ANALYSIS OF THE DURABILITY OF HIGH STRENGTH CONCRETE WITH SUPERABSORVENT POLYMER

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Abstract

The High Strength Concretes (HSC) provided significant advances in civil construction, due its superior strength, efficiency and durability. Due to the high content of cement, low water/cement ratio and mineral additions, it is essential to avoid the emergence of tensile stresses generated autogenous shrinkage and consequently the cracking of structural elements and, therefore, losses in the durability. One strategy to mitigate autogenous shrinkage of HSC is the use of superabsorbent polymers (SAP) as internal curing agent. However, the use of SAP increases the porosity, leaving unconnected voids in the hardened material, which can reduce the durability of it.

This research aims to analyse the influence of the addition of superabsorbent polymer on the durability of Portland cement microconcrete.

In order to compare the influence of the use of shrinkage mitigation agents in durability, the experimental program consists of two mixtures of high strength microconcretes with water/cement ratio equal to 0.35: one used as reference and another one containing 0.3% of SAP. The behaviour of concrete in the hardened state was evaluated by performing the tests: resistance to simple axial compression, modulus of elasticity, migration of chloride ions and absorption by capillarity.

It was verified that the dense microstructure, characteristic of HSC, was preserved even in the presence of pores created by the SAP desorption process, because they are larger and disconnected instead of smaller and continuous pores. In conclusion, the SAP is a promising strategy to mitigate autogenous shrinkage, with a low prejudice to the mechanical properties and even improving the durability.

Keywords: *High Strength Concretes (HSC), Superabsorbent Polymers (SAP), Durability*

1. INTRODUCTION

The development of high strength concrete has provided numerous advances on the productive and economic aspects for civil construction. With the use of plasticizing additives and, later, superplasticizers (SP), it was possible to reduce the water/cement ratio (w/c) of concretes, achieving increasingly higher compressive strengths, without compromising on workability.

Due to the dense and refined microstructure, the low w/c ratio, the mineral additions and the high cement consumption, this concrete is less permeable and more resistant to attack by aggressive agents such as chlorides – sulphates and CO_2 – and presents higher abrasion resistance. However, one of the main factors limiting the use of HSC is the occurrence of a great increase in autogenous shrinkage to which they are susceptible - is especially prominent in concrete with low water-cement ratio below 0.4 - (WYRZYKOWSKI et al., 2018), due to the low w/c, which can cause early cracking that compromises the stability, durability and aesthetics of the structure.

To mitigate this shrinkage, several solutions have already been idealized, but the use of internal cure water with porous materials (such as superabsorbent polymer - SAP - or light aggregates) has been consolidating as the best alternative.

Polymers are superabsorbent and fine synthetic particles capable of absorbing a large amount of liquid from the environment, allowing the formation of water-filled macropores in the cement paste, thereby retaining water within its structure without dissolution (JENSEN and HANSEN, 2001). In a publication derived from the Rilem TC 260-RSC working group, Wyrzykowski et al. (2018) defines SAP as reticulated polyelectrolytes that swell in contact with water or aqueous solutions, resulting in the formation of a hydrogel.

Internal curing using SAP occurs effectively due to the rapid absorption of water by the polymer, which then gradually releases it, reducing the internal moisture content of the concrete. This process occurs over several days or week, with the major portion occurring within the first’s days of hardening.

According to HASHOLT and JENSEN (2015) this internal healing water participates in the hydration process, increasing the degree of hydration of the paste. Thus, hydration reactions are controlled by the total w/c ratio rather than the initial basic w/c ratio of the cement paste. Therefore, the comparison of SAP effectiveness should be based on the same total w/c ratio.

That said, the w/c ratio, by neglecting the water stored in SAP, is called the basic w/c ratio (w/c_b). The incorporated cement water ratio (w/c_{inc}) refers to SAP internal cure water. Therefore, the total w/c would be the sum of the basic water/cement ratio with the incorporated water cement ratio. Agostinho (2019) also concluded that the comparison on SAP efficiency should be based on the same total a/c ratio.

Although a lot of research is underway, there are still gaps about the long-term effects of these polymers on the durability of high strength cementitious materials and whether this internal cure water (w/c_{inc}) actually participates in hydration reactions.

2. MATERIALS AND METHODS

This research aims to analyse the influence of superabsorbent polymer (SAP) addition on the durability of Portland cement microconcrete. It was measured the interference of SAP addition on the mechanical properties of microconcretos by performing the tests: compressive strength and modulus of elasticity. The chloride ion migration assay and the absorption by capillarity was performed to evaluate the interference of SAP addition on durability.

The premise of the research is to maintain the fixed spread of (215 ± 20) mm (based on ABNT NBR 13276: 2016, without applying beats to the table); and the variable SP content. The total w/c ratio used in the present study was constant of 0.35 for both mixtures, the first being the reference admixture and the second containing 0.3% SAP in relation to the cement mass. Table 1 shows the nomenclature of de microcretes used in this research.

Table 1: Nomenclature of the microconcretes

Name	Description
035 REF	Reference mixture with total w/c = 0.35
035 SAP 03	Mixture SAP/C = 0.3% with total w/c = 0.35)

2.1 Materials

For this study, CPV-ARI cement was used, due to its amount of clinker and the fact that it is a cement widely used in HSC. The fine aggregate used in this research is natural and washed river sand from the Corumbá alluvial deposit in the Pires do Rio – Goiás/BR.

The active silica used is of non-densified national origin, from DOW CHEMICAL®. The addition content of 10% in relation to the cement mass was fixed, as recommended by the TC 225-SAP Committee (RILEM, 2012).

The chemical additive GLENIUM® 51, of the high efficiency water reducing type (superplasticizer type II - SPII-N) was the superplasticizer used. Such additive is based on a modified polycarboxylic ether chain that acts as a dispersant of cementitious material.

The superabsorbent polymer used in the work was supplied by Professor Ole Mejlhede Jensen and developed at the Technical University of Denmark (DTU) and is supplied as a dry white powder with spherical particles. It is a covalent crosslinked acrylic acid/acrylamide type polymer produced by the reverse suspension polymerization technique (JENSEN and HANSEN, 2001). The use of 0.3% was enough to mitigate autogenous shrinkage in HSC, not justifying a higher content, as exposed by MANZANO (2016), SANTOS (2016), BORGES and AIDAR (2016).

2.2 Mixtures compositions

The w/c ratio of 0.30 is usual for HSC, which is suggested by the TC 225-SAP organizing committee (RILEM, 2012). However, the mixtures that have internal curing water have a basic w/c ratio (w/c_b) of 0.30 and incorporated w/c ratio (w/c_{inc}) of 0.054, considering the SAP absorption value of 18 g/g. Summing the w/c_b with the w/c_{inc} gives a value of 0.354. By approximation criteria and practicality of execution, total w/c ratio of 0.35 will be used in both mixtures. Details of the composition of the traces can be found in Table 2.

Table 2: Composition of the microcretes (kg/m^3)

Name	Cement	Sand	Active silica	SAP	SP	Water		
						Water (measured)	SAP internal curing eater	Water contained in SP
035 REF	700	1265	70	-	6.3	240.59	-	4.41
035 SAP 03	700	1265	70	2.1	15.4	234.22	31.5	10.78

The mixing script was based on the recommendations presents by the TC 225-SAP Committee (RILEM, 2012). The sand was used in the wet condition, so it is essential in the production process to perform the moisture correction for the dry surface saturated condition (SSS). The determination of this surface moisture was performed by the Chapman Bottle (ABNT NBR 9775: 2011) moments before the production of microconcretes.

2.3 Methods

To evaluate the **compressive strength**, 50 x 100 mm cylindrical specimens were used and the tops of the specimens were adjusted by grinding. The method was performed according to ABNT NBR 5739:2018 and the specimens were tested at the ages of 1, 7 and 28 days.

Regarding the **modulus of elasticity** test, the methodology used followed the ABNT NBR 8522: 2017, at 28 days of age. Initially, the tensile strength (Fc) of two specimens was determined and an upper limit stress equal to 30% Fc and a lower limit of 0.5 MPa was established. Then three other specimens were subjected to four loading and unloading cycles at a rate of 0.45 ± 0.15 MPa/s.

For the **chloride ion migration** test, the methodology proposed by NT BUILD 492: 2011 – Chloride migration coefficient from non-steady-state migration experiments – was followed. The specimens measuring 100 x 200 mm, were cut into four equal 100 x 50 mm parts after 28 days of curing, and the two central parts were used in the test. The samples underwent vacuum preconditioning. After this preconditioning, the samples were transferred to the test apparatus. Fig. 1 shows the schematic drawing suggested by the standard for the construction of the test apparatus and the apparatus made according to the normative specifications.

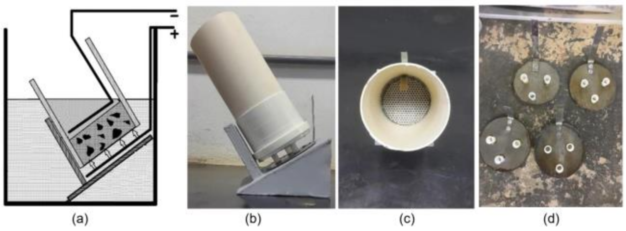

Figure 1: (a) Schematic drawing of the chloride migration test apparatus suggested by NT BUILD 492: 2011; (b) Side view of the migration test apparatus; c) Top view of the migration test apparatus; d) Lower plate used to position the test apparatus.

The plastic containers are filled with 10% sodium chloride cathodic solution by mass of water. Each apparatus was filled with an anodic solution of sodium hydroxide in distilled water (1.2g NaOH for every 100g water). From this, all devices were connected in parallel and initially the voltage was set to 30 volts, as can be seen in Fig. 2.

Figure 2: Chloride chloride migration test in progress

At the end of the test, the samples were ruptured by diametral compression and a 0.1 molar silver nitrate solution was sprayed onto the fractured surface of the specimen. The chemical reaction between silver nitrate and chloride impregnated in concrete results in silver chloride salt, being possible to measure chloride penetration. Concluding the measuring, it becomes possible to calculate the non-steady state chloride diffusion/migration coefficient.

The **capillary water absorption** test was performed according to the recommendations of ABNT NBR 9779: 2012, using 3 cylindrical specimens measuring 50 x 100 mm. The test was performed on the specimens at 28 days of age.

3. RESULTS AND DISCUSSION

Figure 3 shows the **compressive strength** results of the microconcrete containing 0.3% SAP addition to the reference mixture for ages 1, 7 and 28 days. It is observed that the SAP causes a decrease in compressive strength with 1 day cure, promoting a reduction of around 35% over the reference. At this early age, the reference microconcrete obtained a resistance value of 40.16 MPa and the mixture containing SAP a value of 25.92 MPa.

However, at 7 days, it is observed that SAP no longer brings damage to the resistance. The reference mixture obtained a value of 57.96 MPa and the mixture containing SAP showed 57.29 MPa, representing a difference of about 1%. At 28 days, the reference microconcrete obtained 72.87 MPa, compared to 72.59 MPa of the superabsorbent polymer mixture. Again, the difference between the observed values was 1%, which cannot be considered a reduction. That is, at 7 days and at 28 days, SAP did not harm the mechanical properties of concrete.

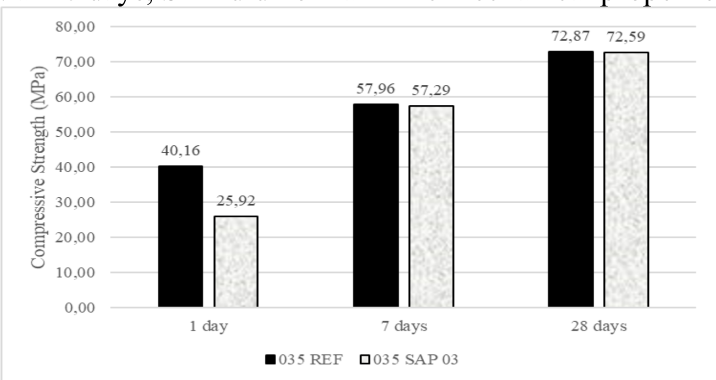

Figure 3: Results of simple compressive strength at ages 1, 7 and 28 days.

It is important to emphasize that several studies report the loss of mechanical resistance caused by SAP, among them DUDZIAK and MECHTCHERINE (2010); SILVA (2014) and SANTOS (2016). Though, all the above authors added extra water to the SAP-containing mixtures; so they compared traits with even basic w/c.

Nevertheless, the results obtained in this research corroborate the theory that in fact SAP internal healing water is part of the hydration process. Thus, the initially observed reduction in resistance is probably due to an increase in microconcrete porosity due to the introduction of SAP particles, since when they come into contact with water they absorb and increase in volume. Over time, there is the desorption of the polymer particle. During cement hydration, when the external relative humidity becomes lower, SAP releases the water inside the cement into the cementitious medium and reduces in volume.

Figure 4 shows the results of **modulus of elasticity** of microconcrete containing 0.3% SAP addition to the reference mixture at 28 days. The use of SAP triggered a 9% increase over the reference microconcrete. The reference mixture obtained a modulus value of 34.9 GPa and the mixture containing SAP, 38.1 GPa. This increase is probably due to advanced cement hydration, which may compensate for the reduction in strength caused by the high porosity left by the polymer (SANTOS, 2016).

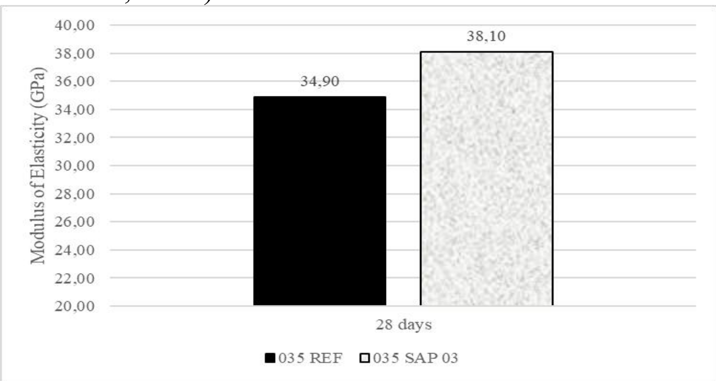

Figure 4: Results of modulus of elasticity at 28 days.

Figure 5 shows the results of **chloride ion migration** test containing 0.3% SAP addition to the reference mixture for the age of 28 days. The reference mixture obtained a migration coefficient value of 2.78 (10^{12} m^2/s) and the mixture containing SAP a value of 1.61 (10^{12} m^2/s). Thus, the value found in the mixture containing SAP is 58% lower than the value found for the reference microconcrete.

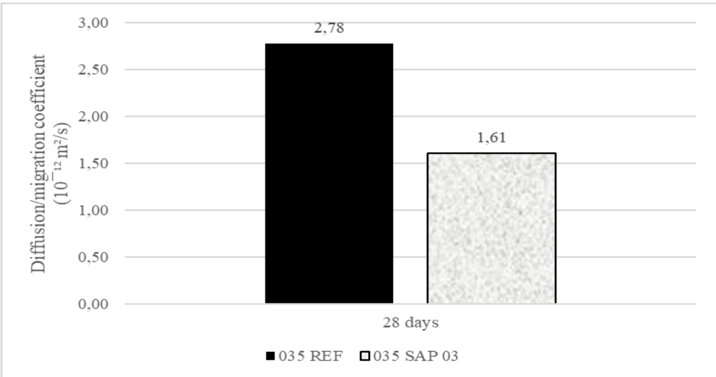

Figure 5: Results of chloride ion migration test at 28 days.

NILSSON, NGO and GJØRV (1998) *apud* NEGREDO (2018) proposed a classification of the concrete resistance to chloride penetration as a function of the diffusion/migration coefficient in the non-steady state regime. By this classification, the reference microconcrete has a very high chloride penetration resistance. Demonstrating that the w/c ratio equal to 0.35 already promotes a pore refinement and a denser microstructure, precisely because it is a high strength concrete.

Figure 6 shows the **capillary absorption results as a function of time** to the two studied mixtures. It is noticeable that in the first hours of the test, the trace containing only SAP had higher absorption values, however over the course of the test, the reference trace reached higher absorptions. When analyzing the absorption after the end of the test, the 035 SAP03 trait, compared to the REF trait, had a 12% lower absorption value.

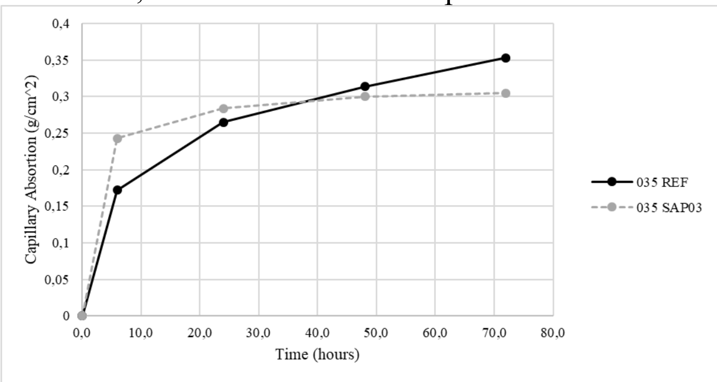

Figure 6: Capillary absorption results as a function of time.

To explain a lower absorption of trace 035 SAP03 when compared to the reference two hypotheses are raised. The first of these is that the additional porosity caused by polymer detachment is poorly interconnected, positively influencing the absorption property, that is, decreasing it by creating a tortuous, disconnected network. The second hypothesis is related to the reduction of self-drying due to the addition of superabsorbent polymer, thus reducing the microfissure of the composite, thus creating a more integral cementitious matrix and thus presenting a lower absorption capacity.

4. CONCLUSIONS

- Regarding mechanical properties, a small reduction (35%) of resistance was observed at the age of 1 day, which is justified by the rapid absorption of SAP upon contact with water. However, at the age of 28 days, the SAP-containing mixture recovered the resistance initially lost, reaching the resistance observed in the reference trait. In addition, adding 0.3% SAP represented a 7% increase in elasticity modulus. Given the above, SAP does not harm such mechanical properties.
- In the capillarity absorption test, the mixture cointaining SAP had a higher performance, that is, it presented lower absorption values (12%). Improvement in chloride ion migration results by adding SAP (42% reduction in diffusion/migration coefficient) reiterates that the addition of polymer results in the maintenance of dense microstructure.
- The voids left by the desorption process form a tortuous, discontinuous and barely permeable net. Therefore, SAP does not harm the durability of microconcretes, promoting even a certain improvement, which should be further investigated and evaluated. It is recommended to perform the accelerated carbonation, electrical and surface resistivity, immersion absorption tests.
- Finally, the data collected in this research reiterate that the most appropriate comparison of SAP effects when added to mixtures as an internal curing agent is in fact using a reference composition with the same total w/c rather than w/c basic, as it is currently widespread in the academic community.
- Therefore, it is observed that dense microstructure, characteristic of CAR, was preserved even in the presence of pores created by the use of SAP, because they are larger and disconnected pores instead of smaller and continuous pores.

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