Evaluation of external sulfate attack (Na₂SO₄ and MgSO₄): Portland cement mortars containing fillers

Avaliação do ataque externo por sulfato (Na₂SO₄ e MgSO₄): Argamassas de cimento Portland contendo fíleres

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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 with limestone filler and, with a quartz filler, 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 fillers generate different results, the quartz filler presented a mitigating behaviour towards the sulfate, and the limestone filler was harmful to Portland cement mortars, in both physical and chemical characteristics.

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 fíler calcário, e, CPV – ARI com substituição parcial por 10%, em massa, de fíler quartzoso) 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 pelos dos diferentes fíleres geram diferentes resultados, o fíler quartzoso apresentou um comportamento mitigativo frente ao ataque por sulfato, porém, o fíler calcário apresentou comportamento deletério tanto pela avaliação física, quanto mineralógica.

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

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1. Introduction

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 typical form of sulfate attack, associated with the formation of gypsum and the secondary ettringite formation, is the most common, resulting from the diffusion of sulfate ions from an external source [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]. The mechanism of attack for the anion (SO_4^{2-}) is very close for each of the associated cation, on the other hand, each cation has a distinct interaction with the cementitious matrix. Also, the ratio anion/cation in solution for each salt (Na_2SO_4, $MgSO_4$, $CaSO_4$, etc.) is also variable, since the molecular mass is dependent on the mass of each of the atoms.

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 Ca(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 [$Mg(OH)_2$] (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 use of fillers in the composition of cementitious products is widely discussed in the literature [2,16–18]. It is known that such materials can influence the physical, mechanical and chemical characteristics of the concrete, even if it is an inert material. Three physical effects of fillers can be observed when used in cementitious materials [16]. Two of these, cement dilution and improved particle packing, are direct consequences of the substitution or addition of these fineness particles, while the third effect is related to the improvement of the nucleation of the cement grain. Regarding the hydration of Portland cement, such materials can modify the kinetics of this phenomenon, especially at lower ages due to the heterogeneous nucleation [16].

However, the blended cements containing fillers are more vulnerable to sulfate attack distresses (at longer exposure periods) when compared with supplementary cementitious materials [12,19–23]. Mostly because fillers do not consume part of the portlandite generated in the cement hydration process, favoring the formation of gypsum and later, secondary ettringite [17,24,25].

An example of the long-term exposure of fillers, Tosun-Felekoglu [26] presented results from samples with different amount of C_3A (4.6% and 11.2%) and limestone filler (0%, 5%, 10%, 20% and 40% % in partial replacement of the cement) exposed to both magnesium and sodium sulfate at two different temperatures (5 and 20 °C). The author concludes that the deterioration of the
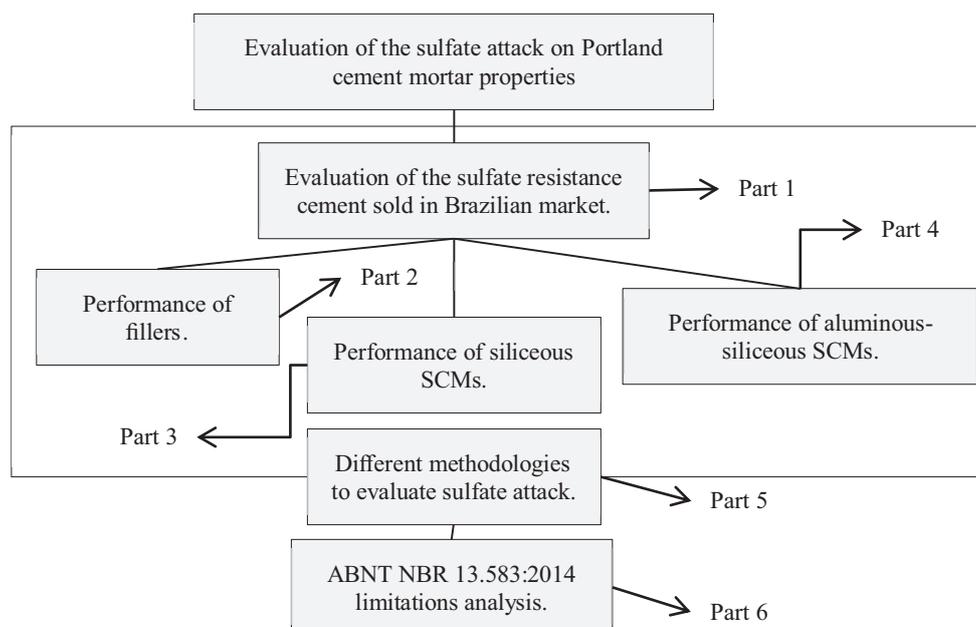
Figure 1
Division of the research project to evaluate sulfate attack on the properties of Portland cement mortars

samples was much more significant in concretes containing C$_3$A content in the range of 11.2% in both solutions, and this has become even more critical in conditions where there are higher cement substitution levels Portland by limestone filler. The increase in the amount of limestone filler had increased the permeability of the samples, and, there was an increase in the formation of thaumasite that had been aggravated at low temperatures.

The limestone filler added may also present some reactive activity with Portland cement [27]. A small portion of this material can be consumed and form calcium monocarboaluminate hydrated, which can influence and delay the conversion of AFt into AFm [28].

The presence of limestone filler can also be harmful when exposed to sulfate ions, especially when exposed at lower temperatures (below 15 ºC). Due to the release of carbonates from the filler particles, which combinate with sulfate and potentially form thaumasite [14,17,19,20,24,25].

The present paper is the second 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 can be seen in [29].

2. Research significance

The use of different types of fillers 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 (OPC, with limestone and quartz filler) 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.

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$_2$Oeq	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	—	—

3.1 Materials

Portland cement with high early age strength CPV - ARI (PC) was used as a control group (containing 4.9% of carbonaceous material) and also replaced partially (10% by weight) by the limestone filler and quartz filler.

The PC used 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 5%, according to ABNT NBR 5733/2010). 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.

In this study, two different types of filler were selected, limestone filler (LF) and quartz filler (QF), which correspond to different total amount of carbonaceous materials in the mixes, i.e. control group equal to 5%, LF group equal to 15% (5% from the cement + 10% of limestone filler, corresponding to the new regulations regarding the use of limestone filler in blended cement), and QF group equal to 5% of carbonaceous materials + 10% of quartz filler. Both fillers were characterized for loss on ignition, specific gravity, BET and particle size distribution. The mineralogical properties of both fillers were also characterized using XRD tests. The analysis was performed from 5º to 75º 2θ, with an angular pitch of 0.02º 2θ and time per step of 1 second. It was used copper anode tube, 40 kV / 30 mA and divergent slot of 1º. 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 SiO$_2$ 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 + LF and PC + QF) and

3 final exposure solutions: Control (water + calcium hydroxide), Na_2SO_4 and $MgSO_4$ 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 (cement + filler)-to-sand ratio of 1.0/3.2, by mass, and water to "binder" ratio of 0.60. 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.

b) Exposure solutions

The concentration of anhydrous sodium sulfate, in accordance with ABNT NBR 13.853/2014, was 100g of Na_2SO_4/L of solution (0.704 mol/L); which means that the concentration of SO_4^{2-} (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 $MgSO_4$/L of solution). Finally, the solution volume-to-samples volume ratio was fixed as 4.0/1.0 [13,14,29,30], 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 [27] 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 [27].

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.

Table 2

Chemical and physical properties of the limestone filler and quartz filler

	Limestone filler	Quartz filler
CaO	42.77	—
SiO_2	1.62	94.45
Al_2O_3	0.95	2.76
Fe_2O_3	0.24	—
MgO	8.25	—
SO_3	0.66	1.18
K_2O	0.17	0.29
Insoluble residue	0.14	0.05
Loss on ignition	45.2	1.3
BET (m²/kg)	1,413	1,227
Specific gravity	2.70	2.60

4. Results and discussions

The results of the tests will be presented and discussed in this section, firstly length variation of and then the results related to mechanical properties.

4.1 Physical and chemical characterization of the filler materials

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.

Both fillers have higher surface specific area and lower specific gravity than PC. The limestone filler had magnesium oxide content of 8.25% according to its chemical composition, which means that this material is not classified as limestone, but as magnesian limestone, since the MgO content is in between 5% and 12% [31] and it can be classified as Type B of Fillers (ASTM C1797). On the other hand, the chemical composition of the quartz filler (Type C of Fillers according to ASTM C1797), as expected, had a high content of silicon dioxide, close to 95%. The XRD patterns of the limestone and quartz filler, respectively, are shown in Figure 2. Calcite ($CaCO_3$), dolomite ($CaCO_3.MgCO_3$) and quartz (SiO_2) were identified as the main mineralogical phases in the samples.

In Figure 3, the particle size distributions of the cement and fillers are presented. The limestone and quartz fillers have D50 around 10-15 μm, both higher than the cement average, around 6 μm. However, this does not necessarily mean that the fillers grains will not influence the nucleation and hydration of the cement particles [16,32,33]. As an example, for all anhydrous cement particles larger than 10 μm (approximately 31% of the cement grains), 50% of the QF particles and approximately 40% of LF will be equal to or lower than those of Portland cement grains, which means that some fillers particles can still change the hydration kinetics of the cement. However, the randomization of the mixture between the binder particles should be considered as well.

4.2 Length variation analysis

The results of the analysis of length variation of the samples over
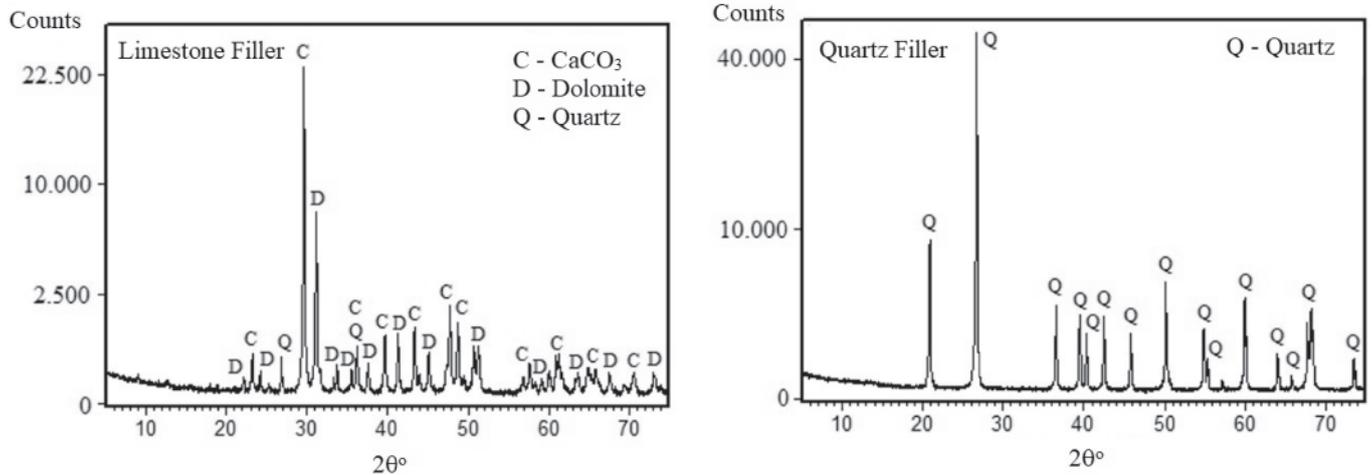
Figure 2
X-ray diffractograms of limestone filler and quartz filler

the 20 weeks of exposure (140 days) in both aggressive solutions are presented in Figure 4.

The methodology of the discussion will initially debate the length variations presented for an exposure period of 42 days (6 weeks) since the test was based on NBR 13.583. Then, the discussion of the behaviour of the studied groups will be discussed individually for the extended time of exposure (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 [34], 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 SO_4^{2-} content in solution was kept constant at 6.76%, it was observed that only the FQ series exposed to sodium sulfate presented resistance (expansion equal to 0.02%), considering the limit of 0.03% at 42 days (6 weeks).

On the other hand, the expansion of mortars bars exposed to magnesium sulfate was more harmful 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. Also, for one mole of magnesium sulfate the available amount of SO_4^{2-} in solution also becomes higher due to the influence of the sulfate ion on the molar mass of the $MgSO_4$ molecule. Moreover, in $MgSO_4$ the brucite precipitation also acts a pH-buffer in the sulfate solution.

The comparative analysis between the averages results, Tukey's test, for 6 weeks of exposure, can be seen in Figure 5. Thus, it should be mentioned that the PC and LF groups exposed to sodium sulfate, as well as PC and QF for exposed to magnesium sulfate can be considered statistically equivalent. 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). However, in the PC x QF and LF x QF comparisons exposed to sodium sulfate presented significant differences in the results, the QF had 59% lower induced expansion than the other samples. The PC x LF and LF x QF samples exposed to magnesium sulfate also showed significant variations in the results. For magnesium sulfate, the QF samples presented statistical similarity to the control group and the samples containing LF showed worse results (66% greater than the control group).

As can be seen in Figure 4 the groups LF and QF, have mitigated the effect of sodium sulfate attack or at least have shown results similar to the control group at 140 days of exposure, as can be seen in Figure 6, which shows the comparative analysis of the averages, Tukey's Test. The impact of the fillers, at least for low replacement levels, such as 10%, was more significant for exposure to sodium sulfate solution so that the QF presented a good performance to induced expansion when compared with the control group (50% lower expansion values) and LF decreases the expansion to values close to 14%. On the other hand, for exposure to magnesium sulfate attack, all series can be considered as equivalents (Figure 6). However, such similarities are positive, since the replacement of the Portland cement did not cause losses in performance.
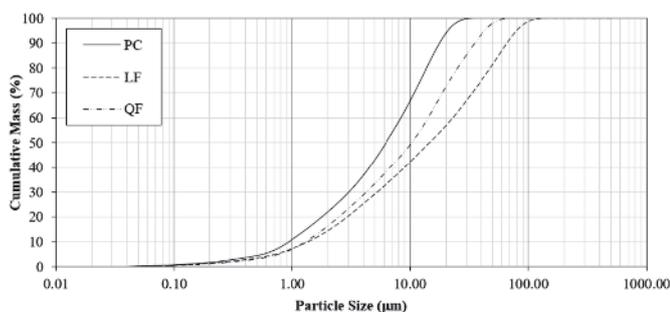
Figure 3
Particle size distribution of the cement, limestone filler and quartz filler
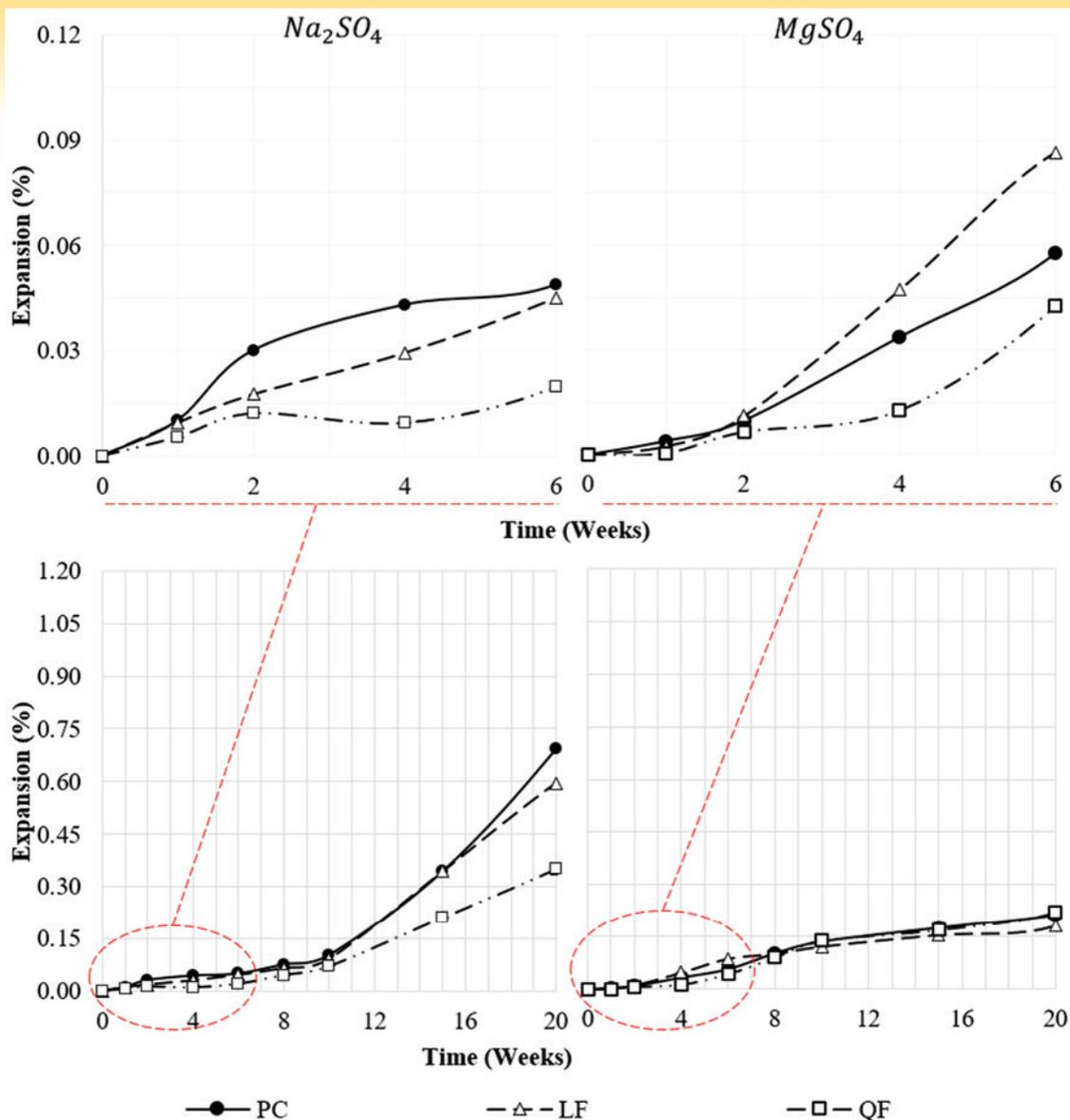
Figure 4
Expansion of the mortar bars ARI, LF and QF exposed to solutions of Na_2SO_4 and $MgSO_4$ (0.7 mol/L) for 42 and 140 days (6 and 20 weeks)
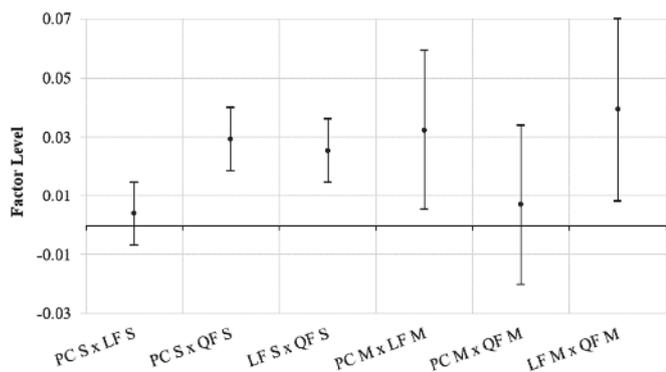
Figure 5
Comparative analysis of the averages, Tukey's test, for 6 weeks of exposure among the series studied, for a significance level of 5% (S-sodium sulfate and M-Magnesium sulfate)
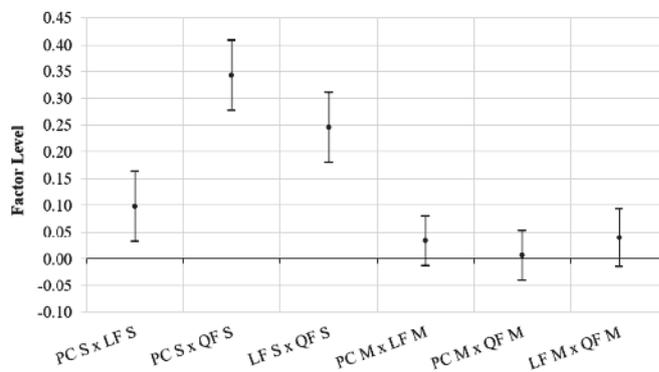
Figure 6
Comparative analysis of the averages, Tukey's test, for 20 weeks of exposure among the series studied, for a significance level of 5% (S-sodium sulfate and M-Magnesium sulfate)
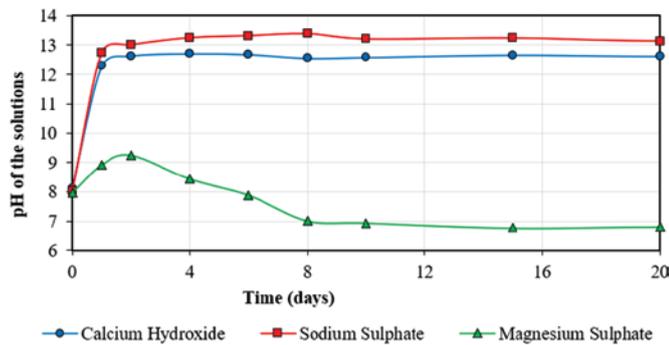
Figure 7
Comparative pH analysis of Ca(OH)$_2$, Na$_2$SO$_4$ and MgSO$_4$ solutions over 20 weeks (140 days)

The first product formed from the interaction between magnesium sulfate and Portland cement hydrated products is brucite (magnesium hydroxide), in which the electron affinity magnesium ion replaces the portlandite calcium ions. Such material is presented as a gel filling the voids of the mortars and can precipitate on the surface along with the gypsum and compositions of hydrated magnesium sulfate [2,3,8,11,17,35–37].

According to authors [3,8,37], after the mortar bars are immersed in the solution, it tends to have an increase in the pH of the solution (initially close to 7-8) for a range of 9 - 10 due to the interaction with the portlandite of the pores of the samples, and, parallel with this phenomenon, there is the formation of brucite, gypsum and ettringite on the surface of the mortar bars. With the excessive formation of brucite and gypsum, the pH of the pore solution begins to decrease, since such these materials have lower solubility than the portlandite. Therefore, releasing less OH⁻ to the solution. Then, at lower pH in mortar pores solution (around 7) there is the destabilization of the C-S-H, which begins to release calcium ions to increases the pH. However, this process, besides the decalcification of calcium silicate hydrate (CSH), allows the
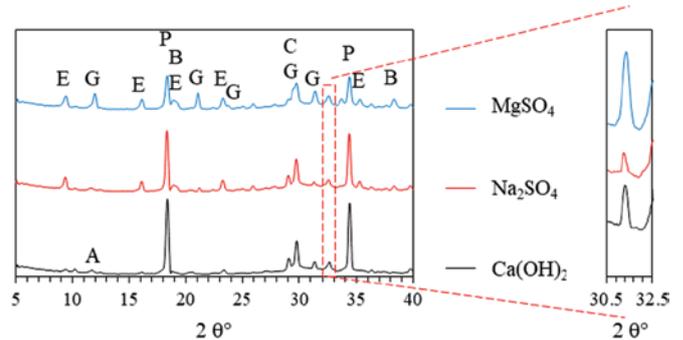
Figure 9
LF diffractograms after 20 weeks of exposure to Ca(OH)$_2$, Na$_2$SO$_4$ and MgSO$_4$.
Monocarboluminate (A), brucite (B), calcite (C), ettringite (E), gypsum (G) and portlandite (P)

formation of magnesium silicate hydrate (MSH) that does not have the cementitious capacity.

Nevertheless, the calcium ions cannot stimulate the increases in pH of the solution, because the Ca²⁺ ends up interacting with sulfate ions and precipitate due to the low solubility of the calcium sulfate. To analyze such statement, for the present study, pH measurements were carried out along the analyzed periods of exposure, and Figure 7 presents the comparative pH along the evaluation between three studied solutions (i.e. control, sodium sulfate and magnesium sulfate).

4.3 Mineralogical analysis

The obtained diffractograms for all series for each exposure conditions can be seen in Figure 8, Figure 9 and Figure 10. Compared to calcium hydroxide exposure solution, it can be observed that PC, LF, and QF presented a higher intensity the peaks related to ettringite crystals (E) for exposure in
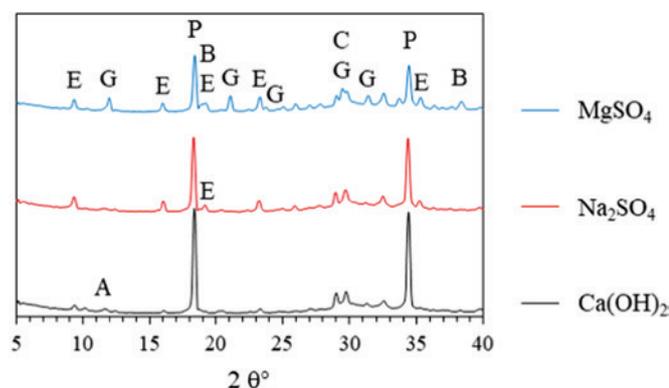
Figure 8
PC diffractograms after 20 weeks of exposure to Ca(OH)$_2$, Na$_2$SO$_4$ and MgSO$_4$.
Monocarboluminate (A), brucite (B), calcite (C), ettringite (E), gypsum (G) and portlandite (P)
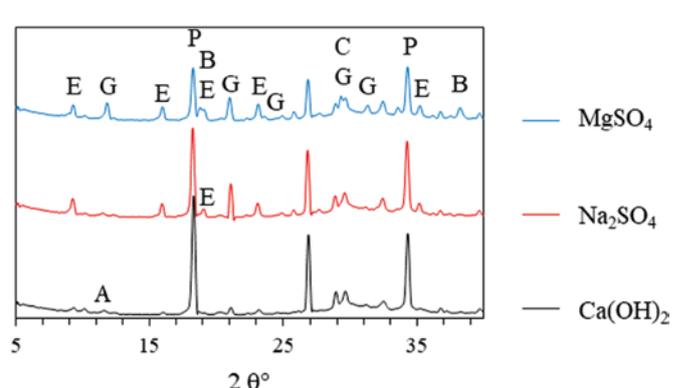
Figure 10
QF diffractograms after 20 weeks of exposure to Ca(OH)$_2$, Na$_2$SO$_4$ and MgSO$_4$.
Monocarboluminate (A), brucite (B), calcite (C), ettringite (E), gypsum (G) and portlandite (P)

both sulfate solutions, as well as consumption of the portlandite. In the position close to 12.00° 2θ related to gypsum (11.65° 2θ, card number 03-0044) and calcium monocarboaluminate hydrate (11.68° 2θ, card number 14-0083) formation, can be seen an increase for exposure of the sample in a magnesium sulfate solution. The formation of gypsum in this condition of exposure can be associated, among other factors, to the de-stabilization of the ettringite and C-S-H due to the lower pH in the pore solution of the samples and with the reaction between $MgSO_4$ and calcium hydroxide [17,36]. The later can be easily explained by the higher consumption of the portlandite (34.19° 2θ, card number 02-0968) due to the exposure to magnesium sulfate, leading to a higher gypsum formation, reduction of the pH, destabilization of CSH and ettringite (9.14° 2θ, card number 13-0350), suitable with data presented in the literature [3,10–12,36].

The groups containing fillers materials (LF and QF), in general, mitigated or, at least, kept similar the effects in the induced expansion of sodium sulfate attack when compared to PC. The fact that the composition LF presented greater degradation than QF due to Na_2SO_4, can be plausibly explained by the high pH of the sodium sulfate solution after reaction with mortar samples. After formation of gypsum and ettringite, Na_2SO_4 releases a large amount of Na+ in the pore solution of the mortar bars. As seen the LF group presented higher peak count at 31.33° 2θ (Figure 9) in comparison with PC and QF, this peak is be associated with the presence of two main minerals: gypsum and dolomite (i.e. from the mineralogical formation of the magnesian limestone filler used). Comparing the three diffractograms showed in Figure 9, the exposure to sodium sulfate presented a significant consumption of Dolomite (at 31.33 ° 2θ) when compared with the different exposure conditions, as well as there is an increase in the peak of calcite at 29.5° 2θ. One of the possible explanations for dolomite consumption can be the "dedolomitization" process caused by ion exchange between the Ca^{2+}, Mg^{2+} and CO_3^{2-} ions in the solid phase and alkali ions (i.e. Na+) in the pore solution, as the occurrence in alkali-carbonate reaction [38–43]. As already mentioned, the source of the limestone filler can be classified as magnesian limestone rock, and, based on CSA A23.2-26A, "Determination of Potential Alkali-Carbonate Reactivity of Quarried Carbonate Rocks by Chemical Composition", this rock (source of the limestone filler) can be classified as potential to the reactivity of alkali-carbonate reaction, as indicated in Figure 11, the red zone indicated is the potential reactivity zone of ACR occurrence, based on the chemical composition of the material. Then, the red dot indicated is related to the chemical combination of the magnesian limestone filler used (i.e. CaO content of 42.77%, MgO content of 8.25% and Al_2O_3 content of 0.95%, with CaO/MgO ratio equal to 5.18), placed in the red zone.

Also, carbonate molecules from the limestone filler can also be "consumed" to reacts with the ettringite particles (replacing the sulfate ions), or with unhydrated aluminate particles, to form of calcium monocarboaluminate hydrate [27,28]. In the comparison between the diffractograms, it is possible to see a slightly decreases on ettringite peaks, which may confirm the above statement.

4.4 Mechanical properties

The compressive strength is an essential parameter to be considered regarding the degree of sulfate attack [11,44], as well as the flexural strength which gives important data regarding the microcrack propagation within the cement paste [19,45]. According to Marciano [28] publication, tensile strength is not a good parameter for monitoring the degradation due to sulfate attack, either flexural strength or splitting tensile strength (Brazilian test), especially for short exposure time. However, Biczók [1] and Irassar [29] commented that the flexural strength test shows that the strength increases with exposure to sulfate attack up to a limit point, from which it starts to decrease. According to Irassar [29], it is possible to take from this parabolic behavior of the results the micro-cracking start time point of the samples. Which matches with the point at derivate is equal to zero. 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 12 and Figure 13).

Figure 12 and Figure 13 show an increase in early strength comparing both sulfate solutions with the control solution, attributable to pore filled by sulfate attack products, (i.e. gypsum, ettringite, brucite, etc.), once these "empty" void are now filled with "solid" material, they have their density increased and also there is more contact area to absorb the applied load. However, the formed sulfate attack products continue to gain volume so far, at the point that tensile strength is overcome and then there is the beginning of micro-cracks on cement paste [44]. So, at 6 weeks of exposure, the strength of the mortar bars, even for flexural tensile or compressive, is still increasing, which became difficult to compare the "damage" caused by the sulfate attack.

In general, it was observed during the 20 weeks of exposure to sodium and magnesium sulfate solutions that the individual
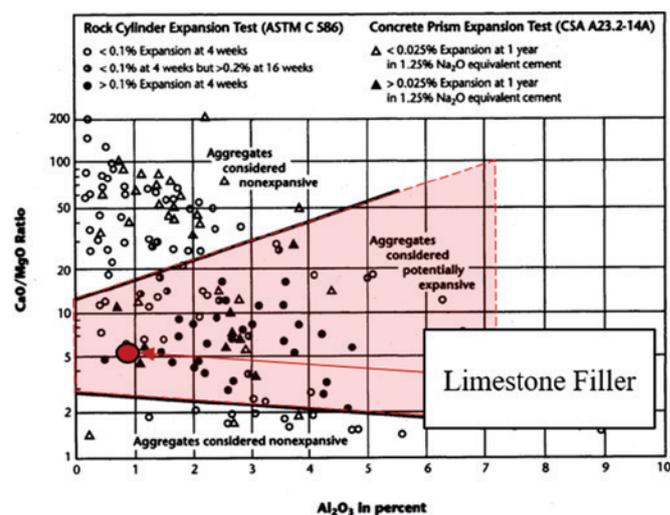
Figure 11

Illustration of the division between non-expansive and potentially expansive aggregates on basis of chemical composition. Source: CSA A23.2-26A
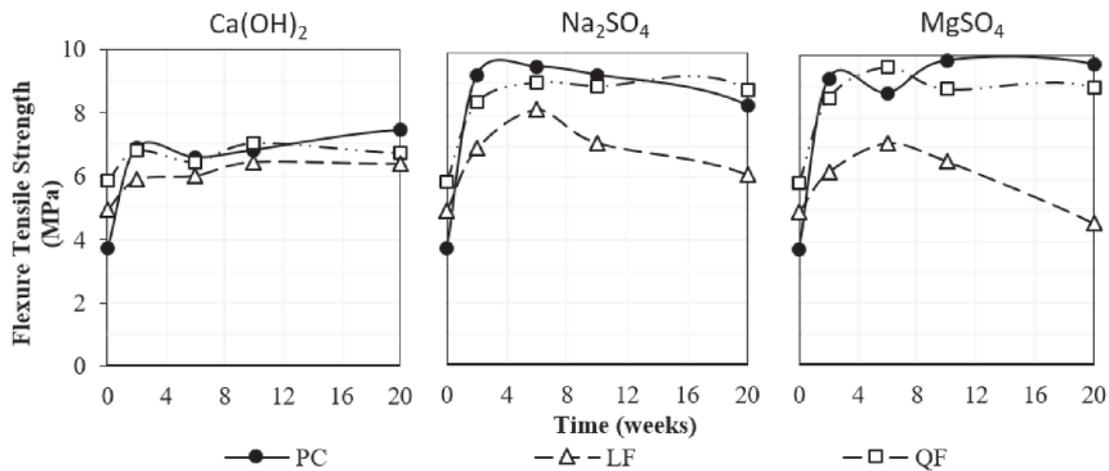
Figure 12
Flexural Tensile strength of the samples up to 20 weeks of exposure in the three different solutions [Ca(OH)$_2$, Na$_2$SO$_4$ and MgSO$_4$]

behaviour of each filler group distinguishes between them, even considering that both materials are inert fillers with close physical properties. When exposed to Na$_2$SO$_4$, QF showed results statistically similar to the control group PC (Figure 14 and Figure 15), as well as the same behaviour in flexural tensile strength can be seen for QF when exposed to magnesium sulfate attack; however, for compressive strength, QF and PC are not statistically similar, indicating that the behaviour of QF was slightly better than PC.

On the other hand, LF has not shown any similarities with QF and PC (Figure 14 and Figure 15) and based on the flexural and compressive strength data presented in Figure 12 and Figure 13, the use of the magnesian limestone filler was worse in terms of mechanical losses. In one hand, replacing the Portland cement by LF decreases the total amount of aluminates, as result, decreases the potentiality of ettringite formation, which can explain

the similarities in the induced expansion results. Though, considering that the water-to-cement ration changed, (from 0.60 to 0.66) since it was kept the water-to-"binder" ratio constant (as 0.60), there are changes in the microstructure of the mortar bars; however, the same behaviour should be addressed to QF as well, but both fillers behave differently. Therefore, a plausible explanation for the obtained results for LF can be its physical and chemical properties. Physically, as presented in Figure 3, the limestone filler has a larger average for particle size distribution, which increases, even more, the porosity and replacing the finer Portland cement particles, decreasing the quality of the microstructure of the mortar bars. Chemically, as already discussed, the significant amount of magnesium in the limestone filler may contribute to a process of dedolomitization of the LF in the mortar bars, especially when exposed to Na$_2$SO$_4$.
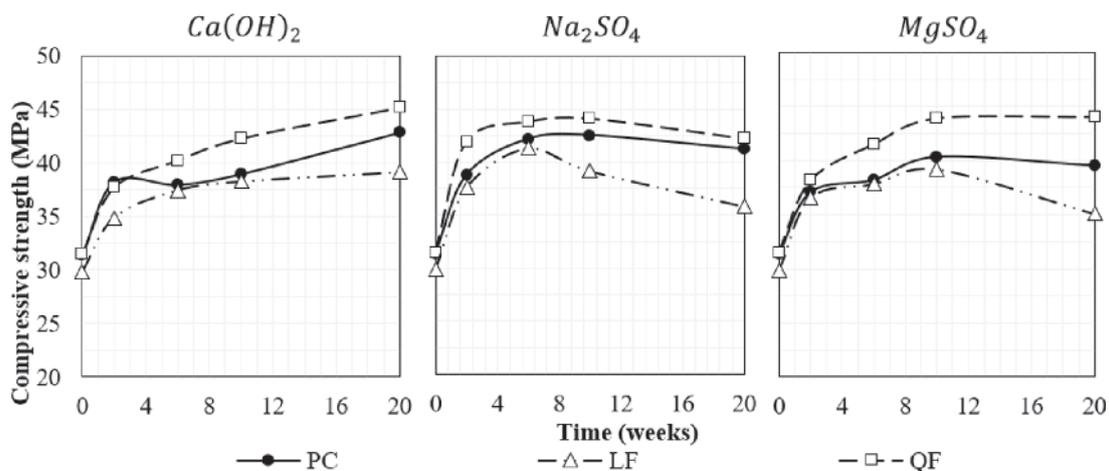
Figure 13
Compressive strength of the samples up to 20 weeks of exposure in the three different solutions [Ca(OH)$_2$, Na$_2$SO$_4$ and MgSO$_4$]
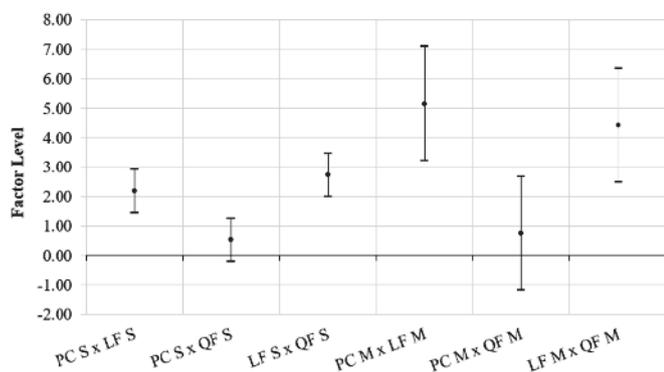
Figure 14
Comparison between averages of flexural tensile strength losses (tukey test for a significance level of 5%) of the same series for different aggressive solutions (S - sodium sulfate and M - magnesium sulfate) for 20 weeks of exposure

Figure 15
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

The loss in strength for exposure to magnesium sulfate attack (comparatively higher than sodium sulfate attack for PC and LF) is associated with the decalcification of CSH, and, consequently, formation of MSH particles, which have little or no binding characteristics [3,10,11,17,36]. Thus, these results are consistent with the theory and experiments analyzed in the literature. The losses in strength are much more significant than the actual linear induced expansion of samples exposed to magnesium sulfate attack. Therefore, the evaluation only of length variation can lead to erroneous conclusions that, since magnesium sulfate attack does not generate great expansions values in concrete, mortars or cement pastes, when compared in the same exposure period for the solution of Na_2SO_4. However, such results show a contrary reality, leading to the analysis of the sulfate attack may be insufficient when evaluated only by linear dimensional variation.

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 filler particles in the mortars mitigated the induced expansion due to sodium sulfate attack, on higher values for quartz and smaller for limestone fillers. The exposure to magnesium sulfate solution did not show the same behaviour, the replacement of the cement by fillers did not mitigate the expansion, but at least QF and LF 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, which decreases the flexural tensile and compressive strength of the samples due to instability and decalcification of the CSH, plus the damage caused by gypsum and ettringite formation;
- Sodium sulfate solution affected differently the induced ex-

pansion and strength loss of Quartz Filler and the Limestone Filler groups. The fine particles of LF show more instability due to the presence of Na^{2+} ions (for Na_2SO_4 exposure) and the XRD analysis showed that the peak of dolomite decreased and there was also increase in the peak of calcite (LF released Mg into the solution) due to sodium sulfate attack;
- Comparing the expansion caused by Na_2SO_4 with $MgSO_4$, for the shorter exposure time (6 weeks as NBR 13,583 recommendations) the different mixes presented higher induced expansion values for the latest. On the other hand, with long-term exposure conditions (i.e. 20 weeks) this behaviour has changed, so that exposure to Na_2SO_4 causes higher values of induced expansion.
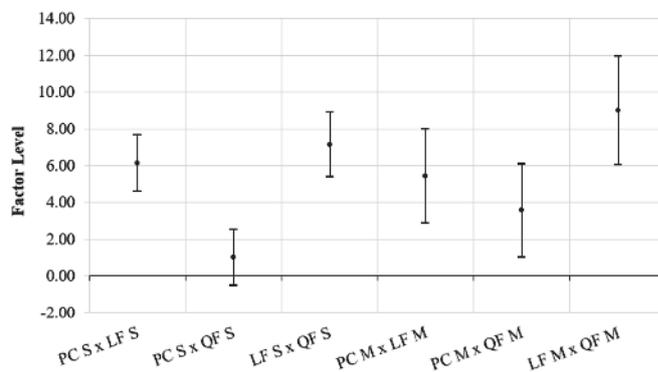
Sulfate attack tests with long exposure period, such as 20 weeks or more, are important to better understand and characterize degradation processes of Portland cement composites due to different types of sulfate (sodium sulfate attack, magnesium sulfate attack, etc.).

6. Acknowledgment

7. References

[1]   N.M. Al-Akhras, Durability of metakaolin concrete to sulfate attack, Cem. Concr. Res. 36 (2006) 1727– 1734. doi:10.1016/j.cemconres.2006.03.026.

[2]   P.K. Mehta, P.J.M. Monteiro, Concrete: Microstructure, Properties, and Materials, 3rd Edition, 2013. doi:10.1036/0071462899.

[3]   M. Santhanam, M.D. Cohen, J. Olek, Mechanism of sulfate attack: A fresh look - Part 2. Proposed mechanisms, Cem. Concr. Res. 33 (2003) 341–346. doi:10.1016/S0008-8846(02)00958-4.

[4]   A. Neville, The confused world of sulfate attack on concrete, Cem. Concr. Res. (2004). doi:10.1016/j.cemconres.2004.04.004.

[5]   P.J.M. Monteiro, K.E. Kurtis, Time to failure for concrete exposed to severe sulfate attack, Cem. Concr. Res. (2003). doi:10.1016/S0008-8846(02)01097-9.

[6]   W. Müllauer, R.E. Beddoe, D. Heinz, Sulfate attack expansion mechanisms, Cem. Concr. Res. 52 (2013) 208–215. doi:10.1016/j.cemconres.2013.07.005.

[7]   M. Santhanam, M.D. Cohen, J. Olek, Sulfate attack research - Whither now?, Cem. Concr. Res. 31 (2001) 845–851. doi:10.1016/S0008-8846(01)00510-5.

[8]   M. Santhanam, M.D. Cohen, J. Olek, Mechanism of sulfate attack: A fresh look Part 1: Summary of experimental results, Cem. Concr. Res. 32 (2002) 915–921.

[9]   B. Chatveera, P. Lertwattanaruk, Evaluation of sulfate resistance of cement mortars containing black rice husk ash, J. Environ. Manage. 60 (2009) 435–1441. doi:10.1016/j.jenvman.2008.09.001.

[10]   K. Behfarnia, O. Farshadfar, The effects of pozzolanic binders and polypropylene fibers on durability of SCC to magnesium sulfate attack, Constr. Build. Mater. 38 (2013) 64–71. doi:10.1016/j.conbuildmat.2012.08.035.

[11]   A.M. Diab, A.E.M. Awad, H.E. Elyamany, A.E.M. Abd El-moaty, Guidelines in compressive strength assessment of concrete modified with silica fume due to magnesium sulfate attack, Constr. Build. Mater. 36 (2012) 311–318. doi:10.1016/j.conbuildmat.2012.04.075.

[12]   N. Saca, M. Georgescu, Behavior of ternary blended cements containing limestone filler and fly ash in magnesium sulfate solution at low temperature, Constr. Build. Mater. 71 (2014) 246–253. doi:10.1016/j.conbuildmat.2014.08.037.

[13]   J. Hoppe Filho, D.J. De Souza, M.H.F. Medeiros, E. Pereira, K.F. Portella, Concrete attack by sodium sulfate: mineral additions as a mitigation tool, Cerâmica. 61 (2015) 168–177. doi:10.1590/0366-69132015613581905.

[14]   D.J. Souza, L.Y. Yamashita, F. Dranka, M.H.F. Medeiros, R.A. Medeiros-Junior, Repair Mortars Incorporating Multi-walled Carbon Nanotubes: Shrinkage and Sodium Sulfate Attack, J. Mater. Civ. Eng. 29 (2017) 1–12. doi:10.1061/(ASCE)MT.1943-5533.0002105.

[15]   M.D. Cohen, A. Bentur, Durability of Portland Cement-Silica Fume Pastes in Magnesium Sulfate and Sodium Sulfate Solutions, ACI Mater. J. 85 (1988) 148–157.

[16]   P. Lawrence, M. Cyr, E. Ringot, Mineral admixtures in mortars, Cem. Concr. Res. 33 (2003) 1939 – 1947. doi:10.1016/S0008-8846(03)00183-2.

[17]   S.T. Lee, R.D. Hooton, H.S. Jung, D.H. Park, C.S. Choi, Effect of limestone filler on the deterioration of mortars and pastes exposed to sulfate solutions at ambient temperature, Cem. Concr. Res. (2008). doi:10.1016/j.cemconres.2007.08.003.

[18]   B. Lothenbach, K. Scrivener, R.D. Hooton, Supplementary cementitious materials, Cem. Concr. Res. 41 (2011) 1244–1256. doi:10.1016/j.cemconres.2010.12.001.

[19]   E.F. Irassar, M. González, V. Rahhal, Sulphate resistance of type V cements with limestone filler and natural pozzolana, Cem. Concr. Compos. 22 (2000) 361–368. doi:10.1016/S0958-9465(00)00019-6.

[20]   E.F. Irassar, Sulfate attack on cementitious materials containing limestone filler - A review, Cem. Concr. Res. (2009). doi:10.1016/j.cemconres.2008.11.007.

[21]   N. Mavropoulou, N. Katsiotis, J. Giannakopoulos, K. Koutsodontis, D. Papageorgiou, E. Chaniotakis, M. Katsioti, P.E. Tsakiridis, Durability evaluation of cement exposed to combined action of chloride and sulphate ions at elevated temperature: The role of limestone filler, Constr. Build. Mater. 124 (2016) 558–565. doi:10.1016/j.conbuildmat.2016.07.134.

[22]   J. Sun, Z. Chen, Influences of limestone powder on the resistance of concretes to the chloride ion penetration and sulfate attack, Powder Technol. 338 (2018) 725–733. doi:10.1016/j.powtec.2018.07.041.

[23]   F. Abubaker, C. Lynsdale, J. Cripps, Investigation of concrete-clay interaction with regards to the thaumasite form of sulfate attack, Constr. Build. Mater. 67 (2014) 88–94. doi:10.1016/j.conbuildmat.2013.10.033.

[24]   A. Skaropoulou, K. Sotiriadis, G. Kakali, S. Tsivilis, Use of mineral admixtures to improve the resistance of limestone cement concrete against thaumasite form of sulfate attack, Cem. Concr. Compos. 37 (2013) 267–275. doi:10.1016/j.cemconcomp.2013.01.007.

[25]   A. Skaropoulou, S. Tsivilis, G. Kakali, J.H. Sharp, R.N. Swamy, Long term behavior of Portland limestone cement mortars exposed to magnesium sulfate attack, Cem. Concr. Compos. 31 (2009) 628–636. doi:10.1016/j.cemconcomp.2009.06.003.

[26]   K. Tosun-Felekoğlu, The effect of C 3A content on sulfate durability of Portland limestone cement mortars, Constr. Build. Mater. 36 (2012) 437–447. doi:10.1016/j.conbuildmat.2012.04.091.

[27]   T. Matschei, B. Lothenbach, F.P. Glasser, The role of calcium carbonate in cement hydration, Cem. Concr. Res. 37 (2007) 551–558. doi:10.1016/j.cemconres.2006.10.013.

[28]   G. Kakali, S. Tsivilis, E. Aggeli, M. Bati, Hydration products of C 3 A, C 3 S and Portland cement in the presence of CaCO 3, Cem. Concr. Res. 30 (2000) 1073–1077. doi:10.1016/S0008-8846(00)00292-1.

[29]   D.J. De Souza, M.H.F. Medeiros, J. Hoppe Filho, Evaluation of the SR Portland cement against sodium and magnesium sulfate attack: a physical and comparative analysis of mortars, Rev. IBRACON Estruturas e Mater. 11 (2018) 1053–1075. doi:10.1590/s1983-41952018000500009.

[30]   M.H.F. de Medeiros, D.J. Souza, J.H. Filho, C.S. Adorno, V.A. Quarcioni, E. Pereira, Red-clay waste and limestone filler added in Portland cement composite: effects on sulfate attack and alkali-silica reaction, Rev. Mater. 21 (2016) 282–300. doi:10.1590/S1517-707620160002.0028.

[31]   J.L. Wilson, Limestone and dolomite reservoirs, 1st Edi-tio, U.S. Dept. of the Interior, Bureau of Mines, 1980.

[32]   M. Cyr, P. Lawrence, E. Ringot, Efficiency of mineral ad-mixtures in mortars: Quantification of the physical and chemical effects of fine admixtures in relation with com-pressive strength, Cem. Concr. Res. 36 (2006) 264–277. doi:10.1016/j.cemconres.2005.07.001.

[33]   M. Cyr, P. Lawrence, E. Ringot, Mineral admixtures in mortars: Quantification of the physical effects of inert materials on short-term hydration, Cem. Concr. Res. 35 (2005) 719–730. doi:10.1016/j.cemconres.2004.05.030.

[34]   Z.A. Marciano, Desenvolvimento de um método acelerado para avaliação da resistência de argamassas de cimento Portland expostas à solução de sulfato de sódio., 1993.

[35]   D. Bonen, M.D. Cohen, Magnesium sulfate attack on portland cement paste-I. Microstructural analysis, Cem. Concr. Res. 22 (1992) 169–180. doi:10.1016/0008-8846(92)90147-N.

[36]   S.T. Lee, H.Y. Moon, R.N. Swamy, Sulfate attack and role of silica fume in resisting strength loss, Cem. Con-cr. Compos. 27 (2005) 65–76. doi:10.1016/j.cemcon-comp.2003.11.003.

[37]   Z. Makhloufi, S. Aggoun, B. Benabed, E.H. Kadri, M. Be-derina, Effect of magnesium sulfate on the durability of limestone mortars based on quaternary blended cements, Cem. Concr. Compos. 65 (2016) 186–199. doi:10.1016/j.cemconcomp.2015.10.020.

[38]   S.W. Forster, G.S. Barger, R.L. Boone, M.S. Hammer, J.F. Lamond, D.S. Lane, R.E. Miller, S.E. Parker, A. Pergalsky, J.S. Pierce, M.Q. Robert, J.W. Schmitt, D.C. Stark, R.E. Tobin, Report on Alkali-Aggregate Reactivity Reported by ACI Committee 221, (1998).

[39]   P. Štukovnik, M. Marinšek, B. Mirtič, V. Bokan Bosiljkov, In-fluence of alkali carbonate reaction on compressive strength of mortars with air lime binder, Constr. Build. Mater. 75 (2015) 247–254. doi:10.1016/j.conbuildmat.2014.11.024.

[40]   T. Prinčič, P. Štukovnik, S. Pejovnik, G. De Schutter, V. Bokan Bosiljkov, Observations on dedolomitization of carbonate concrete aggregates, implications for ACR and expansion, Cem. Concr. Res. 54 (2013) 151–160. doi:10.1016/j.cemconres.2013.09.005.

[41]   M. Beyene, A. Snyder, R.J. Lee, M. Blaszkiewicz, Alkali Silica Reaction (ASR) as a root cause of distress in a concrete made from Alkali Carbonate Reaction (ACR) potentially susceptible aggregates, Cem. Concr. Res. 51 (2013) 85–95. doi:10.1016/j.cemconres.2013.04.014.

[42]   A.M. López-Buendía, V. Climent, P. Verdú, Lithological influence of aggregate in the alkali-carbonate reaction, Cem. Concr. Res. 36 (2006) 1490–1500. doi:10.1016/j.cemconres.2006.05.032.

[43]   B. Fournier, M.-A. Bérubé, Alkali-aggregate reaction in concrete: a review of basic concepts and engineer-ing implications, Can. J. Civ. Eng. 27 (2000) 167–191. doi:10.1139/cjce-27-2-167.

[44]   W. Ouyang, J. Chen, M. Jiang, Evolution of surface hard-ness of concrete under sulfate attack, Constr. Build. Ma-ter. (2014). doi:10.1016/j.conbuildmat.2013.11.107.

[45]   E.F. Irassar, Prediction and Relation With Flex-ural Strength, 20 (1990) 209–218. doi:10.1197/j.aem.2005.06.022.