgSO₄ and c) indication of the surface gel formed due to MgSO₄.

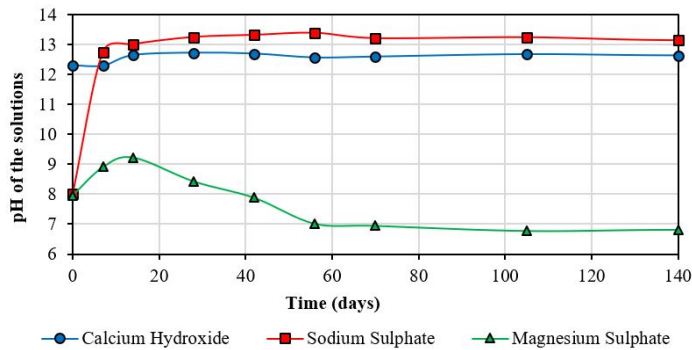


Figure 8: Comparative pH analysis of Ca(OH)₂, Na₂SO₄ and MgSO₄ solutions over 20 weeks (140 days).

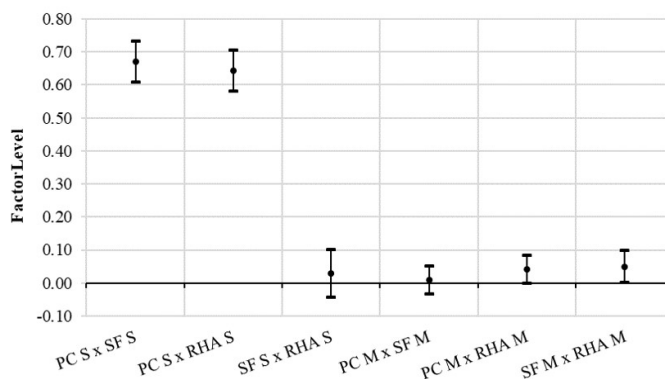


Figure 9: Comparative analysis of the averages, Tukey's test, for 20 weeks of exposure among the series studied, for a significance level of 5% (S-sodium sulfate and M-Magnesium sulfate).

4.3 Mineralogical analysis

The obtained diffractograms for all series for each exposure conditions can be seen in Figure 10, Figure 11 and Figure 12. Compared to calcium hydroxide exposure solution, it can be observed that PC, SF, and RHA presented a higher intensity the peaks related to ettringite crystals (E) for exposure in both sulfate solutions, as well as consumption of the portlandite.

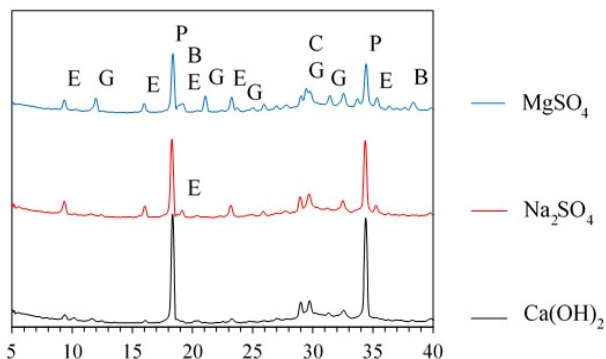


Figure 10: CPV-ARI diffractograms after 20 weeks of exposure to Ca(OH)_2 , Na_2SO_4 and MgSO_4 . Monocarboluminate (A), brucite (B), calcite (C), ettringite (E), gypsum (G) and portlandite (P).

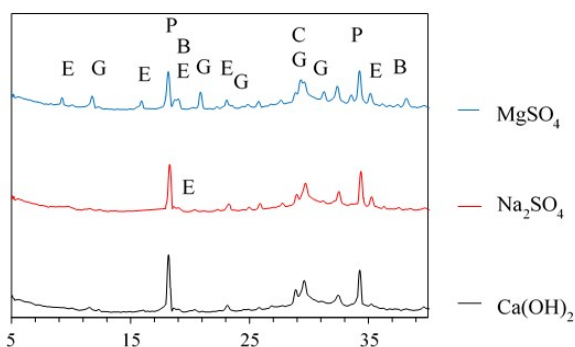


Figure 11: SF diffractograms after 20 weeks of exposure to Ca(OH)_2 , Na_2SO_4 and MgSO_4 . Monocarboluminate (A), brucite (B), calcite (C), ettringite (E), gypsum (G) and portlandite (P).

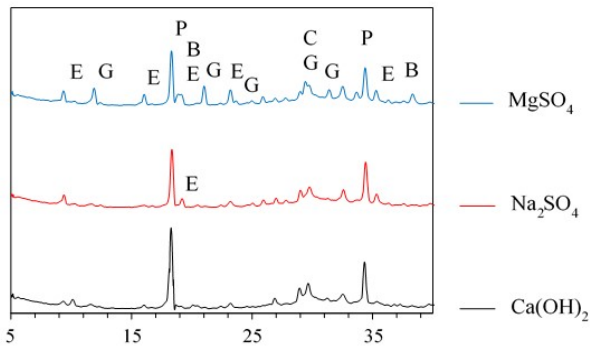


Figure 12: RHA diffractograms after 20 weeks of exposure to Ca(OH)_2 , Na_2SO_4 and MgSO_4 . Monocarboluminate (A), brucite (B), calcite (C), ettringite (E), gypsum (G) and portlandite (P).

SF and RHA mortar samples have their mineralogical composition relatively close to each other, both are highly siliceous materials and with low aluminate contents, in about 2% of the mass. Then, their behaviour under sulfate attack are similar in both aggressive solutions. For calcium hydroxide exposure solution, RHA present on its XRD patterns, small peaks related to the formation of ettringite, indicating the presence of the remaining primary ettringite.

For the exposure to the magnesium sulfate solution, SF and RHA groups presented similar counts than the CPV-ARI for ettringite formation at $9.14^\circ 2\theta$, and, at the same time, slightly higher peaks of gypsum (peak at $12.00^\circ 2\theta$), indicating that the alkaline reserve consumption in the pozzolanic reaction may have contributed with the decalcification of the C-S-H particles, producing more M-S-H (not possible to identify with XRD), releasing calcium to react with SO_4^{2-} ions to form gypsum. Moreover, as observed in the exposure to the calcium hydroxide solution, the group with the SCMs showed significant consumption of portlandite, indicating the occurrence of an intense pozzolanic activity, specially considering the replacement of the cement by 10% by mass.

4.4 Mechanical properties

The compressive and tensile strength are essential parameter to be considered regarding the degree of sulfate attack [11], [50], as well as the flexural strength which gives important data regarding the microcrack propagation within the cement paste [51], [52]. Is common in the literature that samples exposed to the sodium sulfate solutions have their strength increased at an initial exposure time and then, for a long time of exposure, there are strength loss (Figure 13 and Figure 14). The statistical analysis of the obtained data can be seen in Figure 15 and Figure 16.

In general, the influence of the aggressive solutions increases the flexural in the samples. It is also seen that both aggressive solutions showed similar behavior in the samples according, for example, to the results obtained by Huang et al. [53]. Supplementary cementitious materials, in general, can reduce the porosity of the cementitious matrix and the interfacial transition zone (ITZ). This fact leads to an improvement in both compressive and tensile strengths, with the last being on smaller scale until there is an increase in the cement hydration products present in the ITZ. Moreover, while there are high levels of portlandite in this region, the tensile strength will remain unchanged. Thus, the addition of the SCMs can cause a significant increase of the strength since there is formation of more C-S-H particles in this region, then, the interference of the ITZ in the strength of the mortar starts to decrease.

It can be seen in Figure 13 and Figure 14 that the samples exposed to the calcium hydroxide solution, in general, increase the strength (flexural or compressive) as a function of time, even though showing some variations in 6 and 10 weeks. Moreover, it is assumed that the bars did not developed cracks at the evaluation period, as expected since the mortars remained in ideal conditions of curing. On the other hand, when subjected to sulfate solutions, CPV – ARI, for example, show even higher increase in strength over time, until certain point at which micro-cracking begins, then the losses in strength starts. CPV-ARI showed earlier degradation due to the exposure to sodium sulfate solution and slower damaging processes when exposed to magnesium sulfate attack. Indicating, in this case, that Na_2SO_4 was more aggressive to this composition. However, SF and RHA samples presented opposite behavior when than CPV-ARI samples. In other words, SF and RHA delayed the micro-crack starting point for exposure to sodium sulfate but accelerated the degradation when exposed to magnesium sulfate, at least for measurement of compressive strength.

As well known, the tensile strength is more sensitive to any crack formation in the concrete, mortars, etc, different authors [6], [54], [55] stated that, does not matter the mechanism of deterioration of the concrete, if there is crack formation there is reduction in the capacity of the concrete on tensile stresses. However, considering the expansion levels and the flexural strength results seems that the groups of samples containing SF and RHA did not developed crack, at least, during the period of evaluation. Yet, the compressive strength results indicate significant losses for both composition when exposed to $MgSO_4$.

The Ca/Si ratio of the samples varied due to the replacement of the cement by the highly siliceous SCMs. According to Tikalsky et al. [56], Bellmann and Stark [57] and Lothenbach et al. [19], the decrease in this ratio implies in a reduction in the amount of portlandite after hydration, therefore, the composition can be more resistant to sodium sulfate attack. On the other hand, for magnesium sulfate attack, such reduction results in a composition more susceptible to the damage [3], [8]. Thus, for both cases, what was seen was, precisely, a behavior of the samples according to information obtained in the literature.

In general, it is observed during the 20 weeks of exposure that the individual behavior of each series distinguishes between both aggressive solutions, indicating, once again, that the cations associated with the sulfate ions also influence the degree of the attack. For example, the SF and RHA groups presented at 20 weeks just a little variation in strength when exposed to Na_2SO_4 and can be considered as highly resistant to attack by this type of sulfate. However, the same series when exposed to $MgSO_4$ showed high losses in compressive strength, about 8.6% for RHA and 9.8% for SF, corresponding to losses of 5.4 MPa and 5.9 MPa, respectively. This loss of compressive strength is associated with the decomposition of C-S-H particles, and, consequently, formation of M-S-H, which have little or no binder capacity.

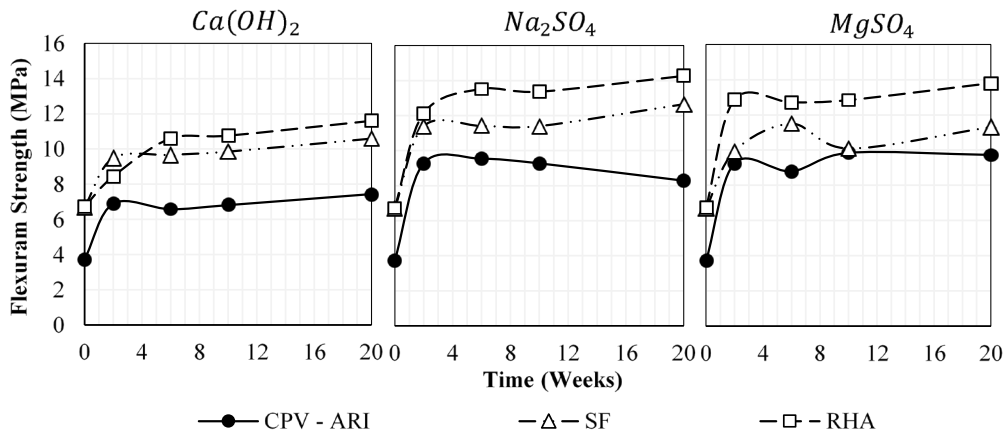


Figure 13: Flexural Tensile strength of the samples up to 20 weeks of exposure in the three different solutions [$Ca(OH)_2$, Na_2SO_4 e $MgSO_4$].

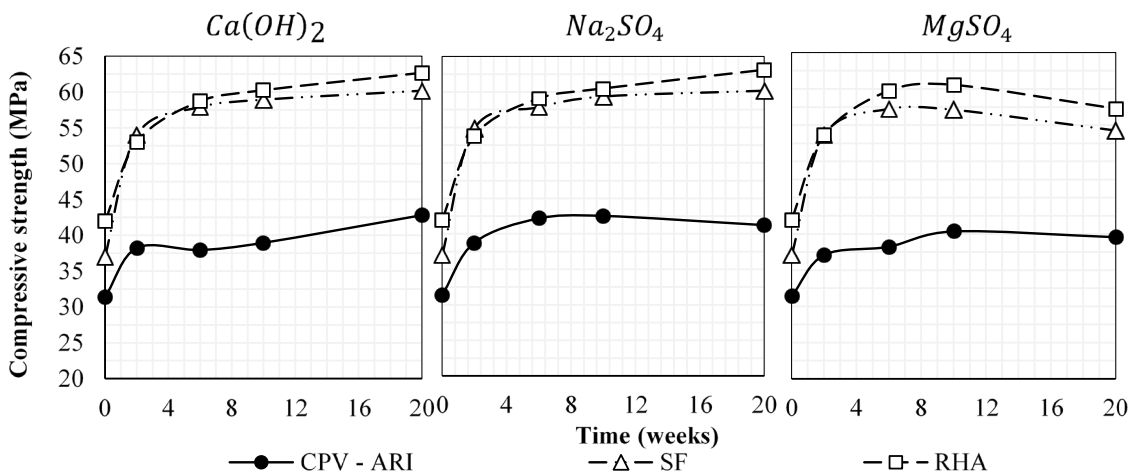


Figure 14: Compressive strength of the samples up to 20 weeks of exposure in the three different solutions [$Ca(OH)_2$, Na_2SO_4 e $MgSO_4$].

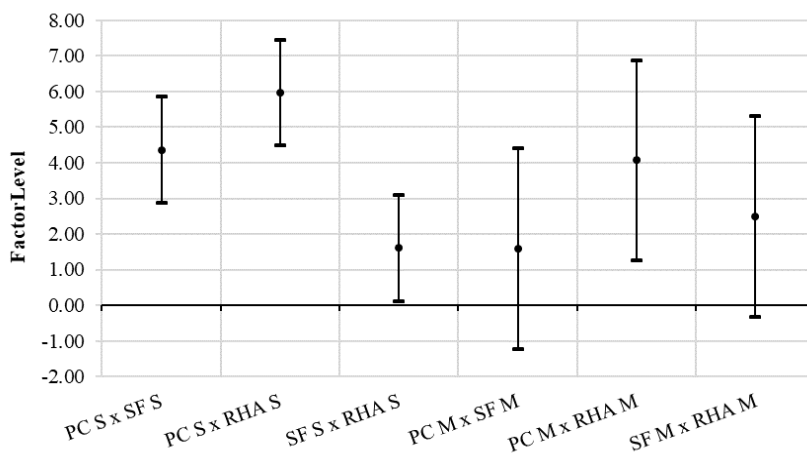


Figure 15: Comparison between averages of Flexural strength losses (Tukey test for a significance level of 5%) of the same series for different aggressive solutions (S - sodium sulfate and M - magnesium sulfate) for 20 weeks of exposure.

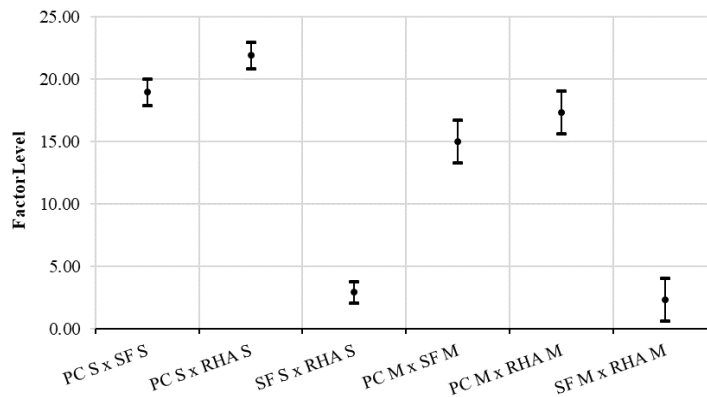


Figure 16: Comparison between averages of compressive strength losses (Tukey test for a significance level of 5%) of the same series for different aggressive solutions (S - sodium sulfate and M - magnesium sulfate) for 20 weeks of exposure.

Likewise, these results are reliable with the theory and experiments analyzed in the literature, such as those of Santhanam et al. [8], Diab et al. [11], that is, the loss in compressive strength is much more significant than the actual expansion of the samples containing higher amount of reactive SiO_2 when exposed to magnesium sulfate attack. These results bring important information regarding the degradation of the sulfate attack, especially when it makes a parallel with real concrete structures since these are always projected based on compressive strength. At the same time, such degradation was not observed for linear dimensional expansion, so it was confirmed that “quantify” sulfate attack only using one-dimensional behavior can lead to errors in decision-making to define the materials to be used at the field.

5 CONCLUSIONS

Based on the results of this experimental investigation under tidal environment, the following conclusions are drawn:

- The partial replacement (10% by mass) of the cement by supplementary cementing materials in the mortars mitigated significantly the induced expansion due to sodium sulfate attack. The exposure to magnesium sulfate solution did not show the same behaviour, the use of SF and RHA were statistically similar to the control group;
- When exposed to sodium sulfate attack, the pH increased along time and has an influence on the test results (i.e. length variation and mechanical analysis), since higher pH maintains the stability of CSH and Ettringite particles. For MgSO_4 the pH decreases to values close to 7, affecting the stability of the CSH, reducing, significantly the compressive strength of the SF and RHA;
- Comparing the expansion caused by both sulfate solutions, at short (i.e. 6 weeks as per NBR 13,583) and long-term (i.e. 20 weeks) exposure conditions, MgSO_4 developed higher expansion levels than sodium sulfate attack for both mortars made of PC plus SCMs. Yet, for the control group made only by PC, the long-term exposure to Na_2SO_4 lead to a much higher induced-expansion than MgSO_4 ;
- Sulfate attack tests with long exposure period, such as 20 weeks or more, are important to better understand and characterize degradation processes of Portland cement composites due to different types of sulfate (sodium sulfate attack, magnesium sulfate attack, etc.);
- Finally, it was clear from the obtained results the importance of knowing, precisely the type of sulfate to which the cementitious material will be exposed. In other words, groups of samples considerable resist to Na_2SO_4 had higher damage when exposed to MgSO_4 . This reinforces, once again, that the approach to classify the capacity of each binder composition if is resistant of not to sulfate attack is always dependent of the different types of sulfate solutions present in the environment.

ACKNOWLEDGMENT

The authors would like to thank the support of the Graduation Program in Civil Construction Engineering at Federal University of Paraná (DCC-PPGECC-UFPR), the Ponta Grossa State University (UEPG), the Federal University of Western Bahia (UFOB), the National Council for Scientific and Technological Development (CNPq) and the

Coordination for the Improvement of Higher Education Personnel (CAPES), De Souza benefits from a Vanier scholarship financed by NSERC (Natural Science and Engineering Research Council of Canada).

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Author contribution: Souza, Medeiros and Hoppe Filho conceived of the presented idea. Souza developed the theory and performed the computations. Souza performed all the tests presented. Medeiros and Hoppe Filho encouraged Souza to investigate the external sulfate attack on mortar samples containing siliceous SCMs and supervised the findings of this work. All authors discussed the results and contributed to the final manuscript.

Editors: Pelisser Fernando Pelisser, José Luiz Antunes de Oliveira e Sousa, Guilherme Aris Parsekian.