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Experimental study of the mechanical properties and durability of self-compacting mortars with nano materials (SiO_2 and TiO_2)

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HIGHLIGHTS

- Updated research on the application of nano materials (SiO_2 and TiO_2) in the production of self-compacting mortars.
- Feasibility analysis of nano materials in self-compacting mortars mixes.
- Analysis of the properties of self-compacting mortars with nano materials in fresh and hardened states.
- Compressive and flexural strength, porosity, water absorption and carbonation penetration are discussed.

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ABSTRACT

Cement, as well as the remaining constituents of self-compacting mortars, must be carefully selected, in order to obtain an adequate composition with a granular mix as compact as possible and a good performance in the fresh state (self-compacting effect) and the hardened state (mechanical and durability-related behavior). Therefore in this work the possibility of incorporating nano particles in self-compacting mortars was studied. Nano materials are very reactive due mostly to their high specific surface and show a great potential to improve the properties of these mortars, both in mechanical and durability terms.

In this work two nano materials were used, nano silica (nano SiO_2) in colloidal state and nano titanium (nano TiO_2) in amorphous state, in two types of self-compacting mortars (ratio binder:sand of 1:1 and 1:2). The self-compacting mortar mixes have the same water/cement ratio and 30% of replacement of cement with fly ashes. The influence of nano materials nano-SiO_2 and nano-TiO_2 on the fresh and hardened state properties of these self-compacting mortars was studied. The results show that the use of nano materials in repair and rehabilitation mortars has significant potential but still needs to be optimized.

1. Introduction

Fly ash (FA) is one of the most used industrial wastes in the cement and concrete industry as an addition and they have many advantages, such as a reduction of cement consumption, an increase of concrete's workability, and a potential increase of concrete's durability and mechanical strength at later ages. However, the retarding effect on the evolution of mechanical strength in the first ages may, in some cases, represent a significant drawback. Even though this effect may be favorable for some applications, such as casting of large volume elements [1], in most cases the effect is uncalled for. In order to compensate it many methods have been experimented to accelerate the hydration process in the early ages in binary mixes of cement and fly ash including grinding processes of the components [2], chemical activation of the fly ash [3], hydrothermal treatments [4,5], among others.

Recently nano silica (nano-SiO_2) was introduced in the study of mortars and/or concrete and various studies have demonstrated that, even at small contents, it can improve the mechanical properties of these cementitious mixes [6]. According to Nazari and Riahi [1], it was possible to increase the compressive strength by 70% with the addition of 4% of nano-SiO_2 (in cement mass). Similarly Shih et al. [6] demonstrated that an addition of 0.6% of colloidal nano-SiO_2 can increase the compressive strength of cement pastes by 43.8%. Li et al. [7] refer that, with the addition of 3% and 5% of SiO_2 in cement-based mortars, the 28-day compressive strength increases by 13.8% and 17.5% respectively. Zhang et al. [2] e Li

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et al. [7] refer significant improvements of the mechanical properties of cementitious mixes with large replacement of cement with pozzolanic additions such as fly ash and/or blast furnace slag, together with nano-SiO_2.

However there are two important problems to be considered related to the use of nano-SiO_2 in powder. The first refers to the particles dispersion at the mixing stage of the mortars or concrete and the second to the loss of workability due essentially to the high specific surface of the particles. It is stressed that in the works referred to in the previous paragraphs mechanical dispersion techniques or ultra-sounds were used and in some cases the authors refer the application of systems of treatment of the particles surface. An inadequate dispersion may cause a least favorable of the compressive strength [8], among other effects.

When considering the use of binary mixes of fly ash and nano-SiO_2, the individual benefits of each of them can certainly contribute to offset the problems of the other: reactive nano-SiO_2 can improve the mechanical properties in the early ages (unlike fly ash) while fly ash can improve the workability (contrarily to nano-SiO_2). As for the dispersion problem of the nano-SiO_2 powder particles, it is possible to replace them by water-based mixtures of colloidal nano-SiO_2.

With the evolution of the study of nano materials applied on construction materials, nano titanium (nano-TiO_2) has been widely studied in various fields including the elimination of residual waters and exhaustion gases and the improvement of the mechanical and durability properties of concrete [4]. Nazari and Riahi [1] studied the influence of various nano materials on the mechanical performance and microstructure of concrete. These authors refer an increase of density of concrete with a significant improvement both at the mechanical and durability level as the content of nano-TiO_2 in the mix increases. They justify these trends with an acceleration of the formation of calcium-silicate-hydrate gel (C–S–H) due to greater volume of calcium hydroxide ($Ca(OH)_2$) crystals especially in the first ages. Li et al. [2] and Zhang et al. [9] demonstrate that the use of nano-SiO_2 and nano-TiO_2 causes a significant improvement of the refinement if concrete's porous structure, increasing its resistance to chlorides penetration. Fujishima et al. [8] also studied the influence of the use of nano particles on the mechanical strength of concrete and obtained similar results to those of Li et al. [2] and Zhang et al. [9]. The excellent photo-catalytic properties of nano-TiO_2 must also be highlighted: when incorporated in concrete production, they can contribute to the decomposition process of pollutant gases in the atmosphere, simultaneously improving the performance of concrete.

2. Literature review

Jawahar et al. [11] investigated the use of the mini slump cone test to optimize the super plasticiser (S_P) and viscosity modifying agent (VMA) contents in SCMs. The SCMs mixes had 35% replacement of cement with class F FA and two different water/cement (W/C) ratios by weight: 0.32 and 0.36. It is observed that, for the same cementitious proportions, the optimum S_P content was the same for the mixes with 0.32 and 0.36 W/C. Mortar mixes with 0.36 W/C showed an increase in the rate of flow, i.e. lower viscosity at each level of S_P content than that of mixes with 0.32 W/C. It is also observed that a minimum VMA content was required in the mortar mixes with 0.36 W/C in order to stop bleeding, whereas no VMA was required in the mortar mixes with 0.32 W/C as no bleeding was observed at the optimum S_P content. In practical terms, it was seen that the mini slump cone test is the best choice for SCM tests to evaluate the mortar spread and its viscosity (T_{20}). Also, it was seen that the sand content in mortar does not affect the optimum S_P content (saturation point) when the cementitious proportions remain constant.

Nepomuceno and Oliveira [13] reported an experimental study on the mortar phase for SCC. A series of SCMs were produced with similar flow properties, measured by spread and mini V-funnel tests, adequate to produce SCC. The water content and the modified carboxylic S_P content were determined experimentally for each mortar. Different contents of cement replacement materials were used in binary blends, each one combining one of the two types of cement with one of the three mineral additions selected: limestone filer (LF), granite filler (GF) and FA. Each of the binary blends of powders was combined in five proportions in volume with the fine aggregate (V_P/V_s). Mortars were tested for compressive strength at 28 days and this value was related to the water/cement ratio, the percentage of cement replacement materials, and the V_P/V_s parameter. The analysis revealed the possibility of establishing adequate mortar parameters to obtain simultaneously self-compatibility and the required compressive strength of self-compacting concrete.

Porro et al. [14] mentioned that the use of Nano-SiO_2 particles increases the compression strength of cement pastes. They also stated that this phenomenon is not due to the pozzolanic reaction, because calcium hydroxide consumption was very low but, instead, to the increase of silica compounds that, in turn, contribute to a denser microstructure.

Hui et al. [15] studied the mechanical properties of nano-Fe_2O_3 and nano-SiO_2 cement mortars were experimentally studied. The experimental results showed that the compressive and flexural strengths at 7 and 28 days of the cement mortars mixed with the nano-particles were higher than those of a plain cement mortar. Therefore, it is feasible to add nano-particles to improve the mechanical properties of concrete. The SEM study of the microstructures between the cement mortar mixed with the nano-particles and the plain cement mortar showed that the nano-Fe_2O_3 and nano-SiO_2 filled up the pores and reduced the Ca$(OH)_2$ compound between the hydrates. These mechanisms explained the supreme mechanical performance of the cement mortars with nano-particles.

Arefi et al. [16] did research on the compressive, tensile and flexural strength of cement mortar containing Al_2O_3 nanoparticles at 1%, 3% and 5% by weight of cement. The results show that the mechanical properties of samples containing 1% and 3% Al_2O_3 nanoparticles are better than those of the ordinary cement mortar. But, by increasing Al_2O_3 nanoparticles to 5%, the mechanical properties decreased severely. A SEM study of the microstructure of cement mortar containing nanoparticles and ordinary cement mortar showed that Al_2O_3 nanoparticles reduced the $CaOH_2$ crystals, filled the pores and increased the density of cement mortar.

Oltulu and Sahin [17] studied the addition of both nano-SiO_2, nano-Al_2O_3 and nano-Fe_2O_3 powders and their binary and ternary combinations on the compressive strength and capillary water absorption of cement mortars containing FA. The powder content used corresponded to 0.5%, 1.25% and 2.5% of the binder for all mixes. The authors concluded that the addition of any single type of oxide powders at 1.25% increased the compressive strength of the mortars more efficiently than the other proportions. The use of NS + NA powders at 1.25% maximized the compressive strength relative to the control specimen. For all binary powder combinations, the rate of increase in strength reached generally their peak at 28 days and gradually decreased through aging. Of all the groups, the best results were obtained in the mortars added with NS + NA + NF powders at 1.25%. For this specific mortar, 7–32% increase in compressive strength and 14% decrease in capillary absorption occurred relative to the control specimen.

Meng et al. [18] studied the effect of nano-TiO_2 on the mechanical properties of cement mortar. The test results indicated that

when cement was replaced with nano-TiO_2, the strength of the cement mortar at early ages increased a lot and the fluidity and strength at later ages decreased significantly. It seems that the main reason for the improvement of strength is the decrease and modification of the orientation index for the nucleus function, rather than the increasing amount of hydration products. They also concluded that, by adding superplasticizer and slag powder to the cement mortar, the fluidity and strength at older ages of the cement mortar with nano-TiO_2 changed.

Nazari et al. [19] investigated the compressive strength and workability of concrete by partial replacement of cement with nano-phase TiO_2 particles. TiO_2 nanoparticles with an average diameter of 15 nm were used with contents of 0.5%, 0.1%, 1.5% and 2.0% by cement weight. They concluded that the use of nano-TiO_2 particles up to a maximum replacement level of 2.0% produces concrete with improved strength. However, the maximum strength of concrete was gained at 1.0% of cement replacement. The workability of fresh concrete decreased when the content of TiO_2 nanoparticles increased. They also concluded that partial replacement of cement with nano-phase TiO_2 particles improves the compressive strength of concrete but decreases its workability.

3. Experimental programme

The main objective of this work is to study the strength and durability properties of self-compacting mortars (SCMs) with incorporation of nano silica (nano-SiO_2) and nano titanium (nano-TiO_2) in 1:1 and 1:2 mixes (ratio binder:sand of 1:1 and 1:2). For this purpose, $4 \times 4 \times 16$ cm specimens were cast with various contents of nano-SiO_2 (colloidal state) and nano-TiO_2 (amorphous state) for compressive and flexural testing of 1:1 and 1:2 SCMs. Specimens with 100 mm diameter and 300 mm length were cast to test durability properties like porosity, water absorption and carbonation.

3.1. Materials

The following materials were used: cement complying with NP EN 197-1 [20] (cement type I-42.5 R with specific gravity of 3.14), whose chemical composition and grading are provided in Tables 1 and 2; a mineral addition – fly ash (FA) – complying with NP EN 450-1 [21] and NP EN 450-2 [22] with specific gravity of 2.30, whose chemical composition and grading are provided in Tables 1 and 2; two siliceous sands complying with NP EN 12620 [23], one coarse (0/4) with specific gravity of 2.55, fineness modulus of 3.70 and water absorption of 1.10% and one fine (0/1) with specific gravity of 2.58, fineness modulus of 2.03 and water absorption of 0.70%; a third-generation high-performance water-reducing admixture (S_P) complying with NP EN 934-1 [24] and NP EN 934-2 [25] (a modified polycarboxylic high-range water-reducing admixture in liquid form with a density of 1.07); tap water complying with NP EN 1008 [26].

In this study, two types of nano materials, nano-SiO_2 (colloidal state) and nano-TiO_2 (amorphous), with various contents were used. The specific surface area of nano-SiO_2 is 260 m^2/g and that of nano-TiO_2 is 50 m^2/g. The average particle size of both nano materials is 20 nm. The pH of the nano-SiO_2 solutions is between 9.4 and 10.4 whereas for nano-TiO_2 it is 3.4–4.5.

Table 1
Chemical composition of the raw materials.

Chemical composition of raw materials (%)*	CEM I	FA
Al_2O_3	5.24	24.70
$CaCO_3$	–	–
CaO (free)	0.81	0.30
CaO (total)	62.71	2.63
Cl^-	0.01	<0.01
Fe_2O_3	3.17	5.40
K_2O	–	1.11
MgO	2.23	1.01
Na_2O	–	0.89
SiO_2	19.59	54.70
SO_3	3.13	1.38
TiO_2	–	–
Insoluble residue	1.37	–
Loss of ignition	2.94	5.10

* These data are indicative values provided by the manufacturers.

Table 2
Grading of the raw materials.

Particle size, in microns*	Passing %	
	CEM I	FA
1000	100	100
100	98	96
10	38	45
1	5	2
0.1	0	0

* These data are indicative values provided by the manufacturers.

3.2. Mix proportions

In this work two self-compacting mortars were selected (ratio binder:sand 1:1 and 1:2). As seen in Table 3, to each of these mortars nano-TiO_2 in amorphous state was added at 0.50%, 0.75% and 1.00% of cement mass (NTA, NTB and NTC respectively). Similarly nano-SiO_2 in colloidal state (30% of nano silica) was added at 0.75%, 1.50% e 3.00% of cement mass (NSP, NSQ and NSR respectively). In the second group of mortars it was necessary to compensate the apparent mixing water content due to the colloidal state of the addition. All the SCM mixes had the same effective W/C ratio and 30% of replacement of cement with fly ash.

3.3. Mortar mixture procedure

As found out by various authors [13,27–31], the mixing procedure has a significant influence on the self-compacting mortars fresh-state properties, namely on the optimization of the use of superplasticizers. They confirmed that the mixing time until the superplasticizer is added is not irrelevant to its efficiency and consequently it alters the self-compatibility conditions of these mortars.

Based on the analysis of the proposals of these authors and bearing in mind the experience collected so far, the mixing procedure adopted by Domone [27] and Jin and Domone [28] was selected, very similar to the one used by Nepomuceno [13] and Liu [29].

The complete mixing sequence takes 10 min and starts with the insertion of the fine aggregates (sands) and fine materials and their mixing for approximately 1 min. The first water fraction, corresponding to 80% of the whole mixing water, is then slowly added, without interrupting the mixing process for a further 1 min, in order to optimize the homogenization. The second water fraction (the remaining 20%), mixed with the superplasticizer, is also slowly added without interrupting the mixing process. The mixing proceeds at it normal speed for another 5 min. The mixer is then switched off and the mix rests for 2 min. If necessary, this phase can be used to clean the mixer's paddle. Before starting the fresh-state tests, the mix restarts for 1 min, always at the normal speed.

3.4. Test methods and sample preparation

3.4.1. Mini-cone slump-flow test for SCM

The determination of the slump-flow average diameter through the mini slump-flow test using a conical mould allows determining the G_m parameter. Given that there are still no normative references for this test, the choice was to follow the test procedures used by Nepomuceno and Oliveira [13], based in turn on Okamura et al. [32]:

$$G_m = \left(\frac{D_m}{D_0}\right)^2 - 1 \quad (1)$$

where G_m = relative slump-flow area; D_m = slump-flow average diameter, in mm; D_0 = initial diameter in the cone's base, in mm.

The admissible range established by Nepomuceno and Oliveira [13] for the value of G_m, considering what best suits the accomplishment of SCC, is 5.3–5.9. As per EPG guidelines [33], all the SCM mixes have slump flow of 240 mm to 260 mm.

3.4.2. Mini V-funnel test for SCM

The determination of the flow time using the mini V-funnel test allows calculating the R_m parameter. Since there are still no normative references for this test, the choice was to follow the test procedures used by Nepomuceno and Oliveira [13], based in turn on Okamura et al. [32].

The result of this test is presented directly by the flow time (t), measured in seconds:

$$R_m = \frac{10}{t} \quad (2)$$

where R_m = relative flow velocity, in s^{-1}; t = flow time, in s.

Table 3
Mix proportions of all mortars.

Mix proportions		CEM I	Fly ash	$Sand_{0/1}$	$Sand_{0/4}$	Water	W/C	S_P*	Binder/sand**	Paste volume
1:1	Weight (kg/m^3)	665	286	485	485	286	0.43	5.0	1.0	
	Volume (m^3)	0.212	0.124	0.190	0.190	0.286		0.0045		0.622
1:2	Weight (kg/m^3)	490	210	695	695	211	0.43	7.35	0.50	
	Volume (m^3)	0.156	0.091	0.273	0.273	0.211		0.0067		0.458

* S_P (% mass cement): $mix_{1:1}$ = 0.75 and $mix_{1:2}$ = 1.50.
** Ratio binder: sand of 1:1 and 1:2.

The admissible range established by Nepomuceno and Oliveira [13] the value of R_m, considering what best suits the compliance with SCC characteristics, is 1.14–1.30. As per EPG guidelines [33], all the SCM mixes have mini V-Funnel time of 7–11 s.

3.4.3. Compressive and flexural strength test

The compressive and flexural strength tests were performed according to the procedures described in NP EN 1015-11 [34], at 7, 28 and 91 days, in three 160 × 40 × 40 mm prismatic specimens. They were initially tested for flexural strength, which resulted in two halves that were then tested for compressive strength.

3.4.4. Immersion water absorption

The water absorption (total volume of penetrable pores) was determined according to the procedure described in LNEC E 394 [35], in three 100 mm cubic moulds, at 28 and 91 days. Three mass values were obtained: apparent mass of saturated samples after immersion to constant weight (i.e. until the incremental increase in mass was less than 0.1%), mass in the air while they were still saturated, and mass of dry samples (oven dried at 105 ± 5 °C to constant weight, i.e. until the increase in mass was less than 0.5%).

3.4.5. Carbonation resistance

Specification LNEC-E391 [37] and recommendation RILEM CPC-18 [38] were used to determine carbonation resistance. A 100 mm diameter and approximately 50 mm thick sample of each SCC mix was tested after 14, 28, 56 and 91 days of exposure in the CO_2 chamber. All the specimens tested were subjected to wet curing by immersion in water at 20 ± 2 °C until 14 days prior to the start of the test, i.e. placing in the carbonation chamber. At that time, the specimens were sectioned and their tops protected with an insulating coating. Then, the specimens were conditioned at 20 ± 2 °C and 50% RH until they were placed in the carbonation chamber (28 days). The chamber had 5 ± 1% of CO_2, at 60 ± 5% RH and 23 ± 3 °C. After the required time of exposure to these conditions the specimens were removed from the chamber, broken into four pieces and the carbonation depth was measured using a colorimetric method (with phenolphthalein at 0.1%).

4. Tests results and discussion

4.1. Fresh-state properties

The fresh-state performance of self-compacting mortars depends on many factors, the most relevant of which were mentioned in Section 1. However, it is stressed that the objective in terms of spread and mini V-funnel test results was simply to comply with the workability parameters defined in the reference documents [13,27–31], in order to reach self-compatibility, which was successfully done for all the mixes produced.

Table 4 and Fig. 1 present a summary of the fresh-state results for all the mixes studied. As expected, there is a decrease of spread and flowability with the addition of both nano-TiO_2 and nano-SiO_2 for both mortar families (ratios 1:1 and 1:2).

The flowability evaluated by the mini V-funnel shows a minor scatter in the 1:1 family mixes (independently of the nano material used). As for the 1:2 family mixes, there is a minor scatter with the R_m values always between 0.77 s^{-1} e 0.89 s^{-1}. However, the spread losses of the 1:2 mixes is almost nil independently of the nano material used by comparison with the reference mortar, contrarily to the 1:1 mixes.

The results presented, relating to the mixes with nano-SiO_2, can be confirmed by the work of Senff et al. [36,44]. These authors studied the effect of nano-SiO_2 on the fresh-state behavior of cementitious mortars and mention unequivocally that, as the nano-SiO_2 content progressively increases (0%, 1.0%, 1.5%, 2.0% and 2.5% in cement weight), the yield stress after 75 min is −126.4%, −4.3%, −14.7%, +38.1% and +66.5% (relative to the maximum test time – 150 min – for the 2.5% nano-silica containing sample), respectively.

Table 4
Mini-cone slump-flow and mini V-funnel test results.

Mix	Mini-cone slump-flow		Mini-V-funnel	
	D_m (mm)	G_m	t (s)	R_m (s^{-1})
1:1	310.0	8.6	7.4	1.35
NT1A (0.5%NT)	283.0	7.0	7.8	1.28
NT1B (0.75%NT)	275.0	6.6	7.9	1.27
NT1C (1.00%NT)	260.0	5.8	9.7	1.03
NS1P (0.75%NS)	284.0	7.07	7.6	1.32
NS1Q (1.50%NS)	282.5	7.0	9.0	1.11
NS1R (3.00%NS)	265.0	6.0	9.9	1.01
1:2	300.0	8.0	10.4	0.96
NT2A (0.5%NT)	297.5	7.9	11.2	0.89
NT2B (0.75%NT)	292.5	7.6	12.0	0.83
NT2C (1.00%NT)	290.0	7.4	12.7	0.79
NS2P (0.75%NS)	297.5	7.9	12.6	0.79
NS2Q (1.50%NS)	292.5	7.6	12.8	0.78
NS2R (3.00%NS)	285.0	7.0	13.0	0.77

NS = nano-SiO_2; NT = nano-TiO_2.

According to Sections 1 and 2, and as occurred in both our work and that of various authors [36,39,43,44], it is possible to state that the use of additions with a specific surface higher than that of the cement particles (as is the case of nano-SiO_2), implies a higher consumption both of water and of superplasticizer to maintain the same level of workability of an equivalent mix without the use of this nano-material.

Regarding the use of the nano-TiO_2, it is possible to compare the results of our work with those of Senff et al. [44]. These authors mention a significant increase of the torque values and yield stress with the addition of nano-TiO_2 with a corresponding decrease of the open testing time.

Generally it can be stated that the influence of both nano-SiO_2 and nano-TiO_2 on the fresh-state performance of the mortars is more significant for the 1:1 family in terms of flow. In the remaining cases, the workability losses are minimal and perfectly within the reference values.

4.2. Compressive and flexural strength test

The results of the uniaxial compressive and flexural tests for all mixes produced are presented in Table 5 and Figs. 2–4.

These elements show a clearer growth of the early-age (7 days) compressive strength of the mixes with nano-SiO_2 (in both the 1:1 and 1:2 families). As for the mixes with nano-TiO_2 (in both the 1:1 and 1:2 families), they show a more monotonic evolution of the compressive strength beyond the early ages. For older ages it is found that all mixes reach compressive strength values higher than

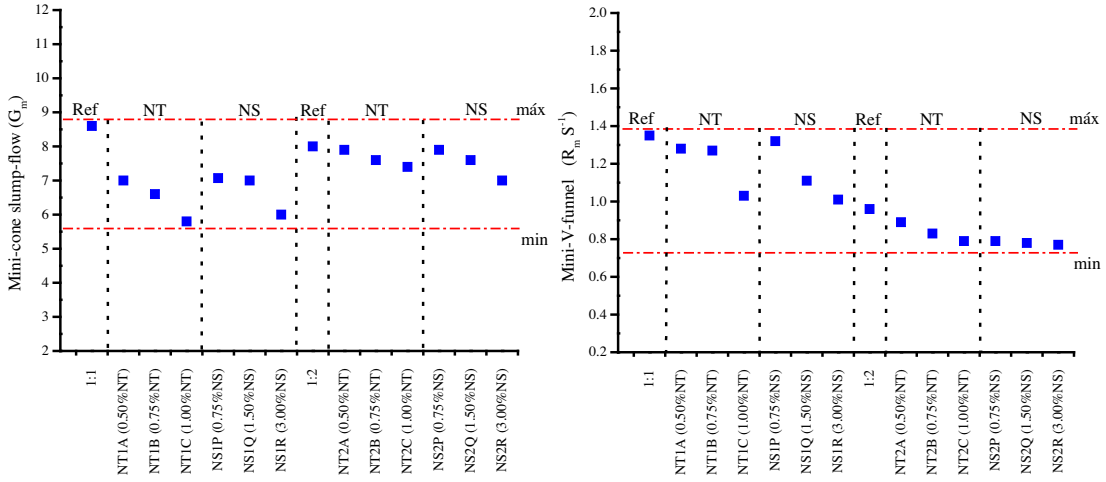

Fig. 1. Mini-cone slump-flow (left) and mini V-funnel (right) test results.

Table 5
Compressive, flexural strength and water absorption test results.

Mix	Compressive strength (MPa)			Hardening coefficients (compressive strength)			Flexural strength (MPa)			Porosity (%)
	7 days	28 days	91 days	7 days	28 days	91 days	7 days	28 days	91 days	28 days
1:1	75.5	91.4	106.3	0.83	1.00	1.16	10.5	10.7	14.2	6.2
NT1A (0.5%NT)	75.3	87	108.1	0.82	1.00	1.18	8.2	13.1	14.9	6.4
NT1B (0.75%NT)	66.9	84.2	99	0.73	1.00	1.08	6.9	12.9	13.4	6.4
NT1C (1.00%NT)	54.5	83.1	88.1	0.60	1.00	0.96	7	13	13.1	6.5
NS1P (0.75%NS)	73.2	88.4	96.7	0.80	1.00	1.06	13.8	13.4	14.8	7.1
NS1Q (1.50%NS)	71.6	86.3	94.7	0.78	1.00	1.04	11.8	12.5	13.7	7.2
NS1R (3.00%NS)	70	84.2	94.2	0.77	1.00	1.03	8.4	12	12.8	7.6
1:2	74.2	94.9	101.6	0.81	1.00	1.11	8.8	12.9	13.5	4.1
NT2A (0.5%NT)	73.4	92	104.1	0.80	1.00	1.14	11.1	11.8	13.7	5.5
NT2B (0.75%NT)	69.3	87.8	98.8	0.76	1.00	1.08	12.4	13.6	11.8	5.8
NT2C (1.00%NT)	62.2	76.6	92.7	0.68	1.00	1.01	10.2	12.1	9.9	5.9
NS2P (0.75%NS)	73.6	90.4	98.9	0.81	1.00	1.08	12	13.5	14.5	6.5
NS2Q (1.50%NS)	71.9	86.3	95.4	0.79	1.00	1.04	12.2	13	14.2	6.7
NS2R (3.00%NS)	70.3	83.3	92	0.77	1.00	1.01	11	11.5	13.8	6.9

NS = nano-SiO_2; NT = nano-TiO_2.

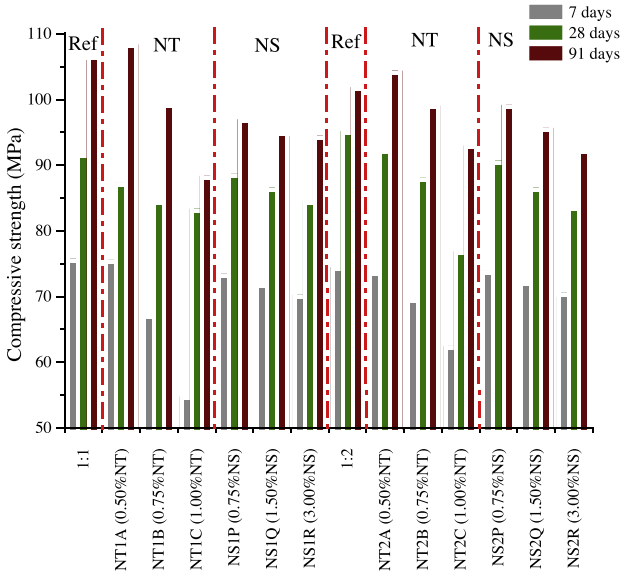

Fig. 2. 7-, 28- and 91-day compressive strength of all mixes.

90 MPa (except for the NT1C mix), with very similar values for the equivalent mixes with each of the nano materials.

These differences may be seen both in the graphs of mechanical strength *versus* age (Fig. 3) and in those of mechanical strength *versus* replacement ratio (Fig. 4). In terms of absolute values, for both families studied and as expected, the compressive strength increases with age and decreases with the nano materials addition ratio.

The hardening coefficients presented in Table 5 confirm what was referred in the beginning of this section, i.e. the 7-day compressive strength of the 1.00% mixes of nano-TiO_2 is generally lower than that of the remaining mixes. With the exception of the NT1C and NT2C mixes, they all showed values higher than 70% of those at 28 days (independently of the nano material used). None of the 7-day strength values is higher than 83% of the corresponding values at 28 days. At older ages the compressive strength tends to stabilize, increasing at the most 18% relative to the 28-day value (NT1A mix) and 14% for the NT2A mix. Increasing the addition of both nano-SiO_2 and nano-TiO_2 generally decreases the hardening coefficient, by less than 10% in most mixes.

According to Table 5, the scatter of the flexural strength results is lower than of the compressive strength results. There is also a less significant increase of the results with the addition of both nano-TiO_2 and nano-SiO_2. For older ages (91 days) the flexural

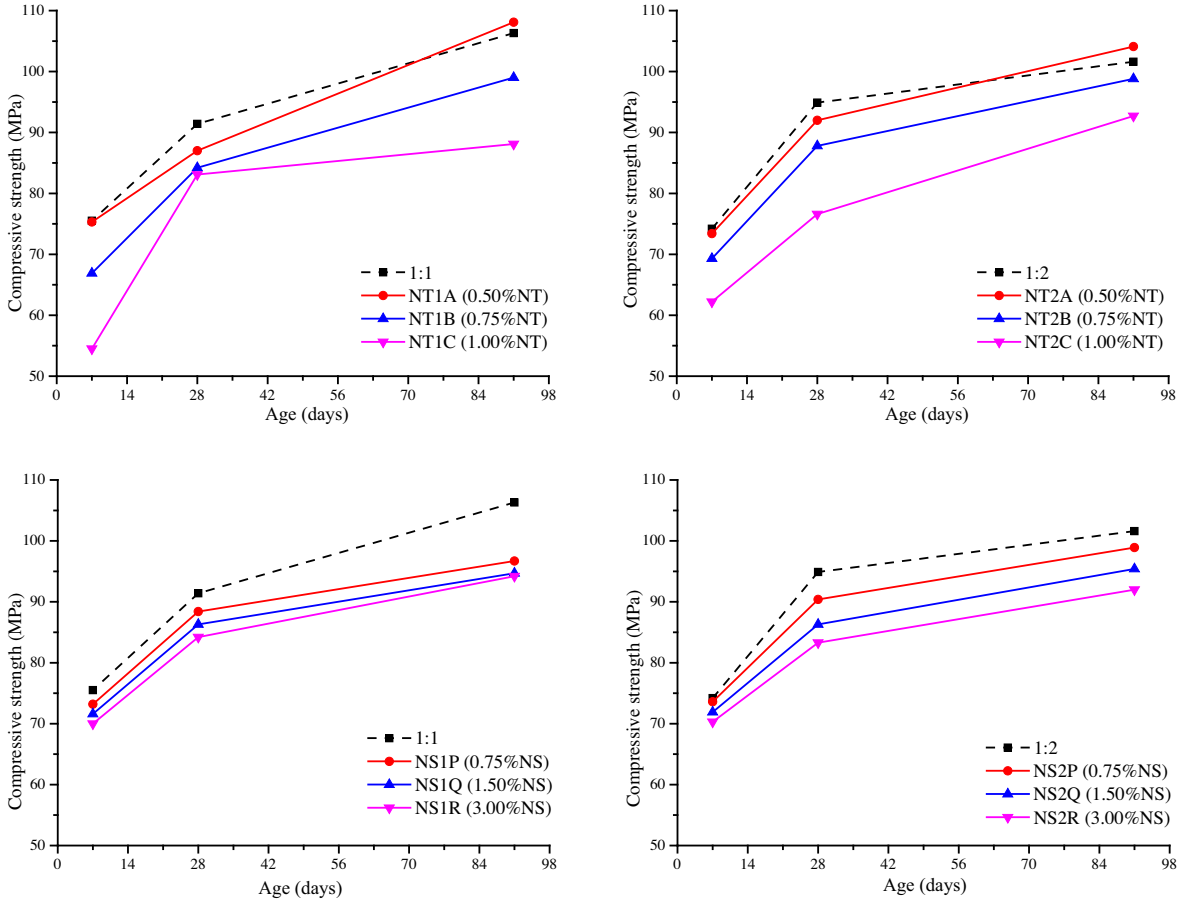

Fig. 3. Compressive strength *versus* age for all mixes.

strength of the 1:2 mixes with 3% of nano-SiO_2 increases approximately 4% (relative to the reference mix) while for the 1:1 mixes this increase is almost 20%.

Compared to the results obtained by other studies regarding the mechanical behavior of the type of mixes studied (with nano-SiO_2 and nano-TiO_2), there is some contradictory data. Some authors [36,44,45] mention a practically nil variation of the mechanical strength with the addition both of nano-TiO_2 and nano-SiO_2 when compared to the reference mixes (without nano-materials). As observed in our work, the lower mechanical strength (mainly in more advanced ages) with the addition of the nano-materials under study, when compared to the reference mixes, is usually attributed to the difficult dispersion of the nano-particles in the mixes of both mortars and concrete [36,44–46]. Li [47] mentions that, regarding concrete mixes with fly ash and nano-SiO_2, the high contents of calcium hydroxide (produced in the early stage of the hydration process) can be consumed by the nano-SiO_2, resulting in a lower available quantity of that compound for the pozzolanic reactions with fly ash at more advanced ages, causing a decrease of the mechanical strength of these mixes mainly at those ages.

On the other hand, some authors [48–50] present results with a significant increase of the mechanical strength due to the addition of the nano-materials under study. Shih et al. [48] show gains of 20–25% of the compressive strength of mortars with nano-SiO_2 relative to the reference mixes (without additions). These authors [48–50] generically mention that the improvement observed in the mechanical strength, due to the incorporation of nano-SiO_2, is essentially caused by an increase of the pozzolanic activity, resulting in a higher quantity of calcium silicate hydrate and a denser microstructure, i.e. a microstructure with greater compacity [51].

4.3. Immersion water absorption

The results of the water absorption by immersion test of all the mixes produced are presented in Table 5. These results are also presented graphically in Fig. 5.

This test, performed according to the procedure presented in Section 3.4.4, essentially evaluates the porosity of concrete. However, the test has some limitations, namely that it measures the volume of accessible pores only, usually called open porosity, i.e. this value does not represent the absolute porosity of the material since it does not consider the volume of closed pores.

From Table 5 and Fig. 5 it is found that the water absorption by immersion significantly increases when the nano materials content increases. It is also found that there is a decrease of the absorption from the 1:1 family mixes to the 1:2 family mixes, and consequently with the decrease of the volume paste in the 1:2 mixes. These variations can be confirmed in the reference mixes: 6.2% for the 1:1 mix and 4.1% for the 1:2 mix. However it is stressed that the 1:2 family mixes have a higher change (from the reference value) than the 1:1 family mixes. It can be further seen that the mixes with nano-SiO_2 present water absorption by immersion values slightly higher than those with nano-TiO_2 independently of the mortars family (1:1 or 1:2).

It can be generally stated that the open porosity determined by the water absorption by immersion test (Table 5 and Fig. 5) presents values in agreement with those of other authors in equivalent mixes [1,4,5]. The porosity values are lower for a 0.5% addition of nano-TiO_2 and they are maximum in the mixes with nano-SiO_2 independently of its ratio of incorporation. Regarding the microstructure of the mixes with nano-particles (namely with nano-SiO_2), Li et al. [49] mention that the difficulty in dispersing

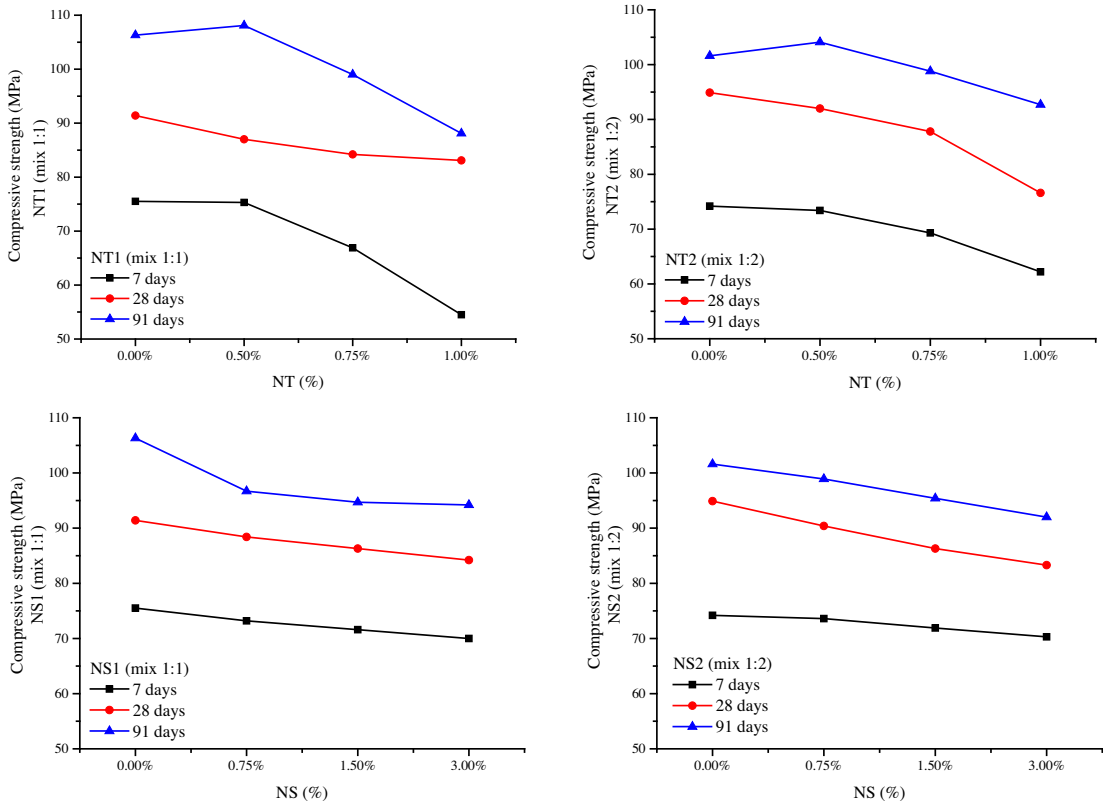

Fig. 4. Compressive strength *versus* NT and NS%.

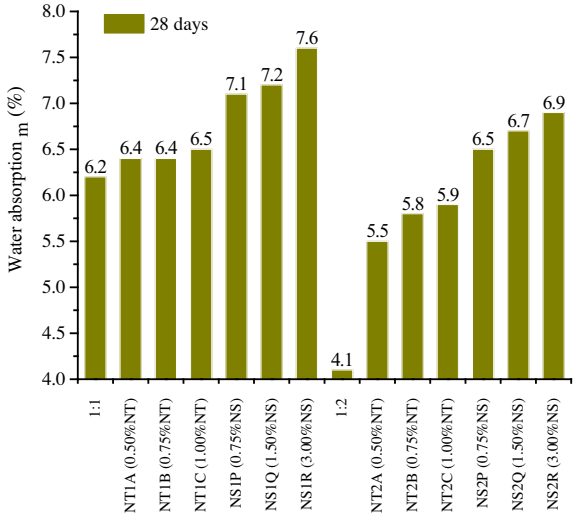

Fig. 5. 28-Day water absorption by immersion of all mixes.

these materials can have as main consequence the appearance of weaker areas, in the form of voids that can cause the formation of a less dense and homogeneous microstructure and, as observed in Section 4.2, a reduction of the mechanical strength.

4.4. Carbonation resistance

The carbonation depth results of all mixes are presented in Table 6. For each of the test ages, the average carbonation depth (d_{kmxd}) is provided. In the table the result "<1" of the carbonation depth means that no measurable carbonation was detected at any of the ages analyzed and consequently the corresponding coefficient is assigned the minimum value of 1 mm/year$^{0.5}$. Fig. 6 presents the carbonation depth in function of the test age (graphs on the left) and of the square root of time (graphs on the right), from which the carbonation coefficients line (also in Table 6) were determined, corresponding to the slope of the linear regression.

Fig. 6 shows the variation of the carbonation depth with time (graphs on the left) and the same depth in function of the square root of time (graphs on the right), from which the respective carbonations coefficients were determined, corresponding to the slope of the regression line (and presented in Table 6).

A preliminary evaluation of the carbonation depth results in Table 6 shows that the 1:1 family mortars with nano-TiO_2 and the mix with 0.75% of nano-SiO_2 did not show any carbonation effect up to 91 days of exposure in the accelerated carbonation chamber. The same occurred in 1:2 family mortars with 0.5% of nano-TiO_2, i.e. these mixes proved to be practically impermeable to carbonation in the time period studied. The remaining mixes had a very similar behavior with carbonation depths always lower than 10 mm, with the exception of the 1:2 mix with an addition of 3% of nano-SiO_2 that showed after 28 days of exposure depths of 15 mm, reaching 20 mm at 91 days (maximum exposure time in this study). The mixes with nano-TiO_2 generally showed lower carbonation depths than those of the mixes with nano-SiO_2. Similarly the 1:1 family mortars showed lower carbonation depths than those of the 1:2 family mortars.

Concrete carbonation may be quantified by the corresponding coefficient, through the variation of the carbonation depth over time, using equation $x = k\sqrt{t}$ ($x = kt^{(1/n)}$ with $n = 2$). The analysis of the graphs on the right in Fig. 6 shows that the equation indeed applies, with reasonable correlation coefficients always above 0.9, with the exception of mix NS2P with $R^2 = 0.892$. However, according to Neville [39] or Bertolini et al. [40], among others, this equation involving the square root of time cannot be applied to non-

Table 6
Depth of carbonation (mm) and corresponding coefficients of all mixes.

Mix	d_{km14d}	d_{km28d}	d_{km56d}	d_{km91d}	K_c (mm/year$^{0.5}$)	R^2
1:1	<1	<1	<1	<1	1	–
NT1A (0.5%NT)	<1	<1	<1	<1	1	–
NT1B (0.75%NT)	<1	<1	<1	<1	1	–
NT1C (1.00%NT)	<1	<1	<1	<1	1	–
NS1P (0.75%NS)	<1	<1	<1	<1	1	–
NS1Q (1.50%NS)	3	4	5	6	11.94	0.973
NS1R (3.00%NS)	4	5	9	10	20.92	0.971
1:2	<1	<1	<1	<1	1	–
NT2A (0.5%NT)	<1	<1	<1	<1	1	–
NT2B (0.75%NT)	2	4	6	8	16.39	0.989
NT2C (1.00%NT)	3	4	5	6	11.94	0.990
NS2P (0.75%NS)	2	3	6	8	41.93	0.892
NS2Q (1.50%NS)	3	4	7	8	19.78	0.960
NS2R (3.00%NS)	5	15	16	20	16.36	0.941

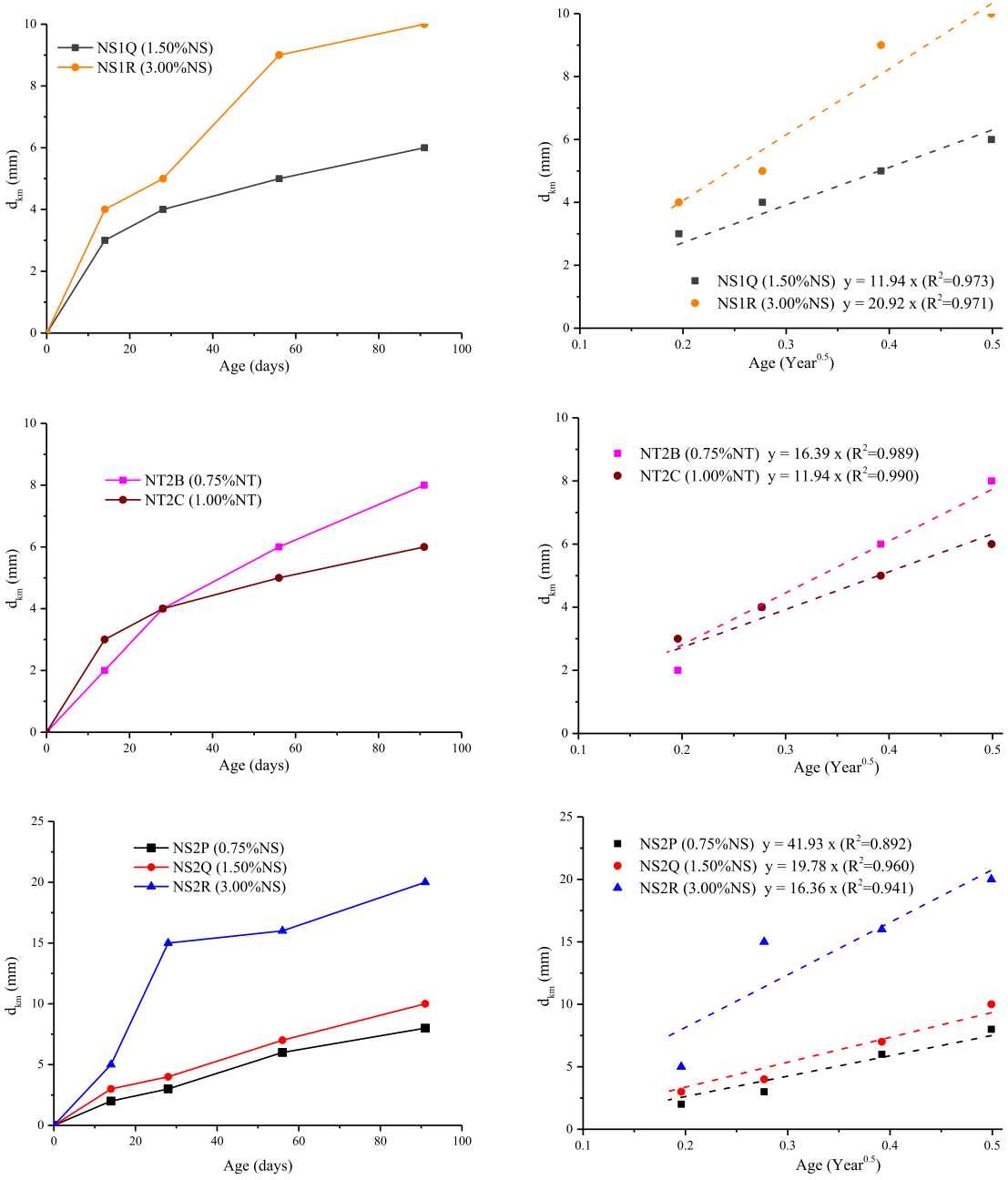

Fig. 6. Depth of carbonation *versus* age and $\sqrt{t}$ for all mixes.

stationary exposure conditions, i.e. natural exposure situations in which the material is subjected to humidity and temperature variations and CO_2 concentration levels significantly lower than those of the accelerated test. Bertolini et al. [40] refer that for cement-based materials under natural exposure conditions the reduction of the carbonation process over time is steeper than that described by the parabolic equation $x = kt^{(1/n)}$ and that in these cases the "n" value tends to be higher than 2. As seen in our work, Bertolini et al. [40] argue that in cement-based materials with high compacity the carbonation process tends to be negligible. Confirming other authors, namely Neville [39], Bertolini et al. [40], Silva and de Brito [41,42], in the more compact mixes of this work carbonation was negligible even after exposure times up to a quarter of a year.

Despite the problems associated with the dispersion of this type of particles [1,4,5,36,44–47,49], numerous authors [45–49] mention the advantages, in terms of compacity of the mixes, mainly with nano-SiO_2. In that sense, Li et al. [49] mention how the nano-SiO_2 can participate in the hydration process, at least as a nucleation point, but mainly generating calcium silicate hydrate through the reaction with calcium hydroxide and consequently causing a higher compacity of the microstructure. This has unequivocal advantages in terms of resistance to the progression of the main degradation mechanisms (namely CO_2 penetration), even when small quantities of nano-SiO_2 are not well dispersed.

5. Conclusions

All self-compacting mortars produced with and without nano materials (SiO_2 and TiO_2) complied with the reference values intended concerning the fresh-state properties, namely those referring to the mini-cone and the mini V-funnel. Despite the differences observed between reference and nano-materials mixes, it is possible to state that all mixes are self-compacting and there are no significant changes to the fresh-state properties with the addition of these nano materials. This is equally true in the 1:1 family mixes and the 1:2 family mixes. It is however pointed out that both nano-materials cause a decrease of the open testing time that should be taken into account in the case of practical applications.

Concerning the hardened-state properties, it is concluded that the compressive strength growth rate decreased with the addition of these nano materials in both the 1:1 and 1:2 mixes. The flexural strength decreases with the addition of nano particles, especially 3.0% of SiO_2 in the 1:1 family and 1.0% de TiO_2 in the 1:2 family, relative to the reference mortars (1:1 and 1:2). As observed by various authors, the negative influence in mechanical strength of the difficulty of dispersion of the nano-particles under study in the mix should be highlighted. Nevertheless, one should also stress that the more significant losses of compressive strength (relative to the reference mix, without nano-materials) were registered in the mixes with nano-TiO_2, with a maximum value at 91 days of approximately 18% in the mix with 1% of nano-TiO_2. The strength losses regarding the mixes with nano-SiO_2 are minimal (always lower than 10% relative to the reference mixes without nano-materials).

The water absorption by immersion (open porosity) increases with the addition both of nano-SiO_2 and nano-TiO_2, relative to the reference mortars (1:1 and 1:2). There is a slight decrease of porosity in the 1:2 family mixes relative to the 1:1 family mixes.

The results allow stating that generally in the case of the 1:1 family mixes, the 1:2 reference mix and the NT2A mix, their greater compacity creates an almost impenetrable barrier to CO_2, significantly retarding its propagation. These high compacity mortars are usually associated to a low water-accessible porosity, which represents the main CO_2 penetration path. As confirmed in Section 4.3 by the water absorption by immersion results, these mixes are the ones with the lowest accessible porosity values and the lowest carbonation coefficients. Concerning the influence of the additions on the degradation mechanism analyzed, the differences found between the nano materials used in terms of carbonation resistance, essentially in the 1:2 family mixes, are highlighted: the mixes with nano-TiO_2 show an improvement.

Acknowledgements

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