RISK ASSESSMENT OF A POTENTIAL EXTERNAL AND INTERNAL SULFATE ATTACK IN POZZOLANIC CEMENTITIOUS MATRICES

AVALIAÇÃO DO POTENCIAL DE OCORRÊNCIA DO ATAQUE POR SULFATOS EXTERNO E INTERNO EM MATRIZES CIMENTÍCIAS POZOLÂNICAS

EVALUACIÓN DE RIESGO DE UN POTENCIAL ATAQUE POR SULFATOS EXTERNO E INTERNO EN MATRICES CEMENTICIAS PUZOLÁNICAS

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ABSTRACT
This work evaluated the behavior of cementitious composites against internal and external attack by sulfates (ISA and ESA, respectively) over time, as well as the mitigating potential of Brazilian cements considered pozzolanic. Three pozzolanic cements called sulfate resistant according to Brazilian standards were evaluated, coming from three regions of Brazil, in addition to a reference cement, with high initial resistance. Based on evaluations by Brazilian (ABNT) and American (ASTM) standardization, it was found that the use of pozzolanic additions to cement brings mainly mechanical and durability improvements in relation to external sulfate attack, however, depending on the standardization adopted, it is not possible to say whether it contributed to the mitigation of this attack. In relation to ISA assessments, no cement proved to be effective. Therefore, among the four cements tested, considering the criteria adopted in the study, no cement could be considered to mitigate expansions caused by both sulfate attacks, external - (ESA) and internal - (ISA).

KEYWORDS
Internal sulfate attack (ISA). External attack by sulfates (ESA). Dellayed ettringite formation (DEF). Pozzolanic cement.

RESUMO
Este trabalho avaliou o comportamento de compósitos cimentícios frente ao ataque interno e externo por sulfatos (ISA e ESA, respectivamente) ao longo do tempo, bem como o potencial mitigador de cimentos brasileiros considerados pozolânicos. Foram avaliados três cimentos pozolânicos denominados resistentes aos sulfatos de acordo com a normalização brasileira, oriundos de três regiões do Brasil, além de um cimento de referência, de alta resistência inicial. A partir de avaliações pela normalização brasileira (ABNT) e americana (ASTM), verificou-se que o emprego de adições pozolânicas ao cimento traz melhorias principalmente mecânicas e de durabilidade em relação ao ataque externo de sulfatos, porém dependendo da normalização adotada, não é possível dizer se colaborou com a mitigação desse ataque. Em relação às avaliações de ISA nenhum cimento mostrou-se efetivo. Sendo assim, entre os quatro cimentos testados, considerando os critérios adotados no estudo, nenhum cimento pôde ser considerado mitigador das expansões causadas por ambos os ataques por sulfatos, externo - (ESA) e interno - (ISA).

PALAVRAS-CHAVE

Ataque interno por sulfatos (ISA). Ataque externo por sulfatos (ESA). Formação de etringita tardia (DEF). Cimento Pozolânico.

RESUMEN

Este estudio evaluó el comportamiento de compuestos cementicios frente al ataque por sulfatos, tanto interno (ISA) como externo (ESA), a lo largo del tiempo, así como el potencial mitigador de cementos brasileños con características puzolánicas. Se analizaron tres cementos puzolánicos, clasificados como resistentes a los sulfatos según la normativa brasileña, procedentes de tres regiones de Brasil, además de un cemento de referencia de alta resistencia inicial. A partir de evaluaciones basadas en las normativas brasileña (ABNT) y estadounidense (ASTM), se verificó que la incorporación de adiciones puzolánicas en el cemento mejora principalmente las propiedades mecánicas y la durabilidad frente al ataque externo por sulfatos. No obstante, según la normativa adoptada, no se pudo determinar con certeza si estas adiciones contribuyen a mitigar dicho ataque. En cuanto a las evaluaciones del ISA, ningún cemento demostró ser efectivo. Por lo tanto, considerando los criterios de este estudio, ninguno de los cuatro cementos analizados pudo ser clasificado como mitigador de las expansiones provocadas por el ataque de sulfatos, ya sea externo (ESA) o interno (ISA).

PALABRAS CLAVE

Ataque interno por sulfatos (ISA), ataque externo por sulfatos (ESA), formação de etringita tardia (DEF), cimento pozolânico.

1. INTRODUCTION

With the aim of increasing durability and improving construction material procurement, there has been a growing concern with pathological manifestations in concrete structures both in Brazil and worldwide, as is the case with expansive reactions, particularly those involving sulfate ions.

When compared with other chemical reactions, those involving sulfates are the most harmful to concrete, because they bring about the formation of expansive products, which in turn leads to matrix tensioning and concrete cracking (NEVILLE, 2015). Sulfates are commonly found in environments where concrete structures are exposed, such as contaminated soils, infiltration water, industrial settings, and sanitation-related construction works. This type of chemical degradation is referred to as an external sulfate attack (ESA) and this type of chemical attack is known as an external sulfate attack (ESA) (TAYLOR; FAMY; SCRIVENER, 2001; SCHIAVINI, 2018).

The deterioration of concrete caused by chemical reactions between cement and sulfate ions from external sources depends on the concentration of these ions and the composition of the cement paste. This attack often manifests cracking and expansion, which increase permeability and allow aggressive water penetration, ultimately accelerating the degradation process (MEHTA and MONTEIRO, 2014).

In addition to sulfates from the external environment, concrete is also subject to internal sulfate attacks (ISA), which lead to the formation of delayed ettringite, or DEF (Delayed Ettringite Formation). The formation of secondary or late ettringite is a complex process which is characterized by the non-formation or thermal decomposition of primary ettringite, and reprecipitation of its crystals in already hardened cementitious matrices. That phenomenon occurs over time, and generates expansions, when the recrystallization of the ettringite (BRYANT, 2011; THIEBAUT *et al.*, 2018). An internal attack can occur when the source is not in the environment but originates from either i) aggregates contaminated with gypsum and/or sulfides, ii) the cement itself, or iii) the thermal decomposition of the primary ettringite. The latter is related to DEF and is linked to concrete that has been subjected to high curing temperatures, usually above 60°C (HASPARYK; KUPERMAN, 2019; PORTTELLA *et al.*, 2021; HASPARYK *et al.*, 2022).The chemical reaction involving internal sulfates has the potential to cause high expansions, premature degradation of concrete and damage to all its properties, directly impacting the durability and longevity of structures (MARTIN *et al.*, 2012; KCHAKECH *et al.*, 2016; HASPARYK, KUPERMAN, 2019).

With regard to preventive measures for ESA, the NBR 16697:2018 standard recommends that sulfate-resistant Portland cements should be used, which are cements that contain 15% to 50% of pozzolanic material in their composition. Since they contain pozzolans in their composition, RS cements provide stability when combined with reactive aggregates (which cause the alkali-silica reaction – RAS). Moreover, in acid attack environments - essentially those involving an "external" sulfate attack. Those materials can also reduce heat of hydration, which makes them suitable for mass placement of concrete at elevated temperatures.

The first recorded occurrence of DEF was in 1987 in Finland, in pre-cast concrete that had been subjected to inadequate heat treatment and exposed to humidity. Following this initial record, other countries around the world also reported the phenomenon in different types of precast elements (LCPC, 2009). In addition to prefabricated components, DEF was also documented as prematurely damaging several bridges in Great Britain, with reports of damage occurring 8 to 20 years after construction. In France, the first cases attributed to DEF were reported in the 1990s in structures aged 5 to 10 years (GODART, 2017).

In addition to those already mentioned, several structures made with cementitious materials have deteriorated due to sulfate attack, as documented. In Switzerland, Romer *et al.* (2003) report damage to tunnel structures in contact with groundwater containing sulfates. In the United Kingdom, Crammond (2002) cites sulfate wear in a variety of constructions, ranging from residential foundations and road bridges to tunnel linings and port staircases. In Germany, Bellmann *et al.* (2012) discuss 20 different cases, including the foundations and structural walls of bridges, tunnel linings, water channels, water reservoirs, mining wastewater processing basins, and sewage manholes.

ISA/DEF is a pathological manifestation that originates from the characteristics of the Portland cement. Mineral admixtures, when incorporated into cement in its grinding process, lead to an improvement in the properties and durability of the composites. Some laboratory studies in Brazil have already examined the advantages of pozzolanic Portland cement (CP IV), - when compared with high early strength Portland cement (CP V-ARI) - for mitigating the problem of DEF (SCHOVANZ,

2019; BRONHOLO, 2020; LANGOSKI, 2021; MELO, 2021 HASPARYK *et al.*, 2022). However, although there was an improvement in the behavior of concrete and reduction of its expansion, a complete mitigation of DEF was not achieved in the more advanced ages.

Another factor that affects the occurrence of DEF is the rise in temperature in the first hours of cement hydration and an increase in the C_3A content (ODLER, 2007; BRYANT, 2011). In light of this, many authors have stated that the use of pozzolans can reduce the heat of hydration (MEHTA; MONTEIRO, 2014; AMINE *et al.*, 2017; NGUYEN *et al.*, 2019).

So far, there have been no preventive standardization procedures with regard to DEF just as there are no efficient corrective measures after it has first emerged, which means that it is is essential either to prevent or control the factors that cause it (SCHOVANZ, 2019; ZHANG et al, 2021; MELO, 2021; HASPARYK *et al.*, 2022). The only established means of ensuring the avoidance of DEF, is to control the high internal temperatures, resulting from hydration heat of cement in concrete structures (HASPAYK, KUPERMAN, 2019, HASPARYK *et al.*, 2022; HASPARYK *et al.*, 2023)).

It should be borne in mind that some studies have demonstrated the long-term inefficiency of fly ash as a means of mitigating DEF (SCHOVANZ *et al.*, 2021; LANGOSKI, 2021; MELO, 2021; MELO *et al.*, 2023; HASPARYK *et al.*, 2023) for temperatures above 60-85 ºC.

This research aims to correlate the behavior of sulfate-resistant cements produced with pozzolanic materials, including fly ash from various sources, with the occurrence of delayed ettringite formation (DEF) and their ability to mitigate both external and internal sulfate attacks.

2. MATERIALS AND METHODS

For the purposes of this study, a specific mixture was prepared with a ratio of 1:2.75 (cement: sand), based on ASTM C-012 (2019), which adopts a water-cement ratio (w/c) of 0.485.

For the evaluation of ISA, cylindrical specimens of (5 x 10) cm were cast for the mechanical tests, following the recommendations of NBR 7215 (ABNT, 2019) which were subjected to thermal curing throughout the period, and prismatic test specimens, measuring (2.5 x 2.5 x 28.5) cm for estimating expansions, in accordance with NBR 13583 (ABNT, 2014), which were also subjected to thermal curing. The ESA evaluation considered prismatic specimens of (2.5 x 2.5 x 28.5) cm to measure expansions in accordance with procedures by NBR 13583 (ABNT, 2014) and ASTM C-1012: 2019). During the research, two types of curing methods were devised, which can be classified as: "thermal cure" and "cure under sodium sulfate solution". These healing combinations can be seen in Table 1.

Type of Attack	Cement	Curing	Specimens
ISA-DEF	(3) CP IV32 - RS (1) CP V-ARI	Thermal curing	Cylindrical & Prismatic
ESA 1	(3) CP IV32 - RS (1) CP V-ARI	Sodium sulfate solution NBR 13583 (2014)	Prismatic
ESA 2	(3) CP IV32 - RS (1) CP V-ARI	Solution of Sodium sulfate ASM C-1012 (2019)	Cubic & Prismatic

Table 1: Conditions of testing
ISA: Internal sulfate attack; **ESA 1 and 2:** External sulfate attacks.

2.1 Materials

The experimental investigations included the following materials: **Binders:** 3 cements, called CP IV-32 RS, sulfate-resistant pozzolanic cements, with several mineral admixtures, but without fly ash. These can be described as follows: a) those with calcined clay (PC-PCC), b) those with acid slag (PC-AS) and, finally, c) cement with incorporation of volcanic material (PC-VO) and 1 cement, called CP IV-ARI reference cement called (PC). **Fine aggregate:** from granitic rock, (Pedreira Anhanguera, Goiânia - GO), innocuous with regard to the alkali-silica reaction - RAS (in order to avoid the occurrence of a couple attack - DEF and RAS, and then only isolate DEF). The aggregate used for the production of mortars has a maximum size of 4.8 mm and a fineness modulus of 2.42. **Potable water:** from the water supply network of the town of Passo Fundo/RS.

With regard to the chemical properties of the studied cements, the loss on ignition was above the standard limit for the PC-AS cement content, which was 6.63 and the norm has a limit of < 6.5, but the other characteristics were within the limits. Regarding the physical properties, all the cements met the standard requirements.

Identifica-tion	Cement	Heat of hydration	
		41 h	72 h
PC	CP V-ARI	297.90	306.70
PC-PCC	CP IV-32-RS	163.10	166.66
PC-AS	CP IV-32-RS	156.60	174.60
PC-VO	CP IV-32-RS	173.20	200.50

Table 2: Heat of hydration of cements.

Table 3 shows the results of the pozzolanic activity of each cement. However, when measured at the age of 8 days, as recommended by the standard NBR 5753 (ABNT, 2016), two cements, (PC-AS and PC-VO), did not show pozzolanicity, and had to be measured at a later age, which suggests a slower pozzolanicity. It is significant that the PC cement is a CP V-ARI cement with no admixture, and thus, considered to be a non-pozzolanic material.

Cement type	Cement type	PA 8 days	PA 15 days
PC	CP V-ARI	NP	NP
PC-PCC	CP IV-32-RS	P	P
PC-AS	CP IV-32-RS	NP	P
PC-VO	CP IV-32-RS	NP	P

Table 3: Pozzolanic activity (PA) at 8 and 15 days.

2.2 Methods

2.2.1. Induction of the ESA

External attacks were assessed in two ways, one following the Brazilian standard requirements (ABNT (Brazilian National Standards) NBR 13583:2014) and the other, in accordance with the American international organization - ASTM (American Standard for Testing and Materials) C-1012:2019.

The main differences between the standards discussed in this study are the trace elements, solution concentration, test temperature, and total analysis time. NBR 13583 (ABNT, 2014 provides faster results on the behavior of cementitious materials in a laboratory environment, with a shorter exposure time to sodium sulfates (42 days). In contrast, ASTM C-1012:2019 tests simulate natural exposure conditions more accurately, with an extended exposure period of 365 days.

The 3 stages of curing in which the mortar bars were subjected to the procedure described in NBR 13583 (ABNT, 2014), are as follows: **1) Initial wet curing:** While still in the molds, the test specimens were taken to the moist chamber for 48 h. After this period, the specimens were demoulded. **2) Intermediate Curing:** The specimens were immersed in water saturated with lime for 12 days at a temperature of (23 ± 2) °C. **3) Final curing:** The specimens were placed in a container containing a sodium sulfate solution (Na_2SO_4), with a concentration of 10%, in accordance with the specifications from NBR 13583 (ABNT, 2014), under a constant temperature of (40 ± 2) °C throughout the test period.

Curing was also conducted by following the procedure described in ASTM C-1012, which comprised 3 stages: **1) Initial wet curing:** The specimens were immersed in water at (35 ± 3) °C for 24 h. After this period, they were demolded, and stage 2 began. **2) Intermediate Curing:** The specimens were immersed in water saturated with lime, until it reached a compressive strength of 20 MPa at a temperature of (23 ± 2) °C. **3) Final curing:** The specimens were placed in a container containing a sodium sulfate solution (Na_2SO_4), with a concentration of 5%, which was prepared in accordance with the ASTM C-1012 specifications, under (23 ± 2) °C during the entire period.

The specimens were submerged in a Na_2SO_4 solution and the dimensional variation was monitored for 180 days, by ASTM C-1012, and for 42 days, by NBR 13583, the latter estimate being extended to the age of 98 days since no stabilization had occurred. The external attack was assessed in two ways – one in compliance with the Brazilian standards (ABNT NBR 13583:2014) and the other in accordance with the American standard (ASTM C-1012:2019).

2.2.2. Induction of the ISA (DEF)

When assessing the internal attack by sulfates, the thermal cycle adopted for thermal curing of the test specimens, called the Brazilian method (HASPARYK *et al.*, 2020; 2022), was employed to induce the occurrence of DEF in the laboratory. This procedure was developed based on a number of works in the literature: (FU, 1997; KCHAKECH *et al.*, 2016; GODART, 2017; MARTIN *et al.*, 2017; RASHIDI *et al.*, 2017; ZHANG *et al.*, 2017; SANCHEZ *et al.*, 2018; GIANNINI *et al.*, 2018; SCHOVANZ, 2019; BRONHOLO, 2020; LANGOSKI, 2021). The only adjustment made for the present study was a change in the type of cement composite, from concrete to mortar. Trials were carried out up to the mortar age of 1 year.

After the CPs had been cast, the mortars went through the stages shown in Figure 1. It should be noted that exposure over time occurs in immersion in water at 38 °C after thermal curing.

1º. *Specimens remained at room temperature for 6 hours;*

2º. *Specimens were stored in a tank with water at an initial temperature of 25 ºC;*

3º. *The heating rate of the water in the tank adopted was 10º/h, until it reached 85 ºC, which was a period that lasted 6 hours;*

4º. *The samples remained for 12 h at a temperature of 85 ºC;*

5º. *After this period, the water in the tank was cooled at the same rate (10 ºC/h), and up to 38 ºC;*

6º. *Specimens remained in this condition (immersed in water, at 38 ºC (±2 ºC)) throughout the established ages for concrete testing i.e., for twelve months.*

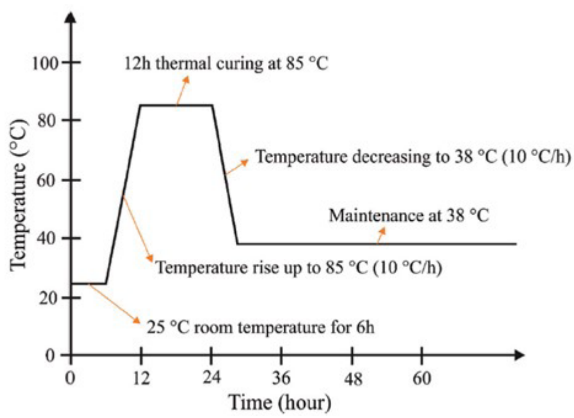

Figure 1: Procedure of DEF induction at laboratory.
Source: Hasparyk *et al.* (2020).

2.2.3. Assessment methods

When assessing the occurrence of ISA in the mortars, the linear dimensional change was determined, by following the recommendations set out in NBR 13583 (ABNT, 2014), although with a prolonged exposure time (1 year). Six prismatic mortar specimens were made for each cement, measuring (2.5 x 2.5 x 28.5) cm. Dimensional assessment was assessed every 7 days in the first 3 ages and, after 28 days of age, every 15 days, up to 1 year. To the measurements were made using a measuring device equipped with a dial indicator with 0.001mm resolution. Readings were performed with the samples positioned vertically, and always with the same face facing up. The readings were carried out in a controlled temperature environment of (23 ± 2) ºC. The linear dimensional variation (expansion or retraction) of individual bars is given by the difference between the value measured at the corresponding exposure time and the initial reading, divided by its effective length, in percentage. The results individual results obtained are rounded to the nearest thousandth and the final result average obtained from the 6 individual bars, rounded to the nearest hundredth. It should be noted that all CPs were molded from a single production, in a mechanical mixer, for each condition under study, in order to guarantee the homogeneity of the composites.

As for the evaluation of ESA by the Brazilian standard, the determination dimensional assessment took up to 98 days and by the American standard, up to 180 days. Six prismatic mortar specimens were molded for each cement also, measuring (2.5 x 2.5 x 28.5) cm. Measurements were assessed every 7 days until 28 days of mortar age, and then, every 15 days, up to the respective ages indicated by each standard. The measuring device, procedure, environment and test tolerance followed the same format as the ISA assessment.

In the evaluation of the internal attack (ISA), the mechanical properties of the mortars were also determined in cylindrical PCs (5 x 10) cm), at the ages of 7, 28, 56, 84, 168, 252 and 365 days. The axial compressive strength was determined in accordance with NBR 7215 (ABNT, 2019), while the tensile strength through diametral compression, in accordance with NBR 7222 (ABNT, 2011), by adapting the size of the specimen to the dimensions of (5 x 10) cm. The equipment used for these tests was a PC 200C press, from the EMIC brand, with capacity of 2000 kN and accuracy of approximately 1% of the applied load. They were I used 4 specimens at each test age.

3. RESULTS

3.1. Evaluation of mortars subject to the required conditions for the development of the ESA

The expansions determined in mortars by applying the Brazilian method as set out in NBR 13583 (ABNT, 2014) are shown in Figure 2 (up to the age of 98 days).

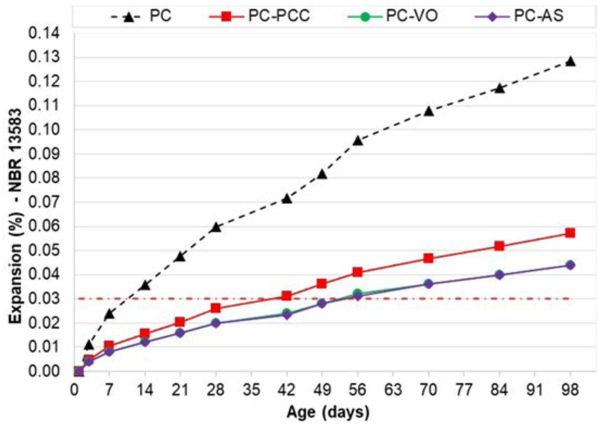

Figure 2: ESA: Expansions according to Brazilian standard NBR 13583 up to 98 days.

The mortars produced and analyzed at the age of 42 days did not exceed the maximum expansion stipulated by the standard, which is 0.03%, except for the PC-PCC and PC mortars, the latter being produced with CP V-ARI cement. However, if the analysis had been conducted after 2 weeks, at 56 days, all the cements would have shown expansions above this limit, which raises concerns about their potential resistance to sulfate ions.

The mortars have a similar behavioral pattern among themselves, in particular PC-AS and PC-VO, which have average expansions that ranged from 0.02% to 0.03% in 28 days, followed by an almost linear pattern of behavior, reaching values between 0.04% and 0.06%, in 98 days. The PC mortar reaches 0.06% expansion after 28 days and 0.13% after 98 days.

When the test time was extended to 98 days, there was no stabilization for any of the three cements assessed. Thus, on the basis of this research study, it can be stated that even if the test extends beyond 42 days, the CP IV-32-RS cements would not be able to prevent the expansions resulting from the external attack of sulfates.

In general, several studies have shown that pozzolanic admixtures are efficient in mitigating the external attack by sulfates (OUYANG *et al.*, 2014; HOPPE FILHO *et al.*, 2015). Hoppe Filho *et al.* (2015) analyzed the influence of various materials, (both inert and active), with regard to these kinds of attacks . The authors found that the reference mortar (with no admixture) obtained an expansion rate of approximately 0.05%; the mineral admixture that achieved the greatest influence on mitigating the attack was silica fume (10% in mass replacement), reducing the expansion to approximately 0.01%, at 42 days. According to the researchers, this positive result was due to the pozzolanic effect of the addition, which reduces the availability of CH that is able to react with sulfate ions, as well as altering the distribution of pores and the interconnectivity of the capillary network; however, studies in this area have not advanced beyond 42 days.

The expansions monitored over a period time, and resulting from the mortars that were subjected to the exposure conditions set out by ASTM C-1012, over 180 days of testing, are shown in Figure 3. The highest rate of growthnand expansions was observed for CP cement V-ARI (PC Blend), which reached 0.085% in the last age.

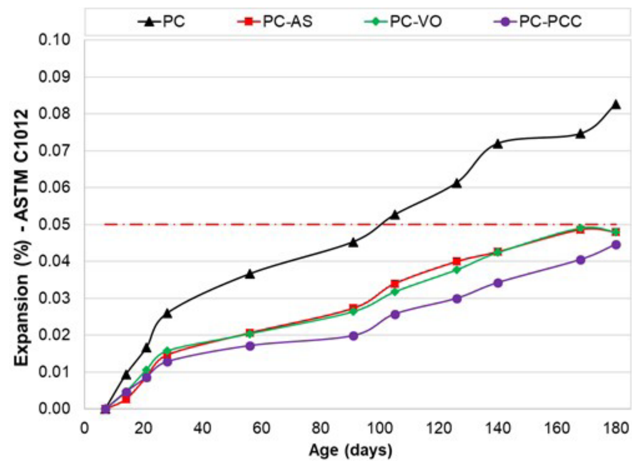

Figure 3: ESA: Expansions according to American standard ASTM C-1012 up to 180 days.

Up to the age of 30 days, there is an important expansion growth rate, followed by a lower rate of acceleration for up to 90 days; then the growth rates increase again up to 6 months of mortar age for all the cements assessed. The highest growth rates and expansions were observed for PC-AS and PC-VO cements, from the pozzolanic cement group, which again have a very similar behavioral pattern. At the end of the tests (180 days) it was found that, with the exception of the PC-PCC mixture, the other two mortars (PC-AS and PC-VO), reached the maximum limit of the American standard, which is 0.05% of expansion, and is a high degree of aggressiveness, as recommended by ASTM C-150:2021. The PC-PCC mixture was close behind, at around 0.45%. The PC mixture with cement, CP V-ARI, reached the standard limit after 100 days, and at the end of the test its expansion was 0.08%.

3.2. Evaluation of mortars induced for ISA

3.2.1. ISA Expansion monitoring

The average expansions obtained in the mortars exposed to the conditions that might result in an ISA, can be observed in Figure 4, and are classified for each evaluated cement.

According to the dimensional variation of the mortar prisms, it was possible to confirm that the PC-VO and PC-AS mortars had the highest expansions at the same age when compared with the PC-PCC mixture, since they were 0.19% and 0.18%, respectively. The expansions were measured in a period of up to 1 year and did not cease, which suggests their potential for continuity over time. The PC mortar, produced with CP V-ARI cement, achived an expansion rate of 0.43% in the last age, more than double that of the other impressions in the same concrete age.

The observed pattern of behavior shows the occurrence of DEF, since, at first, the crystals fill the pores of the matrix and, afterwards, start to cause internal tensions and thus lead to expansions. There are still no parameters to constrain the DEF expansion rate in mortars, by means of the employed method. The only benchmark with regard to attacks by sulfates, (of external origin), is NBR 16697 (ABNT, 2018), which determines that for a cement to be resistant to sulfates (in the case of an external attack) its expansion rate in mortar must be less than, or equal to, 0.03%, at 42 days of age, when tested through the established method in compliance with NBR 13583 (ABNT, 2014). If this limit were used for the DEF, none of these impressions would have expansions below the limit at 42 days and, at the final age of evaluation (1 year). Moreover, all the cements evaluated would reach a rate that is well above 0.03% expansion, with no stabilizating patterns in time.

It should be noted, however, that the CP IV-32-RS type cements that were assessed had a delaying effect on the deleterious expansive process of the DEF, when compared with the CP V-ARI, although the degree of efficiency fluctuated between them. In this study, the most efficient cement with regard to expansion, was the one with calcined clay (PC-PCC), followed by acid slag (PC-AS) and, finally, cement with volcanic material (PC-VO).

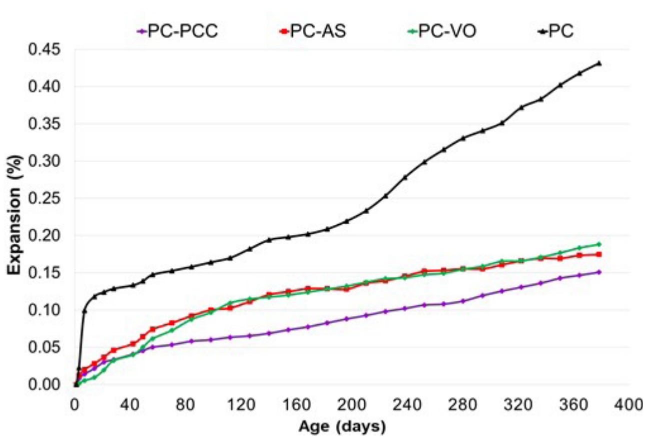

Figure 4: DEF: Mortar expansions over time and up to 400 days.

3.2.2. Monitoring tensile strength

The results displayed in Figure 5 show greater total losses of tensile strength for the PC mortar, which are around 40%, followed by the PC-VO mortar, with falls of around 35% at the age of 1 year, which can be taken as the peak of its strength. The PC-PCC and PC-AS and PC-VO mixtures suffered losses in this property of about 20% and 15%, respectively, at the age of 1 year.

According to Sanchez *et al.* (2018), in the case of concretes that are affected by DEF with expansion levels (ranging from 0.05% to 0.12%), the reduction in tensile strength can reach around 65%. With regard to higher expansion levels (≥0.20%), the reduction rate reaches around 70-80%. In studies conducted by Hasparyk *et al.* (2022) for expansion levels between 0.20% and 0.40%, the reduction in tensile strength was close to 40%.

Langoski *et al.* (2022) showed that expansions above 0.45% promote damages to mechanical properties is very significant, with reductions of around 50%. Furthermore, for expansions of the order of 0.10% there are already clear signs of a beginning of DEF deterioration, since the tensile strength is reduced by around 10% in one year. In the case of the pozzolanic cement in this aforementioned research project with fly ash, the behavioral pattern was different in terms of tensile strength. Expansions above 0.14% involved a decrease of around 18%.

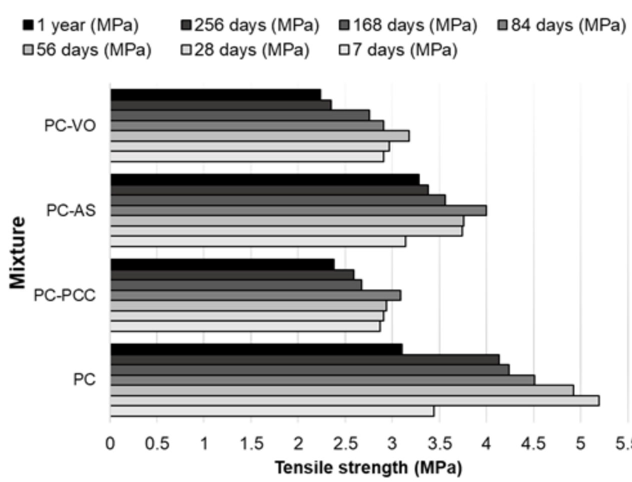

Figure 5: Splitting tensile strength.

3.2.3. Compressive strength

With regard to compressive strength, Figure 6 shows that the mortars that had the biggest fall were those with CP V-ARI (PC), and the PC-PCC mixture, with reductions of around 40%. These mortars reached expansions of 0.15% at the final age of 1 year. The PC-AS and PC-VO mixtures, on the other hand, suffered decreases of around 15%. According to Taylor *et al.* (2001), the microcracking generated by DEF starts in the interfacial transition zone (ITZ), and leads to significant reductions in compressive strength, unlike other expansive reactions, particularly in mixtures containing pozzolanic admixtures.

Tiecher, Langoski and Hasparyk (2022) found intense microcracks, filled pores and massive formations of ettringite in cement paste and in the ITZ, after assessing mortars without mineral admixtures over a period of 1 year.

Current research indicates that DEF modifies the mechanical characteristics of concrete, reducing compressive and tensile strength, in addition to reducing the modulus of elasticity (SCHOVANZ *et al.*, 2021; HASPARYK *et al.*, 2022).

Drops on compressive strength continued over time and, from 6 months to 1 year, with lower reduction rates. It was not possible to determine a unique pattern of behavior in the tested mixtures, but, as the expansions increase, there is a corresponding reduction in compressive strength.

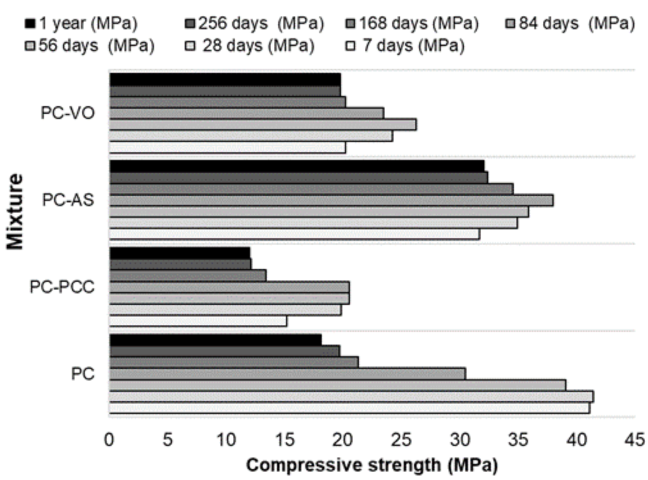

Figure 6: Compressive strength.

In a study with concrete test specimens Pichelin *et al.* (2020) concluded that the compressive strength begins to suffer signs of a decrease when the expansions reach values of 0.17% and 0.25%, during the deterioration stage of the acceleration phase. In this interval the compressive strength may undergo a reduction of the order of 30%, and then stabilize at the end of the acceleration period.

3.3 Relationship between cement characteristics and expansions for ESA and ISA

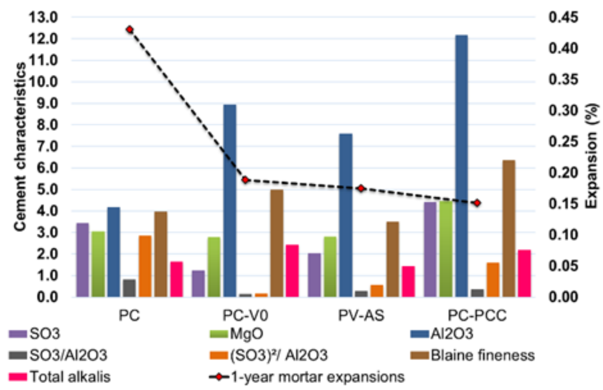

Figure 7: DEF: Properties of cements versus expansion of mortars over time.

Figure 7 shows the relationship between the main chemical parameters of the cements and the expansions obtained in the research.

It can be confirmed that, in general, Al_2O_3 elements above 12% led to smaller expansions by DEF. In addition, as can be seen, the PC-PCC cement had the highest Al_2O_3 content and the PC cement had the lowest, which resulted in the greatest expansion in the study. The same phenomenon occurred for SO_3 and MgO, where the PC-PCC cement had the highest content of these compounds, (4.42% and 4.47%, respectively). Although both ratios involving SO_3 and Al_2O_3 were higher, their values are lower than those mentioned in the literature to determine DEF risks (0.5 and 2.0, respectively), according to Bauer *et al.* (2006).

According to Schmalz (2018), the amount of SO_3, MgO and cement fineness, directly influences DEF and the rate of expansions. Cements with SO_3 content above 2.6% are cited as propensity for the occurrence of DEF is likely, and important levels of MgO, above 1%. The results of the present study demonstrate that all cements contain MgO values well above 1%.

With regard to SO_3, PC and PC-PCC cements had amounts higher than 2.6%, with maximum expansions of 0.43% and 0.15%, respectively, after 1 year of monitoring. The PC impression, which can be considered as the most expansive impression in the study, was made with CP V-ARI cement, and whereas the PC-PCC impression, with the lowest expansion, was produced with CP IV-32-RS cement, its behavior was probably influenced by the use of a pozzolanic cement, with the content of about 25% of calcined clay. This means that an individual analysis of only a single parameter is not enough.

According to Taylor *et al.* (2001), Zhang *et al.* (2002), Bauer *et al.* (2006) and Tosun (2006), the closer the SO_3/Al_2O_3 ratio is to 1, the greater its propensity for DEF development. As can be seen, CP V-ARI cement (PC molding) has the highest SO_3/Al_2O_3 ratio (0.83) and the highest rate of expansion caused by DEF (0.43%). In the case of the other pozzolanic cements, the ratios found are much lower, (always below 0.40), with no clear behavioral pattern between these cements.

Bauer *et al.* (2006) state another ratio $(SO_3)^2/Al_2O_3$. For values greater than 2, there is susceptibility to DEF occurrence. The impressions that have this high ratio, and are close to 2, are PC and PC-PCC. In the case of pozzolanic cements (with the exception of PC-PCC), the ratios found are much lower, with contents below 0.55 (Figure 7).

Another point that needs to be analyzed in Figure 7 is the fineness that affects the expansions, because it influences the porosity of the paste microstructure in the early ages and over time. According to Tosun (2006), in the initial ages the fineness of the cement facilitates the proliferation of the expansions due to the rapid formation of ettringite on the surface of non-hydrated cement particles with high permeability. In the more advanced ages, the rate of DEF formation tends to slow down since it is difficult for the water to penetrate the deeper regions of the non-hydrated cement. Despite the above, no clear pattern of behavior could be observed for this parameter.

In summary, based on the tests and acknowledging that expansive chemical reactions can persist for years, none of the Brazilian cements tested in this study were found to be resistant to sulfate ions, whether of internal or external origin. Sulphate resistant cements should guarantee at least resistance to external sulfate attack; however, this was not observed in the present research.

4. GLOBAL ANALYSIS

Regarding the DEF, the results obtained show that there was a growth of expansions over time for all the tested cements, with high values achieved, as well as damage caused to the mechanical properties

The mechanical properties were prematurely affected for mortar with cement (PC), and experienced high levels of damage when there were significant expansions. As for the tested mortars (PC-PCC; PC-AS and PC - VO), only a delay in the expansion process and deterioration caused by DEF were noted, owing to the presence of admixtures.

In the evaluation of the external attack by sulfates, a comparison between the Brazilian and American standards, showed an incompatibility in the results and behaviors. However, when the timeline for the analysis of the expansions was extended, by employing the NBR method, the expansions did not cease for the pozzolanic cements, which suggests that there was only a slower development of the expansive behavior by DEF.

Under the terms of the Brazilian regulatory standards the expansive behavior of mortars for the ESA must be assessed at an early stage (at the mortar age of 42 days), while the ASTM believes it can be better delineated in time through an assessment of more advanced ages. If the NBR method is applied for the ESA, it is recommended that the analysis time should be extended to at least 3 months, as, in this way, the method will provide more consistent results and be compatible with those of the ASTM. Moreover, if the same NBR limit was adopted for the ASTM, no cement would be regarded as resistant to sulfates.

Another point of observation was that the SO_3 content and the SO_3 and Al_2O_3 ratios had the greatest influences on the expansions in both the ISA and ESA studies. The MgO content of all cements remained above 1%, which shows a propensity for the occurrence of DEF for all the tested mixtures.

In short, since it is well-known that expansive chemical reactions can last for years, Table 4 was devised on the basis of a global analysis of the results. This clearly shows that none of the cements evaluated in this research can be considered to be resistant to sulfate ions, whether of external or internal origin. Cements with the suffix -RS (sulfate resistant) should, at least, ensure resistance against external sulfate attacks, (although this was not

Cement	ISA / DEF	ESA ASTM (0.05%[1])	ESA NBR (98 days[2])	Final Conclusion ESA & ISA
PC	NR	NR	NR	NR
PC-PCC	NR	R	NR	NR
PC-AS	NR	NR	NR	NR
PC-VO	NR	NR	NR	NR

Table 04: Global analysis - ISA & ESA

1 - Limit by ASTM (age: 180 days); 2 – Suggested age of evaluation by this manuscript keeping the same limit of 0.03% from NBR; R – Resistant for sulfates; NR – Nonresistant.

observed), largely owing to the extension of the deadline adopted by the Brazilian standard, NBR 13583 (ABNT, 2014), as well as the reduction of the limit for ASTM C -1012.

5. CONCLUSION

On the basis of the results obtained from the ESA evaluation, it can be concluded that there are differences in the behavior of the mortars, depending on the cement type and the mineral admixture used, as well as between the assessment methodologies. Nonetheless, some of the results between the two tested methods (NBR and ASTM) in the evaluation of the external attack, were found to be incompatible.

Regarding the ESA, according to the ASTM criteria, three of the four cements surpassed the 0.05% limit for extremely aggressive environments, which suggests that they are not resistant to sulfates caused by an external attack. If the limit of 0.03% were also applied to this method, none of the cements would demonstrate resistance. It is noteworthy that the expansions did not cease for any of the mixtures evaluated during the period of assessment, in either of the methods.

Distinct levels of expansion were measured for the ISA and in the case of the PC mixture (CP V-ARI) the expansions were higher, (in the order of 0.43%). The mortars produced with pozzolanic cements (CP IV-32-RS), containing various admixture types, only experienced a delay in the expansion and deterioration process. The expansions did not cease until the last evaluated age, and ranged from 0.15 to 0.19%; in addition, they suffered serious mechanical losses, from which it can be concluded there was damage caused by DEF.

Thus, it was confirmed that the measured mechanical properties were impaired. In terms of tensile strength, decreases of the order of 20 to 40% were found. In the case of compressive strength, there were reductions of up to 40% for CP V-ARI (PC), and with regard to the PC-PCC mixture, the other mixtures had reductions of around 15%. In other words, the tested pozzolanic cements have the potential to reduce the expansions when compared to a cement without any pozzolan (CP V-ARI). However, the incorporation of pozzolanic mineral admixtures at the contents used by the factory, were not enough to mitigate attacks.

Another point to note is that losses of up to 30% in compressive strength are unacceptable, as well as comparable drops in tensile strength. This situation already shows a high degree of aggressiveness and deterioration.

Hence, there is evidence to show that when based on the methods employed and the boundary conditions and constraints adopted, none of the three pozzolanic cements tested, proved to be resistant to sulfates, either in the ESA or ISA/DEF study.

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LZP: data curation, formal analysis, funding acquisition, investigation, supervision, validation, visualization and writing - original draft.

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