# Influence of Delayed Ettringite Formation (DEF) on physical and mechanical properties of concrete

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**Abstract**

*Several concrete elements and structures in Brazil are being diagnosed for DEF distress especially due the internal sulfate reaction (ISR) involving high temperatures from cement hydration heat. Many of them were cast with a national high strength cement. Based on those occurrences, an experimental study was performed in order to research DEF aiming to improve the knowledge on the behavior of cements produced in Brazil. The main purpose of this research was to verify the influence of DEF on the physical and mechanical properties as well as on microstructure characteristics of concrete mixtures submitted to high levels of temperature and moisture. Several specimens of concrete (cylindrical and prismatic ones) were cast at the laboratory and were undergone to a specific thermal up to 85ºC. Thereafter, they were stored in water at 38ºC and monitored over time and up to three months. Compressive strength, Stiffness Damage Tests (SDT) and also qualitative analyses by SEM/EDS were performed in the cylindrical samples; expansions and mass changes were accomplished on prismatic specimens over time. Results have indicated that concrete had undergone DEF with high levels of expansion, negative impacts on the mechanical properties (compressive strength and SDI) and presented typical products from DEF, flagging DEF risks in a real structure over time.*

***Keywords**: concrete; durability; delayed ettringite formation (DEF); heat of hydration; expansion*

## 1. INTRODUCTION

DEF is prone to occur in the presence of sufficient amount of gypsum and aluminates ($C_3A$ and $C_4AF$) during the first hours of hydration in a moist environment and high level of temperature (above 65ºC) [1]. At normal conditions of hydration there is a rapid dissolution of sulfates to form primary ettringite when cement comes in contact with water. On the other hand, crystallization of late ettringite occurs when high level of temperature is achieved at early ages and primary ettringite does not form. Along time, exceeding aluminates are available to contribute to DEF [2].

DEF causes internal tensile stresses that lead to an expansion of the cement matrix that may result in cracking of concrete structures [3]. Several studies point to irreversible damages caused by DEF. For this reason, it is important to prevent high values of temperature and also its evolution, caused by the heat of hydration of the cement or by unsuitable thermal curing [3, 4, 5, 6, 7].

According to Giannini *et al.* (2018), tensile strength and elasticity modulus can be reduced with expansion levels of the order of 0.2-0.3%, whereas the compressive strength is affected with expansions above 1%. In relation to SDI, Sanchez *et al.* (2015) observed a good correlation between SDI, damage index and expansion [8].

High levels of expansion are responsible to impact the mechanical properties of concrete due to cement matrix damages. Considering a high volumetric increase generated by ettringite formation in the presence of water, microstructure changes and the cement matrix micro-cracks increases insofar as DEF progress over time [1, 16, 18, 25].

Some researchers have tested mortar and concretes at laboratory, nonetheless there is no standard method and the differences in the methodologies make a comparison of the results very difficult [3, 9, 10, 11, 12, 13, 14, 15, 16]. There is the need to create standards and also complementary investigations involving also microstructural analyses (e.g. analyses by SEM) to diagnose correctly the type of pathology, since ASR and DEF can present some similar symptoms [17].

Considering the mentioned above, this paper presents the results of an experimental program involving the evaluation of physical, mechanical and microstructural analyses of concrete mixtures affected by DEF in laboratory conditions.

# 2. MATERIALS AND METHODS

## 2.1 Materials

A Brazilian Portland cement of high early strength CP V type (similar to ASTM type III - ASTM C 150) was selected to enable DEF occurrence, i.e., containing a high content of $SO_3$ with $SO_3/Al_2O_3$ higher than 0.70. This cement also presents high fineness (Table 2.1).

Table 2.1: Properties of CP V cement.

| Mechanical Properties | | | Chemical Properties | |
|---|---|---|---|---|
| Characteristics | | Value | Characteristics | Value |
| Compressive Strength (MPa) | 1 day | 25.6 | $Al_2O_3$ (%) | 4.46 |
| | 3 days | 38.6 | $SiO_2$ (%) | 18.86 |
| | 7 days | 44.4 | $Fe_2O_3$ (%) | 2.75 |
| | 28 days | 54.1 | CaO (%) | 61.46 |
| Physical Properties | | | MgO (%) | 3.93 |
| Specific Mass (g/cm³) | | 3.09 | $SO_3$ (%) | 3.28 |
| Le Chatelier test (mm) | | 0.50 | Loss on ignition (%) | 3.37 |
| Setting Time | Initial (h:min) | 03:10 | Insoluble Residue (%) | 0.76 |
| | Final (h:min) | 04:00 | $Na_2O$(%) | 0.23 |
| Normal Consistency (%) | | 29.3 | $K_2O$ (%) | 0.85 |
| Blaine Fineness (cm²/g) | | 4.520 | $Na_2Oeq$ (%) | 0.79 |
| #200 Residue (%) | | 0.03 | Heat of hydration ($J.g^{-1}$) for 41h | 324.42 |
| # 325 Residue (%) | | 0.30 | $Na_2Oeq. = 0.658.K_2O+Na_2O$ | |

The fine aggregates proceeded from natural deposits and the coarse ones from granitic rocks. Both aggregates selected for this research display a non-reactive ASR behavior in field and also at laboratory (less than 0.10% in the AMBT from ASTM C-1260); this condition was defined in order to avoid coupled attack of DEF and ASR. The main aggregate characteristics are presented in Table 2.2.

Table 2.2: Characteristics of fine and coarse aggregates.

| Aggregate | Property | Result |
|---|---|---|
| Fine<br><br>Origin: Natural/Pit | Maximum aggregate size | 4.75 mm |
| | Fineness modulus | 2.56 |
| | Specific Mass | 2.05 g/cm³ |
| | Water absorption | 3.0% |
| | Material passing through #200 sieve | 1.3% |
| Coarse<br><br>Origin: Granite Crushing | Maximum aggregate size | 19.00 mm |
| | Fineness modulus | 6.72 |
| | Specific Mass | 2.68 g/cm³ |
| | Water absorption | 0.40% |
| | Material passing through #200 sieve | 0.32% |

## 2.2 Mix design and exposure environment

Concrete specimens were cast with the mix design presented in Table 2.3. This type of pumped concrete is commonly placed in structures from Hydroelectric Power Plants, such as trunnions beams, containing high cement contents. The curing procedure and exposure environment adopted in the experimental program were defined by the authors of this paper, based on some previous publications such as Fu [9], Kchakech *et al.* [14] and Rashidi *et al.* [12] with adaptations, according to Figure 2.1. The temperature peak of 85ºC and also maintenance period of 12 hours was based on some references such as [1; 8;15;16;18]. The exposure environment over time, with water immersion at 38ºC, was set in order accelerate DEF, as also previously tested by [14; 15].

Table 2.3: Main characteristics of the concrete mix.

| Properties | Results |
|---|---|
| Water-cement ratio | 0.46 |
| Fineness Modulus | 4.809 |
| Natural sand, 4.75 mm (%) | 46.9 |
| Coarse aggregate - 19 mm (%) | 53.1 |
| Polyfunctional admixture (%) | 0.6 |
| Slump (mm) | 110 |
| Air content (%) | 1.5 |
| Cement Content (kg/m³) | 471 |
| Mix design (unit by weight) | 1:1.6:1.9:0.46 |

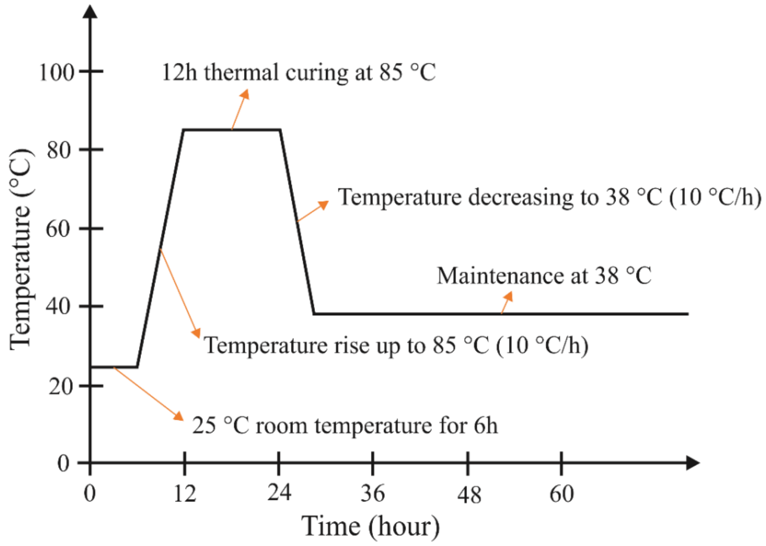



Figure 2.1: Curing process and environment exposure condition [19].

## 2.3 Experimental program

### 2.3.1 Physical characteristics

Dimension, mass variation of concrete samples and also visual characteristics were monitored with a periodicity of 7 days along the three months of test by casting five concrete prisms (75 x 75 x 285 mm). Considering that DEF causes volumetric expansion due to formation of ettringite products that cause tensile stress, this evaluation is very meaningful. Expansions were determined by using a digital comparator according to the Brazilian standard test for ASR (ABNT NBR 15577 – Part 6 [20], similar to ASTM C 1293 [21]). Several photographic records were also performed to evaluate manifestations of DEF along time and their alterations, always at the same side of specimens.

### 2.3.2 Mechanical properties

Mechanical properties were performed in cylindrical specimens (100 x 200 mm). Compressive strength tests were carried out at 7, 28, 56 and 84 days of age whereas Stiffness Damage Index (SDI) was determined at 28, 56 and 84 days, according to Martin *et al.* [15], Giannini *et al.* [16] and Sanchez *et al.* [18] that were pioneer in this test for DEF. The result of SDI comes from the graphical interpretation of hysteresis areas of the SDT (Stiffness Damage Test) which consists of a relation between compressive loads and strain (Figure 2.2) in a cyclic loading, being controlled with 0.1 MPa/s, considering five cycles of loading. For this research, that involved a further comparison between different cements and concrete mixes over time, the loading was fixed to 10 MPa, although it is recommended a loading up to 30-40% of the compressive strength with a limit of 10 MPa.

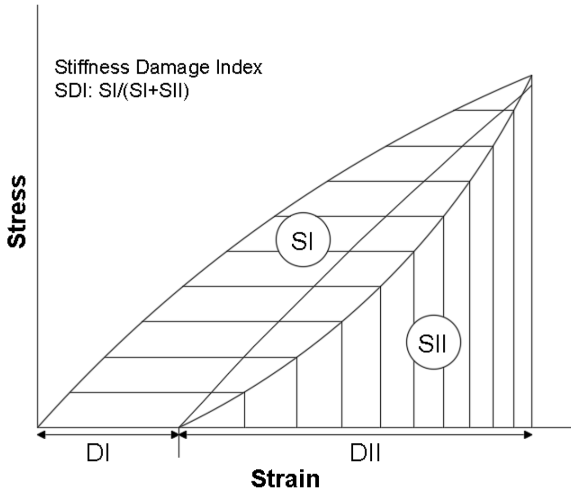



Figure 2.2: Graphic representation of Stiffness Damage Test (SDT) [15, 16, 18].

### 2.3.3 Microstructural analyses

Some microstructural analyses were performed in concrete samples in order to monitor their modifications over time. SEM (VEGA 3-Tescan) and double EDS from Oxford were used during the analyses in fractured samples by using secondary electron (SE) detector. Samples were sputter-coated with gold. Acquisitions were performed with 20 kV acceleration voltages, 18 nm beam current intensity and a 15 mm working distance.

# 3. RESULTS AND DISCUSSION

## 3.1 Physical characteristics

Expansion results from all five concrete prisms and average values along time are reported in Figure 3.1. The rate of expansion growth starts to increase from 1 month, achieving very high values of expansion at 3 months, in the range of 0.5 and 0.6%. Results from Martin *et al.* [15], Amine *et al.* [22] and Giannini *et al.* [16] show high expansions from DEF, of about 1% at 6 months of testing.

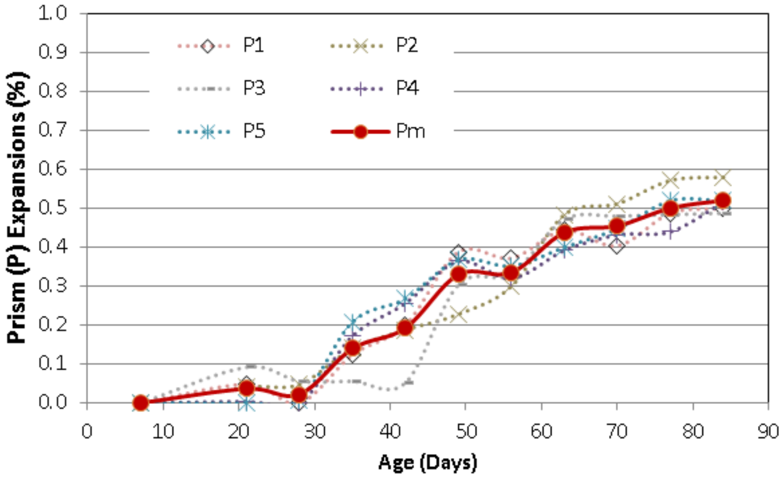



Figure 3.1 - Expansion results from concrete prisms over time.

During monitoring of the weight of concrete prisms it was observed a gradual mass gain along time for all samples, with no stabilization yet up to the age of 84 days. In average, concrete specimens had enhanced their weights by about 1.5% (Figure 3.2).

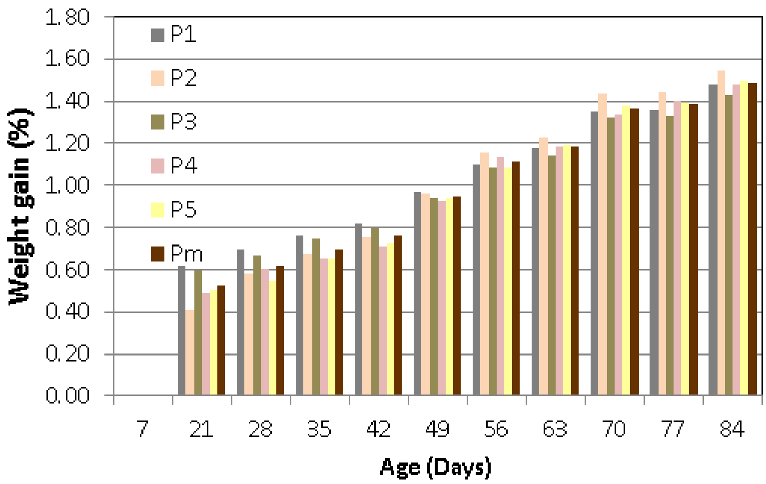



Figure 3.2 – Increase in weight of concrete mixtures.

During visual inspections, it was possible to identify already some symptoms such as white formations at the 56 days; these manifestations had spread over time. At 84 days, all the sides of specimens analyzed were completely covered by white products indicating DEF, according to the microstructural analyses (3.3). In this study, actually cracks were not so evident by visual inspection presumably due to the surface entirely covered even though the expansion level achieved (~0,5%). The following figures register some photos of visual monitoring along time indicating white areas/products.

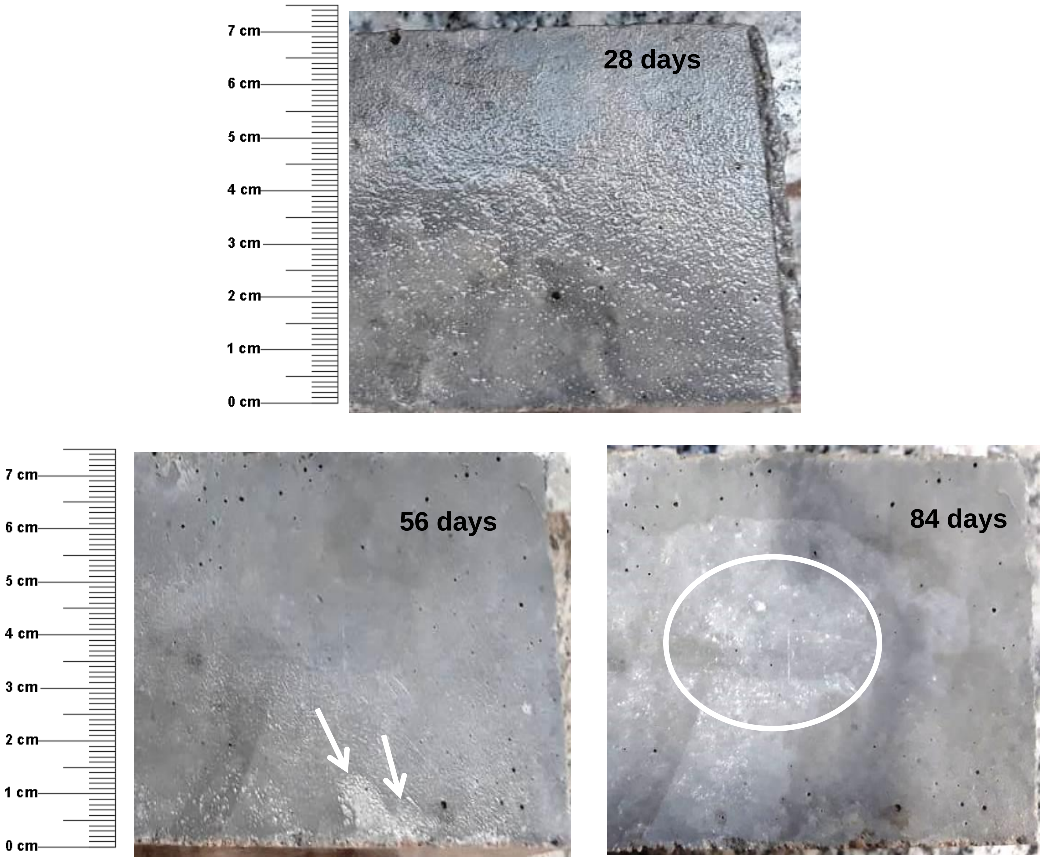



Figure 3.3 – Visual characteristics of concrete prisms along time.

## 3.2 Mechanical properties

Figure 3.4 presents data from mechanical tests of compressive strength versus expansion. Important reduction of values can be noticed as long as expansions progress. By comparing expansions of about 0,35% (2 months) to the first age of evaluation, a high decrease in the compressive strength was noted (about 23%), and more than 10 MPa was lost due to DEF when expansions overpass 0,50% (almost 30%). Those results are in line with the ones presented by Giannini *et al.* [16], Sanchez *et al.* [18] and Jeong *et al.* [25].

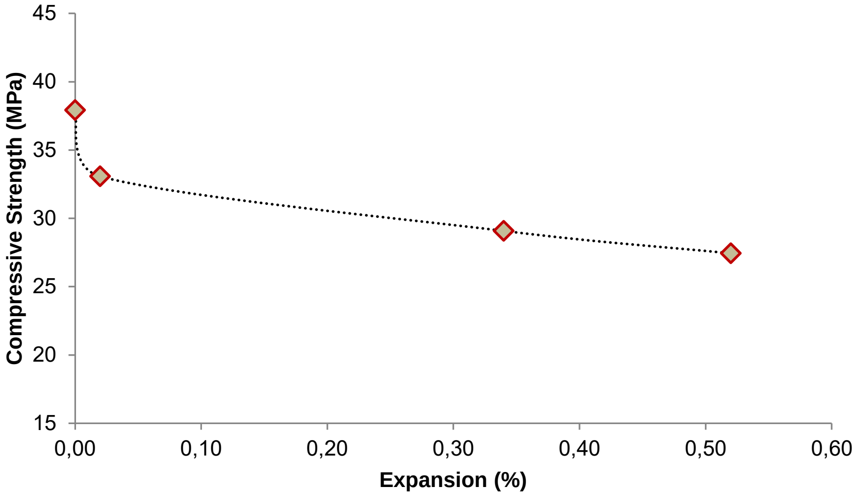



Figure 3.4: Compressive strength results over time.

The results from SDT have indicated a gradual increase of deformations along time as well as expansions (Figure 3.5). The stress-strain curves at 3 months had indicated high level of deformation associated to expressive expansions, and around 0.5%. When comparing one to three months, it is noticed an important increase of SDI from 0.10 to 0.52, respectively. In the SDI study presented by Giannini *et al.* [16], it was verified that as the level of expansion increases the damage symptoms also increase by analyzing hysteresis area, i.e., dissipated energy.

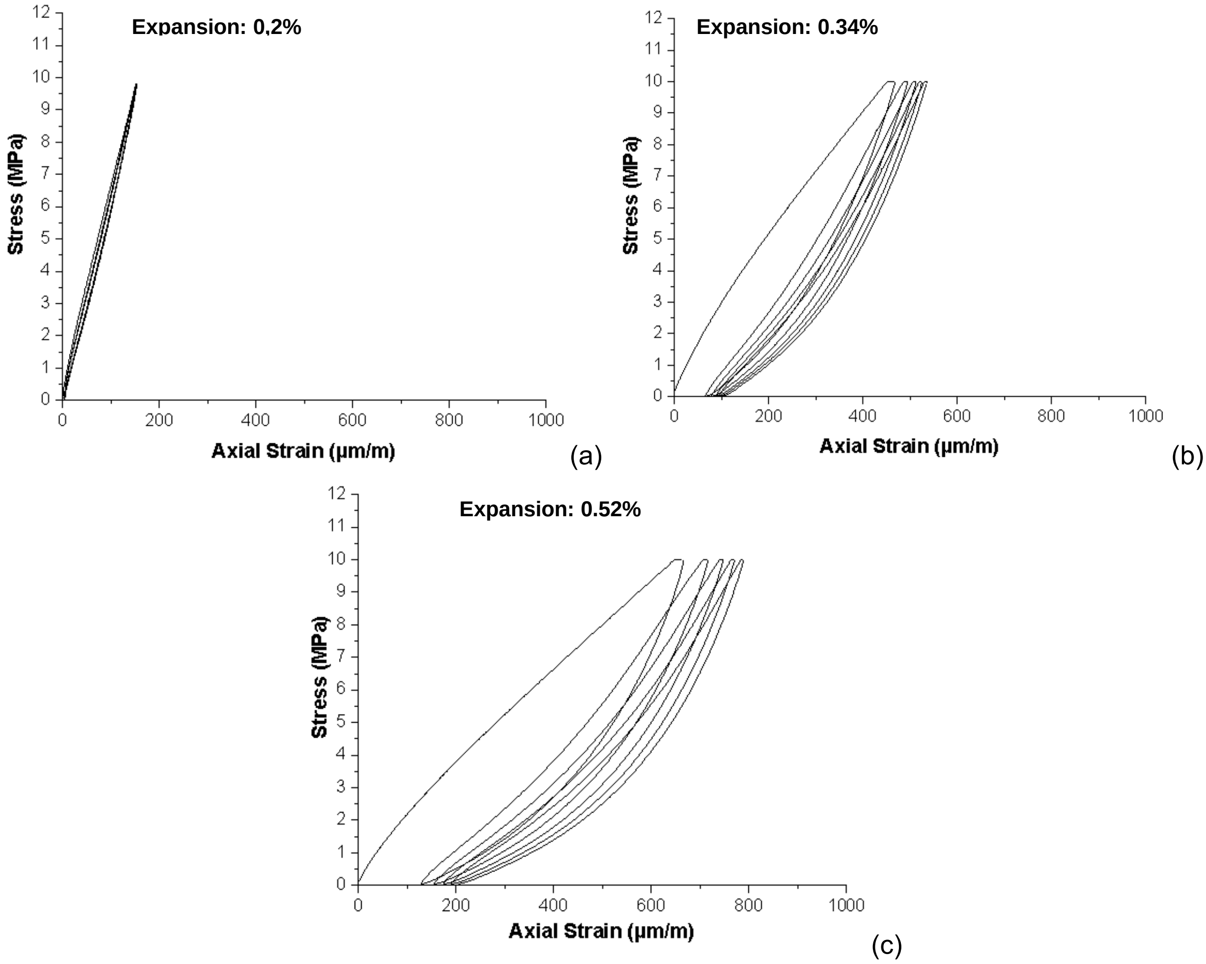
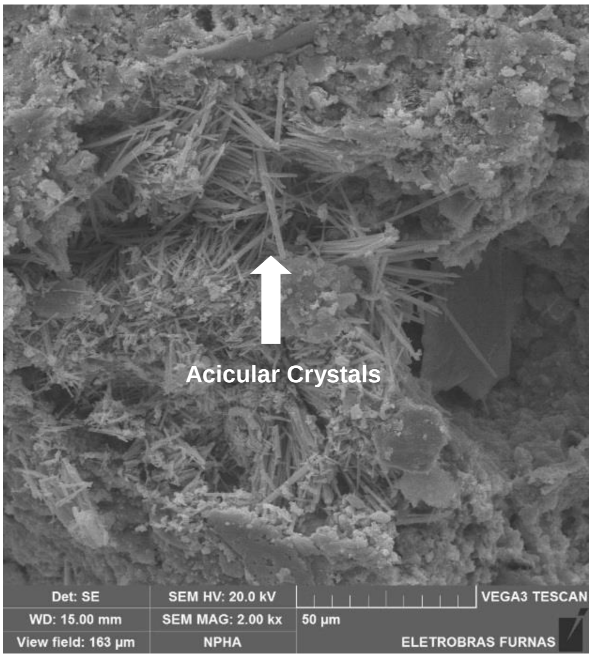


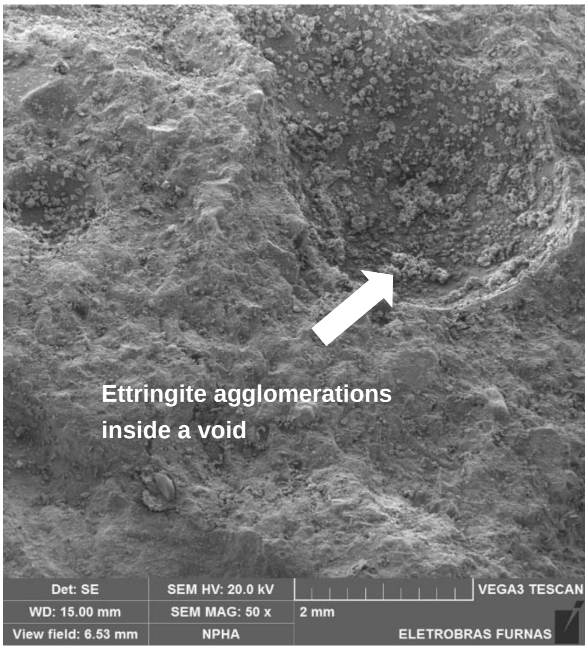

Figure 3.5: Results from SDT over time. (a) 28 days, (b) 56 days and (c) 84 days.

## 3.3 Microstructure results

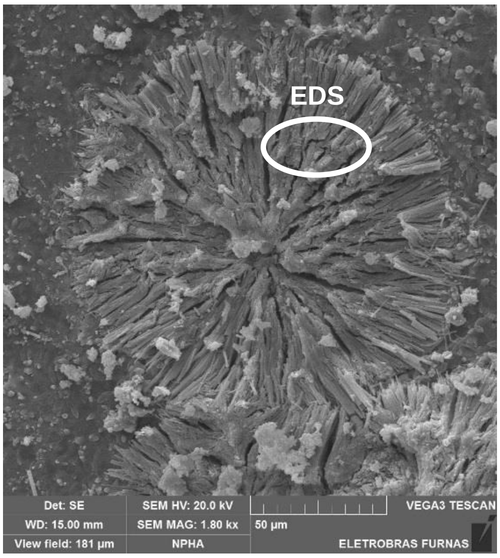
According to SEM/EDS analyses over time, differences were noticed from 28 days of age, with incidences of several ettringite crystals in the cement matrix (Figure 3.6a) whereas at 7 days no evidence was observed. At 56 days, there was an increase of ettringite crystals isolated and also in agglomerations inside voids, and at 84 days, besides late ettringite presence (Figure 3.6b), some detaching of aggregate in the ZT as well as important incidences of powdered material were detected. Figure 3.6c shows local massive ettringite and 3.6d a spectrum from EDS analyses.



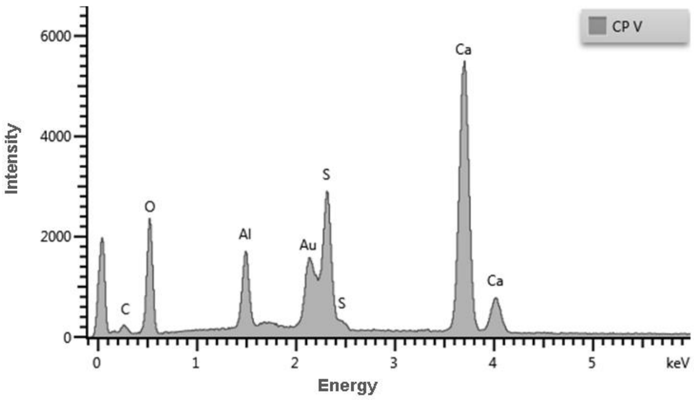

(a) 28 days.




(b) 84 days.




(c) 84 days.




(d) 84 days.

Figure 3.6: SEM/EDS: a), b), c) Micrographs; d) EDS.

Some similar microstructural characteristics were presented by Jensen and Sujjavanich [26] in relation to late ettringite. Their study had involved analyses on foundation concretes suffering from coupled DEF and ASR.

## 4. CONCLUSIONS

The main conclusions from the study presented are:

- The expressive decrease of compressive strength values along time observed in this study at laboratory are in line with DEF occurrence, according to the concrete microstructure, and possible consequences over time, depending on the concrete mixture, its materials and also the exposure environment in the field. Likewise, the stiffness damage index (SDI) was a good marker, indicating an important increase over time, and thus negative impacts of DEF.
- The expansions generated by concretes with a high early strength Portland cement were significant by the age of 3 months, achieving about 0.50%, in average, as well as weight gain. DEF was able to be diagnosed visually along with microscopic analyses in the concrete specimens tested. Several visual white formations and massive products of ettringite in the voids, transition zones and also dispersed along cement matrix by SEM/EDS were viewed.
- The method adopted in this paper to evaluate the incidence of DEF involving the procedure of curing and exposure conditions has shown to be promising, since it was able to diagnose DEF on a specific cement and real mix design, considering the constant presence of water and also a temperature of 38ºC along time. Further studies should be performed in order to complement and also contribute to a standardization of the test method to detect DEF prior to the use of any type of cement.

Finally, as an overview of the experimental program, it is important to point out that the concrete mixtures studied with CP V (high early strength) are prone to suffer DEF, presenting high levels of expansion, negative impacts on the mechanical properties (compressive strength and SDI) and typical products from ISA, i.e., late ettringite formation.

## 5. ACKNOWLEDGMENT

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