Influence of Nano-SiO$_2$, Nano-Al$_2$O$_3$, and Nano-ZnO Additions on Cementitious Matrixes with Different Powder and Steel Fibers Content

Ricardo Carmo$^1$, Hugo Costa$^2$, Eliana Soldado$^3$ and Eduardo Júlio$^4$

Abstract

In the study herein presented three types of nanoparticles, with different dosages, were used, namely nano-SiO$_2$, nano-Al$_2$O$_3$ and nano-ZnO, which were combined with different concrete formulations. The main goal is to improve the eco-efficiency of concrete, using simultaneously a partial replacement of Portland cement by industrial by-products and reduced amounts of nanoparticles, aiming to avoid the reduction, or even enhance, both mechanical and durability properties of the final mixtures. The interaction between the steel fibers added to the matrixes and the nanoparticles is also addressed. To analyze the effects of nanoparticles additions in the properties of both mortar and concrete mixtures, several tests were performed in fresh and hardened states. Durability indicators were also evaluated, namely, capillary absorption, immersion water absorption and carbonation depth. It was concluded that an increase of both flexural and compressive strengths can be obtained with nanoparticles additions, but that effect depends on the powder dosages used in the binder matrixes and on the type and dosages of nanoparticles. Regarding the matrixes with steel fibers, no additional gains were obtained combining simultaneously nanoparticles with those fibers. It was also concluded that the nano-ZnO addition significantly delay the concrete hardening and show a negative effect when combined with the steel fibers.

1. Introduction

In last decades, the high and ultra-high-performance concrete has become an important solution for structural engineering. The improvements of concrete properties, especially the increase of compressive strength contributed to increase the load capacity of structures and to create audacious architectural design. The production of high-performance concrete requires a proper selection of the constituents to be used in the mixture, namely: high strength cements, pozzolanic additions, efficient superplasticizers and fibers additions, the last when enhanced tensile and flexural strengths are needed. Furthermore, it is required to optimize the distribution of the fine particles to increase the packing density and to reduce the porosity of the binding paste, which also contributes directly to enhance the concrete durability. However, the majority of those concrete mixtures requires high dosages of cement and silica fume, contributing to the increase not only the production costs but also the ecological footprint.

More recently, the nanotechnology had important advances, creating new perspectives in several fields that can be explored, such as the properties improvement for the materials used in the construction sector (Bhuvaneswari et al. 2011; Zhu et al. 2004). To answer this challenge, several researches were carried out to study the effects of nanoparticles additions on the properties of mortars and concretes matrixes. The nanoparticles have dimensions of 10 to 300 nanometers and its incorporation on the mixture aims to densify the binding paste, increasing its compactness (Zhu et al. 2004; Sanchez and Sobolev 2010). The nanoparticles also have high reactivity due to their high specific surface area, which increases the pozzolanic reaction and the nucleation effect, accelerating the process of cement hydration (Bhuvaneswari et al. 2011; Zhu et al. 2004; Sanchez and Sobolev 2010; Sobolev and Gutiérrez 2005; Jayapalan et al. 2014; Ghafari et al. 2014). Hence, higher amounts of calcium hydroxide are consumed, and more particles of calcium silicate hydrates (C-S-H) are created, increasing the matrix strength (Sobolev and Gutiérrez 2005; Ghafari et al. 2014). Some studies (Ghafari et al. 2014; Qing et al. 2007) also mention that the interfacial transition zone (ITZ) between the aggregates and the paste is improved with the nanoparticles’ addition. These improvements at micro-scale affect the concrete properties at real scale (Sanchez and Sobolev 2010; Jayapalan et al. 2014; Ghafari et al. 2014; Qing et al. 2007; Heikal et al. 2013; Oltulu and Sahin 2011; Jalal et al. 2012; Jo et al. 2007; Zhang et al. 2014; Li et al. 2004; Collepardi et al. 2002; Said et al. 2012). There are several types of nanoparticles 

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$^1$Professor, CERIS and Polytechnic Institute of Coimbra, Rua Pedro Nunes – Quinta da Nora, 3030-199, Coimbra, Portugal. *Corresponding author, E-mail: carmo@isec.pt
$^2$Professor, CERIS and Polytechnic Institute of Coimbra, Rua Pedro Nunes – Quinta da Nora, 3030-199, Coimbra, Portugal.
$^3$Researcher, Polytechnic Institute of Coimbra, Rua Pedro Nunes – Quinta da Nora, 3030-199, Coimbra, Portugal.
$^4$Full Professor, CERIS, Higher Technical Institute, University of Lisbon, Av. Rovisco Pais, 1049-001 Lisboa Portugal.
but the most commonly used on cement-based mixtures is the nano-SiO\textsubscript{2} (Jo et al. 2007; Zhang et al. 2014). The nano-Al\textsubscript{2}O\textsubscript{3}, nano-Fe\textsubscript{2}O\textsubscript{3}, nano-TiO\textsubscript{2} and nano-ZnO were also studied and used on mortar and concrete cementitious mixtures (Heikal et al. 2013; Oltulu and Sahin 2011; Jo et al. 2007; Zhang et al. 2014; Li et al. 2004). Most studies about this topic were focused on the synthesis process of nanoparticles, on the method to disperse them in the binding paste, on the effects of different types and dosages of nanoparticles on the properties of cementitious materials (Sanchez and Sobolev 2010; Ghafari et al. 2014; Heikal et al. 2013; Jo et al. 2007; Zhang et al. 2014). To summarize the studies already carried out about the last issue, the influence of the nanoparticles on mortars and concretes was separated in three categories, i) effects during the fresh state; ii) behavior in hardened state; iii) durability performance. It was observed that nano-SiO\textsubscript{2} addition promotes the cohesion of the cement paste and reduces the bleeding and segregation (Sobolev and Gutierrez 2005; Collepardi et al. 2002; Saïd et al. 2012). The studies by Qing et al. (2007) and Li et al. (2004) pointed out that an addition of 3% and 4% of nano-SiO\textsubscript{2} increases the temperature of cement hydration. Nazari and Riahi (2011) proved that adding nano-ZnO to concrete mixtures leads to a significant decrease on workability. Another study (Behfarnia and Keivan 2013) related with nano-ZnO concluded that this addition retards the setting time and when high percentages are used the hydration process is stopped. However, another investigation (Nivethitha and Dharmar 2016) concluded that ZnO nanoparticles fill the pores and accelerate the hydration process of cement. Concerning the hardened state, a research showed that the drying shrinkage tend to be higher in mixes with nano-SiO\textsubscript{2} than mortars without nanoparticles but containing silica-fume (Sadrmontzazi et al. 2009). It was also found that the nano-SiO\textsubscript{2} addition increases the compressive strength, but that effect is dependent of the mixture used, i.e., is related with the type and percentage of constituents used (Qing et al. 2007; Li et al. 2004). An experimental work (Zhenhua et al. 2016) revealed an increase of the compressive strength and a major influence on the increase of the Young’s modulus using nano-Al\textsubscript{2}O\textsubscript{3} addition. Those results are justified by the increased density of interfacial transition zone and by the porosity reduction, with nano-Al\textsubscript{2}O\textsubscript{3} additions. Some studies point out that the nano-ZnO\textsubscript{2} and nano-ZnO\textsubscript{2} additions increases the mechanical strength of mortars (Nazari and Riahi 2011; Nivethitha and Dharmar 2016), however this trend is not totally clear because in another study (Behfarnia and Keivan 2013) it was also observed that increasing the percentage of nano-ZnO decreases the compressive strength of concrete. The enhancement of concrete durability can also be obtained with small dosages of nanoparticles, as was verified by Du et al. (2014) when dosages varying between 0.3% and 0.9% of nano-SiO\textsubscript{2} were used. Another study on self-compacting concrete confirmed this trend, where the water absorption, capillary absorption and chloride ions penetration are reduced with the addition of nano-SiO\textsubscript{2} (Jalal et al. 2012). The resistance against sulfate attack increases and the water permeability decreases, with the addition of nano-SiO\textsubscript{2} (Du et al. 2014; Ji 2005; Moslemi et al. 2014). The nano-Al\textsubscript{2}O\textsubscript{3} also contribute to a better durability performance, since a study conducted by Kiachehr and Niloofar (2013) concluded that concrete containing nano-Al\textsubscript{2}O\textsubscript{3} improved the freeze-thaw resistance. In general, the concretes with this type of nanoparticles presents better results comparatively to a similar concrete but containing nano-SiO\textsubscript{2}, excepting on compressive strength that was higher in the last. The study performed by Nivethitha and Dharmar (2016), already mentioned, also found that the nano-ZnO addition increase durability of mortars.

2. Research scope and goals

The huge amounts of concrete consumed annually implies high emissions of CO\textsubscript{2} to the atmosphere, mainly due to cement production, and this fact supports the need for developing new processes and strategies to reduce the environmental impact associated to concrete production. The request for more sustainable and ecofriendly materials in construction industry led to researches aiming the partial replacement of cement and the enhancement of structures durability. This strategy of cement reduction is even more important in high and ultra-high-performance concretes because, in general, high cement proportions are used on their formulation.

The studies about nanoparticles addition and its impact on concrete properties are relatively recent and the results do not present a clear trend yet, being necessary more researches to increase the database and to clarify this approach. The main goals of this study are to simultaneously analyze the influence of three types of nanoparticles (nano-SiO\textsubscript{2}, nano-Al\textsubscript{2}O\textsubscript{3} and nano-ZnO), with different dosages, on the properties of cementitious mortars and concretes, both in fresh and hardened states. The experimental program also aims to define the optimal percentage of nanoparticles that should be added to compensate the partial replacement of Portland cement. The durability performance and the interaction between the nanoparticles and the steel fibers was also tested and analyzed, since there is a lack of conclusive studies about this last topic.

3. Materials, mixtures and tests

3.1 Materials

Different mortar mixtures were studied and based on those results several types of concrete were produced, both incorporating nanoparticles produced by Smart Innovation company. Three types of nanoparticles based on oxides synthetization were used, nano-SiO\textsubscript{2}, nano-Al\textsubscript{2}O\textsubscript{3} and nano-ZnO, with densities of 2220, 3950 and 5410 kg/m\textsuperscript{3}, respectively (Fig. 1). The nanoparticles...
were provided in powder with a purity of 99.5%. The nano-Al₂O₃ and nano-ZnO have particle sizes slightly above the nanoscale (just for the larger dimension), 3 – 20 µm and 0.9 – 5 µm, respectively, resulted from the optimization and cost limitation of the production. The diameter of the nano-SiO₂ range between 70 and 150 nm.

On Fig. 1 the nanoparticles are agglomerated due to Van der Waals force, that is a distance-dependent interaction between molecules. This agglomeration affects the efficiency of the nanoparticles essentially because the specific surface area is reduced, influencing their reactivity and the pozzolanic reaction. So, special attention should be given to the dispersion process to maximize the nanoparticles effects. However, the use of micron-sized particles is an option that should be explored in future studies, considering that this size continues to be very small, comparatively with other constituents, and can continue to be used to fill the pores and create the nucleation effect, beyond the pozzolanic effect.

For the mixtures, Portland cement CEM I 52.5 R and different additions were selected, namely fly ash (FA), limestone filler (LF) and silica fume (SF), with the following densities 3160, 2300, 2700 and 2200 kg/m³, respectively. Two siliceous sands were used, both with a density of 2630 kg/m³ (fine sand – S0/1 mm; medium sand – S0/4 mm) and two coarse aggregates were also used, namely, rolled siliceous gravel-G4/8 mm and crushed limestone gravel-C.L6/14 mm, with densities of 2630 kg/m³ and 2660 kg/m³, respectively (Fig. 2). A superplasticizer (MGS 526), ether and polycarboxylates-based with density of 1060 kg/m³, was used to reduce the water required to maintain a proper workability and the compactness of the mixtures in fresh state. Steel microfibers (Dramix® OL 13/0.20), with 13 mm length and 0.20 mm diameter, were used on some mixtures to increase the tensile strength, ductility and fracture energy (Fig. 3). The fibers were added to analyze their compatibility with the nanoparticles and to evaluate the combined effect of using both additions simultaneously.

### 3.2 Mixtures

The mortars were divided in three series concerning to binder quantity, 550, 750 and 950 kg/m³, obviously resulting in different levels of strength. These mortars were used to formulate concretes with different amounts of binder powder and, consequently, with different levels of strength. For each above-mentioned series, four reference mixtures were produced, one with cement and the others with cement and additions replacing the cement. The goal was defining a database of traditional mixtures that can be used as reference and for comparison with mixtures with nanoparticles. The labeling used was: RA, cement only; RB, 20% of cement was replaced by fly ash (FA) addition; RC, 20% of cement replacement by limestone filler (LF) addition; RD, 20% of cement replacement by 15% of limestone filler and 5% of silica fume (SF) additions (Fig. 4). For each series of binder...
The mixtures with 350 kg/m³ of binder were divided in two series, one with 66% of cement and 34% of limestone filler (C350-1) and another with cement only (C350-2). Again, the three types of nanoparticles were added in two percentages, 1% and 2%. The additions’ selection for concretes was made considering the results obtained on mortars. The air content varied between 2.5% and 1.5% and the water/binder ratio was 0.4 and 0.3 for C350 and C500 series, respectively. The mentioned siliceous sands (S0/1 mm and S0/4 mm) and the coarse aggregates (G4/8 mm and CL6/14 mm) were used in the concrete mixtures. All mixtures were formulated based on the methodology proposed by Costa et al. (2010) and using the adjustment to the Faury’s curve. In total, 13 different concretes were produced. The label used to identify each mixture has the main parameters, for example, C500_Al2 is a mixture with 500 kg/m³ of powder and 2% of nano-Al₂O₃ addition (Table 1).

3.3 Tests on fresh and hardened state

The slump flow test of R750 and R950 mortars occurred by gravity and the flow was determined measuring the average diameter of the spread sample (Fig. 5a). On R550 mortars, the consistency was measured using the slump test table, because those mortars had a plastic consistency (EN 1015-3 1999). On both tests, the diameter of the spread was measured in two orthogonal directions to calculate the average spread. The bulk density of the mortars was determined using a container self-compacting high-performance concrete, corresponding to a powder dosage of about 600 kg/m³, when the coarse aggregates are incorporated.

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with 1.0 liter (Fig. 5b) and the aerometer was used to measure the air content of each mixture (Fig. 5c). The determination of the air content was crucial to define and control the mixtures formulation. The air content may affect significantly the mechanical and durability properties of the mixtures, and depends on the constituents and parameters considered for the binder matrix. In each series, to control all variables, the water/binder ratio, the consistency and the air content were kept constant.

The flexural tests on mortars were performed on prismatic specimens with 40×40×160 mm³ using a universal tension-compression equipment, according to the EN 1015 (1999). Three specimens were used to determine the average tensile flexural strength, $f_t$. On concrete mixtures, four specimens with 100×100×200 mm³, for each type of concrete, were used to perform the splitting test and to determine the tensile strength. The compressive strength, $f_c$, on mortars was determined using the resulting halves of the flexural test, corresponding to six specimens for each age and mixture. The test was carried out using the same equipment and a specific standard device with 40×40 mm² plates, which allowed to apply the compression force on specimens until failure (EN 1015 1999). The tests to determine the compressive strength on concrete were performed in a hydraulic press with a maximum capacity of 3000 kN. The load was applied at a constant rate of 13.5 kN/s in cubes with 150 mm edge, according to EN 12390 (2009). The Young’s modulus of concrete was determined according to the LNEC specification E 397 (1993), using prismatic specimens with 100×100×400 mm³. The load was applied in cycles between two levels and the deformations in 200 mm length were measured using a mechanical strain gauge.

### 3.4 Tests regarding durability performance

The water capillary absorption is a simple test that allows to know some characteristics of concrete matrix, namely, the diameter of the pores. The water goes into the porous network due to pressure differences between the exterior water surface and the surface of the porous network. The capillary absorption coefficient, $S$, is determined based on the absorption velocity of the unsaturated concrete. This test was performed according to the LNEC specification E 393 (1993), using three prismatic specimens with 100×100×200 mm³ for each concrete mixture. To calculate the capillary coefficient, it was necessary to measure the amount of absorbed water per unit area in contact with water. So, the weight of specimens, when they were totally dry and after being in contact with water during a different number of hours, was recorded. The capillary height was also measured at those different instants and perpendicularly to the face in contact with the water (Fig. 6a).

The concrete permeability is related with the open porosity, i.e., with the voids linked with each other through small channels. One way to analyze this prop-

| Constituents | C350-1 | C350-2 | C500 |
|--------------|--------|--------|------|
| CEM I 52.5R  | 230    | 350    | 500  |
| Limestone filler | 120    | 4       | 5    |
| nano-SiO₂    | -      | 4      | -    |
| nano-Al₂O₃   | -      | -      | -    |
| nano-ZnO     | -      | -      | -    |
| Superplasticizer | 0.9    | 2.1    | 6.3  |
| S0/1mm       | 227    | 239    | 138  |
| S0/4mm       | 681    | 718    | 781  |
| G4/8mm       | 187    | 190    | 126  |
| CL6/14mm     | 755    | 770    | 724  |
| Effective water | 161    | 140    | 144  |
| W/C ratio    | 0.70   | 0.40   | 0.40 |
| W/Binder ratio | 0.40   | 0.40   | 0.40 |

### Table 1 Constituents proportion for 1 m³ [kg/m³].

![Fig. 5 Characterization of mortars in fresh state: (a) flow test; (b) density; (c) air content.](image)
tery is through the water absorption at atmospheric pressure. In this study, this test was performed according to the LNEC Specification E 394 (1993), using three cubic specimens with 100 mm edge for each type of concrete (Fig. 6b). The water absorption by immersion is calculated in percentage and corresponds to the difference of the specimens’ weight between being immersed in water and in dry state (the drying was carried out in an oven at 105°C).

To analyze the effect of nanoparticles addition on the carbon dioxide penetration, the accelerated carbonation test was performed, following the LNEC Specification E 391 (1993) and the recommendations of NT Build 357 (1989). This test consists in expose the specimens, during a certain period of time (28, 56 and 90 days), to an environment that is favorable to the accelerated carbonation. In this study a specific chamber was used to create an environment with high concentration of carbon dioxide, 5% and relative humidity of 65% (Fig. 6c). It was required to produce several cylindrical specimens with 100 mm diameter and 50 mm thickness. After expose the specimens to that environment, the carbonation depth was measured, using a phenolphthalein solution.

4. Results and discussion

4.1 Flowability

Figure 7 shows the flowability of the mortars without and with nanoparticles. In general, increasing the binder dosage increases the spreading, despite the reduction of water/binder ratio. The superplasticizer has also an important influence on this behavior, since mixtures with higher cement content allow to use a higher dosage of superplasticizer without segregation. Consequently, it was possible to reduce the W/C ratio and simultaneously ensure a high flowability on those mixtures. So, the high flowability of the mixtures RA750 and RA950 was achieved with some adjustments of the superplasticizer, using respectively 1.25% and 1.5%, in relation to the binder mass. The addition of nanoparticles implied the necessity to increase the superplasticizer dosage to maintain the same air content and similar workability (Fig. 7). In preliminary tests, before the adjustment of the superplasticizer, the mixtures with nano-ZnO addition presented a significant loss of workability, probably due to the elongated shape of those particles. On mixtures with nano-SiO₂ and nano-Al₂O₃ additions, the superplasticizer was also increased around 0.1%, relatively to the reference mixtures, to maintain the target air content.

For the same levels of binder quantity and for each type of nanoparticles, the variation of the percentage of the added nanoparticles did not result in a significant variation of the slump flow. However, when metallic fibers were added the flowability and workability was reduced, as can be seen in RA950 series with ZnO addition (Fig. 8). Mixtures RA950_Zn1 with 1% and 2% of fibers registered a spread reduction of 7.5% and 11.7%, respectively, in mixtures RA950_Zn2 that reduction was 5.9% and 16%, respectively.
4.2 Mechanical properties of mortars

4.2.1 Traditional additions

The mean values of flexural and compressive strengths, at 28 days, of the mixtures RA, RB, RC and RD are shown in Table 2. As already mentioned, the mixtures were divided in three series concerning quantity of binder, which resulted in different flexural and compressive strengths. In most mixtures the compressive strength reduced when cement was replaced by traditional additions. This reduction was higher in mixtures with lower binder dosage (series 550), registering losses of around 15%. In series 750, the strength loss was lower (up to 5%) and in series 950 was neglectable, so the mixtures with limestone filler (RC) or limestone filler combined with silica fume (RD) were those that revealed higher efficiency. The flexural strength follows the opposite behavior, since series 550 showed a reduced loss of strength (about 5%) and series 750 and 950 had a higher strength reduction, up to 60% in series 950 with combined limestone filler and silica fume additions. For a better comparison and understanding, the flexural and compressive strengths are related with the reference mixture RA (Fig. 9).

| Quantity of binder kg/m³ | 550 | 750 | 950 |
|--------------------------|-----|-----|-----|
| Different additions (*)   | RA  | RB  | RC  | RD  | RA  | RB  | RC  | RD  |
| Mean flexural strength (MPa) | 9.5 | 8.8 | 9.1 | 11.8 | 10.7 | 10.8 | 6.7 | 16.8 |
| Mean compressive strength (MPa) | 61.7 | 55.2 | 51.8 | 52.9 | 80.6 | 75.4 | 77.0 | 81.3 | 92.4 | 90.1 | 92.3 | 95.2 |

(*) RA (100%CEM); RB (80%CEM+20%FA); RC (80%CEM+20%LF); RD (80%CEM+15%LF+5%SF)

Fig. 9 Strength ratios between matrices with traditional additions and reference, at 28 days: (a) mean flexural strength and (b) mean compressive strength.

4.2.2 Nanoparticles additions

The ratios between the strength (flexural and compressive) of mixtures with nanoparticles and the reference mixture, RA, are presented in Fig. 10. The results can be analyzed considering the following parameters: i) quantity of binder; ii) type of nanoparticle and iii) percentage
of nanoparticles addition. Surprisingly, the flexural strength of mixtures with nano-ZnO and nano-SiO$_2$ additions was lower than the reference, in certain cases that loss reached 48%. This reduction was more evident on mixtures of series RA950. In mixtures with nano-Al$_2$O$_3$, despite the 20% of flexural strength reduction in some mixtures, the series RA550 had a 15% gain both for 1 and 2% addition. Regarding to the compressive strength, in general, the addition of nanoparticles originated gains of strength up to 15%, being those increases more consistent on mortars with 750 kg/m$^3$ of cement (series 750). The matrices RA550_Zn2 and RA750_Si2 revealed the highest increase.

4.2.3 Nanoparticles and steel fibers additions

As expected, adding steel fibers increased the flexural strength and that increase is related with the dosage of fibers (Fig. 11a). For R550 series, 1% of steel fibers addition increased significantly the flexural strength, 100%, but when the steel fibers addition changed from 1 to 2% that gain was lower, increasing only 25%. However, the influence of steel fibers varied with the quantity of cement used: on R750 series, the increase of flexural strength had practically a linear trend with the percentage of fibers used and; on series R950, the increased strength was more evident for matrixes with 2% of fibers. The compressive strength also increased with the steel fibers addition, but that influence was lower comparatively with the flexural strength. Even so, the increase ranged between 25 to 40% and 45 to 60%, when 1 and 2% of fibers additions were used, respectively (Fig. 11b).

Figure 12 shows the ratio of strength (both flexural and compressive), at 7 days age, between the mixtures with 1 and 2% of nanoparticles combined with 1 and 2% of steel fibers and the reference mixtures. The mixtures with 1% and 2% of ZnO addition presented a very reduced strength of both flexural and compressive, since these mixtures showed an extremely slow hardening, justifying this way such strengths at young age. The mixtures with nano-Al$_2$O$_3$ and nano-SiO$_2$ additions showed better results, generally higher than the reference mixtures. However, the strength variation was very small revealing that the combined effect of fibers and nanoparticles has no relevance. Even so, certain cases with positive results were recorded, where increases of flexural strength of 26% and 21% were registered for RA750_Si1_F1 and RA950_Si1_F2, respectively. The compressive strength presented also some gains, especially the mixtures with nano-Al$_2$O$_3$, presenting an increase of circa 6%.

Considering the same strength ratios between mixtures, but now at 28 days (Fig. 13), it was confirmed that, despite there are some positive effects of the nano-Al$_2$O$_3$ and nano-SiO$_2$ additions on the strength, some losses of strength are also visible. Although the results present some dispersion, mixtures with 2% of steel fibers show a trend to be the best option to be combined with matrixes with 950 kg/m$^3$ of cement: the R950 with 2% of nano-Al$_2$O$_3$ presented an increase of 7% and 12% on flexural and compressive strengths, respectively; the R950 with also 2% of nano-SiO$_2$ combined with 2% of fibers, revealed an increase of the flexural and compressive strengths of 23% and 14%, respectively. This effect was not so clear in mixtures with lower quantity of binder, eventually because the reduction of bond between this type of pastes and the fibers was higher than the effects provided by the nanoparticles’ addition on the interior of the matrix (high reactivity and nucleation effect). It should also be pointed out that, in general, there is no significant influence of the combined effect of nanoparticles with fibers, relatively to the reference mixtures with steel fibers, RA_f. The nano-ZnO is the exception, since some mixtures with nano-ZnO addition present the worst results, with losses of strength up to 23% when 2% of nano-Zn is combined with 2% of fibers. It is noticeable that strength had tended to decrease with the increase of fibers on mixtures with nano-ZnO, which can eventually be explained by a reaction between the ZnO and the fibers cover. To clarify these results and to check if that reaction occurred, additional chemical tests on future research are required.

![Fig. 11 Strength of mortars with steel fibers additions at 28 days: (a) mean flexural strength and (b) mean compressive strength.](image-url)
Fig. 12 Strength ratios between matrixes with nanoparticles and steel fibers additions and the corresponding references with fibers, at 7 days: (a) and (c) mean flexural strength; (b) and (d) mean compressive strength.

Fig. 13 Strength ratios between matrixes with nanoparticles and steel fibers additions and the corresponding references with fibers, at 28 days: (a) and (c) mean flexural strength; (b) and (d) mean compressive strength.
4.3 Concrete with nanoparticles

4.3.1 Mechanical properties

The main mechanical properties of concrete with nanoparticles additions, at 28 days, are presented in Table 3. The overall trend is not clear because the nanoparticles addition had a negligible effect on concrete C350-1 and C500. But contrarily to those concretes, the properties of concrete C350-2 had a clear improvement with the addition of all types of nanoparticles, probably due to the quantity of used Portland cement in this concrete, which may represent an optimal proportion. So, on concrete mixtures, the effect of nanoparticles seems to be more notable for dosages of cement around 350 kg/m$^3$.

Still related to this concrete, it can also be pointed out that the addition of 2% of nano-SiO$_2$ produced slight better results than the 2% of nano-Al$_2$O$_3$, increasing the compressive and tensile strengths and the Young's modulus in 9, 26 and 2%, respectively. The nano-ZnO addition had also a positive influence but only in compressive strength, which increased 14% relatively to the reference concrete. The nano-SiO$_2$ and nano-Al$_2$O$_3$ additions increased significantly the Young's modulus, up to 25%, where the increase percentage depended on the considered powder dosage.

4.3.2 Durability

The water absorption by capillarity is proportional to the square root of time and lower values correspond to a better performance. The absorption coefficient, S, was computed through a linear regression using the measured points, being S the slope of the straight line (Eq. 1), where: A is the amount of absorbed water per area in contact with water, in mg/mm$^2$; $a_0$ is the water initially absorbed by the pores in the contact surface, in mg/mm$^2$, and; S is the absorption coefficient in mg/(mm$^2$×min$^{0.5}$).

$$A = a_0 \times S t^{0.5} \quad (1)$$

The equations determined for each concrete are very near to the experimental points, because the correlation coefficients, $R^2$, are high, varying between 0.93 and 0.98 (Table 4 and Fig. 14). All S coefficients are below to 0.1 mm/min$^{0.5}$, which corresponds to a high-quality concrete.

Table 3 Concrete properties with nanoparticles in hardened state, at 28 days.

|          | C350-1 | C350-2 | C500 |
|----------|--------|--------|------|
|          | Ref    | Si 2%  | Al 2% | Ref    | Si 1%  | Al 2%  | Zn 1% | Ref    | Si 1%  | Al 2%  | Zn 1% |
| $f_{cm}$ (MPa) | 41.7   | 41.2   | 41.1  | 67.8   | 71.2   | 73.7   | 68.1   | 77.2   | 96.0   | 88.3   | 94.8   | 88.3   | 91.3   |
| $f_{ctm}$ (MPa) | 4.8    | 4.1    | 4.5   | 5.7    | 6.7    | 7.2    | 6.9    | 6.2    | 6.5    | 6.9    | 7.4    | 8.2    | 7.4    |
| $E_{cm}$ (GPa)  | 38.7   | 49.2   | 41.9  | 51.4   | 53.8   | 52.6   | 52.6   | 51.4   | 50.3   | 56.5   | 51.4   | 58.0   | 53.2   |

Table 4 Results of capillary and water absorption tests.

|          | C350-1 | C350-2 | C500 |
|----------|--------|--------|------|
|          | Ref    | Si 2%  | Al 2% | Ref    | Si 1%  | Al 2%  | Zn 1% | Ref    | Si 1%  | Al 2%  | Zn 1% |
| Capillary ascent at 72h (mm) | 11.9   | 9.6    | 11.6  | 10.3   | 13.3   | 11.7   | 11.0  | 14.4   | 16.4   | 23.2   | 24.8   | 26.1   | 18.1   |
| $S$ (mg/(mm$^2$×min$^{0.5}$)) | 0.04   | 0.06   | 0.04  | 0.04   | 0.03   | 0.02   | 0.03  | 0.02   | 0.004  | 0.02   | 0.01   | 0.02   | 0.02   |
| $R^2$   | 0.97   | 0.98   | 0.98  | 0.95   | 0.98   | 0.94   | 0.95  | 0.97   | 0.94   | 0.98   | 0.93   | 0.98   | 0.98   |
| Water abs. | w (%)  | 8.4    | 9.4   | 8.2   | 6.8    | 9.9    | 9.8   | 9.5   | 8.3    | 8.9    | 9.9    | 9.4    | 9.3    | 9.3    |

Fig. 14 Water absorbed by capillarity: (a) series C350-1; (b) series C350-2.
and the differences between them are insignificant. These results can be understood taking into consideration that all mixtures had a low, and approximately the same, air content but mainly because the water/(binder powder) ratio is low, 0.4 and 0.3 for C350 and C500, respectively. So, based on these results, it can be concluded that the nanoparticles additions have a lower effect in the open porosity of the matrixes than the air voids and the water/(binder powder) ratio defined. The water absorption test at atmospheric pressure corroborated this trend.

The results of the accelerated carbonation tests presented in Table 5 show that the cement quantity has higher influence on the diffusion of the carbon dioxide into concrete than the effect of nanoparticles addition. Considering these results, it can be stated that the type and dosage of nanoparticles addition does not significantly change the microstructure of the paste. Nevertheless, considering the carbonation depth of C500 with nano-ZnO addition, it is quite visible that this type of nanoparticles influences negatively the carbonation resistance. This result seems to indicate that the hydration products are affected by the nano-ZnO, particularly, when the water/cement ratio is 0.3, but more research is needed to clarify this issue.

### 5. Conclusions

From the experimental study herein presented the following main conclusions can be drawn:

1) The steel fibers addition reduces significantly the flowability and workability of the mixtures, but this effect can be compensated with small adjustments of the superplasticizer dosage.

2) The traditional additions, principally limestone filler and this combined with silica fume, present a good efficiency as cement replacement, mainly on matrixes with high powder dosages (750 and 950 kg/m³), considering the results of compressive strength.

3) The effects of nanoparticles addition on both flexural and compressive strengths do not follow the same trend. The addition of nanoparticles can increase up to 15% the compressive strength, especially when to 2% of nanoparticles are used. This means that, if the goal is to produce a concrete with a certain target for the compressive strength, the nanoparticles can be used to reduce the amount of cement required, comparatively to mixtures without nanoparticles, corroborating the studies carried out by Bahadori and Hosseini (2012) and Sadeghi-Nik et al. (2017).

4) The reduction of the flexural strength can reach 25% and 33% on matrixes with nano-ZnO and nano-SiO₂, respectively. The lack of correlation between flexural and compressive strengths, especially with regard to the effect of nano-ZnO, was not expected, because on conventional concretes those strengths are usually interrelated. It seems that nano-ZnO affects the process of cement hydration, namely, the reaction products calcium-silicate-hydrate and calcium hydroxide, changing the microstructure of the matrixes in a way that influences negatively the flexural strength.

5) The mechanical strengths, flexural and compressive, increase with the steel fibers addition and with its dosage. No additional gain is identified combining simultaneously nanoparticles and steel fibers. However, on early ages, nano-ZnO addition significantly delay the hardening.

6) The mechanical properties of concretes with nanoparticles also show some dispersion. The best results occur when 350 kg/m³ of cement and 2% of nano-SiO₂ or of nano-Al₂O₃ are used.

7) Based on the durability results, it is proved that 1% and 2% of nanoparticles additions is not sufficient to significantly reduce the open porosity of the binder matrix. It can be concluded that the nanoparticles additions have a lower effect in the open porosity of the matrixes than the air content and the water/binder ratio, particularly, when both parameters are low.

Considering the obtained results, it is advisable to carry out more tests aiming to: i) improve the statistical significance of the results; ii) analyze other types of nanoparticles and other synthesis processes, since both factors can significantly influence the results; iii) study the effects of nano-ZnO on the hydration reactions of the cement, particularly, when steel fibers are used and when low water/cement ratio, around 0.3, is defined for the mixtures.

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| Days | Ref 1% | Si 2% | Al 2% | Ref 1% | Si 2% | Al 2% | Zn 1% | Ref 1% | Si 2% | Al 2% | Zn 1% |
|------|--------|-------|-------|--------|-------|-------|-------|--------|-------|-------|-------|
| 28   | 11.0   | 11.4  | 10.2  | 1.4    | 2.7   | 2.7   | 2.2   | 3.2    | 0     | 0     | 0     | 3.8   |
| 56   | 14.8   | 18.5  | 15.7  | 2.1    | 2.9   | 3.5   | 2.8   | 3.6    | 0.4   | 0.7   | 0     | 3.8   |
| 90   | 19.5   | 23.9  | 21.3  | 2.9    | 4.3   | 5.7   | 4.6   | 5.0    | 0     | 0     | 0     | 4.6   |
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