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CIVIL & ENVIRONMENTAL ENGINEERING | RESEARCH ARTICLE

Compatibility analysis between Portland cement type I and micro/nano-SiO₂ in the presence of polycarboxylate-type superplasticizers

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Abstract: This study, assessed the interaction between Portland cement type I and polycarboxylate-type superplasticizers. Five systems were analyzed with the cement-superplasticizer pair being selected from the viewpoint of its rheological behavior using the Marsh cone test. The rheological behavior was analyzed using plain and mineral additions of 5, 10 and 15 wt% and 1, 2, and 3 wt% of silica fume (SF) and nanosilica (nS), respectively. Mechanical and rheological validations were carried out in binary-concretes with nS or SF. The results showed that addition of amorphous silica in different particle sizes has very different rheological results. Particularly, in SF-concretes, the samples exhibited higher susceptibility to bleeding and segregation for higher SF amounts. This limited the application of high SP dosages, but this fact induced a premature slump loss even at the early age. In contrast, nS-concretes tended to have less bleeding, increased packing density and enhanced cohesiveness of the cement matrix. Therefore, higher SP dosages were possible. The results also showed that when mineral additions are applied in concrete mixes the Marsh cone test results of cement pastes must be interpreted carefully. For SF-concretes the numerical results were effectively anticipated by using the Marsh methodology.

ABOUT THE AUTHOR

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PUBLIC INTEREST STATEMENT

Concrete is the most widely used construction material in the world. The primary constituents of concrete are cement, sand, aggregate, and water. In addition, chemical (e.g. superplasticizers) and mineral admixtures (e.g. silica fume or nanoparticles) are often used to modify some physical/chemical properties of concrete. The Portland cement is worldwide the main cementing material, but the energy required to produce a ton of cement is approximately equivalent to emit a ton of CO₂. One of the directions going on to make reductions in CO₂ is to reduce the cement in concrete by adding products such as silica fume. In this sense, the present work report some findings concerning with the behavior of the fresh/hardened state in superplasticized-cement pastes with silica or nanoparticles. The importance of this research relies in determine the compatibility between the cementing materials and chemical/mineral admixtures at the level of the cement paste, before the concrete be cast. By doing this type of experiments the carbon emissions to the environment are reduced.

Nevertheless, in nS-concretes the numerical results of SP doses did not reflect the doses of SP anticipated from the Marsh's experiments. Finally, in the hardened state statistical results showed that compressive and splitting tensile strength in some SF/nS-concretes exhibited an increase of up to 35% with respect to control samples.

Subjects: Materials Science; Nanoscience & Nanotechnology; Civil, Environmental and Geotechnical Engineering

Keywords: Marsh cone test; nanosilica; silica fume; fresh state concrete; compression test; splitting test

1. Introduction

The Marsh cone test represents a rheological indicator for a particular Portland cement (PC)-superplasticizer (SP) combination by studying the resulting paste performance (Aitcin, 1998). It is normally assumed that the Marsh's methodology reveals the same trend as the yield shear stress as long as the cement paste follows a Bingham model (Agulló, Toralles-Carbonari, Gettu, & Aguado, 1999; Banfill, 1991; De Larrard, 1999; Tattersall, 1991). This becomes relevant when high-performance concrete is the target, since its low water-binder (w/b) ratios (usually $w/b \leq 0.35$) require the use of compatible PC-SP systems (Hallal, Kadri, Ezziane, Kadri, & Khelafi, 2010). Hereon, the term compatibility shall be understood as that which characterizes the PC-SP-SF or PC-SP-nS interactions reflected in: (i) low flow time (FT) at 5 min, (ii) low saturation dosage (SD), and (iii) negligible fluidity loss (ΔFT) at 60 min. The difference between the FT at 60 and 5 min is then defined as the ΔFT (Hallal et al., 2010). Plain compatible systems require: a FT between 60 and 90 s, ΔFT tending to zero or negative, and values of SD between 0.0 and 1.0 wt% by-mass-of-cementitious materials (Aitcin, 1998). SD is defined as the point beyond which at 5 min, there is no significant fluidity increase (Agulló et al., 1999; Aitcin, 1998; Hallal et al., 2010).

Polycarboxylate-type SPs are one of the most employed chemical admixtures for concrete due to its capacity of producing concrete with: (i) high fluidity, (ii) high strength, and (iii) superior dispersing force and retention effects even at low w/b ratios (Yamada, Ogawa, & Hanehara, 2001). However, the SPs dispersing force and its retention capacity seem to be affected by some components of the cement (Felekoğlu, Tosun, & Baradan, 2011; Hallal et al., 2010) or by variations in the mixing sequence (Agulló et al., 1999; Aitcin, 1998; Hallal et al., 2010; Yamada et al., 2001). Recently, the concrete industry has become more interested in the study of that PC-SP incompatibility (Felekoğlu et al., 2011; Plank & Sachsenhauser, 2009; Plank, Sachsenhauser, & de Reese, 2010; Zingg et al., 2009). Accordingly, even when a particular kind of cement and a particular SP is satisfactory (e.g. based on acceptable standards, such as ASTM) from a rheological point of view, the resultant PC-SP couple may not be compatible (Aitcin, 1998).

Nowadays, the use of mineral additions such as SF or fly ash has increased as a result of noted improvements in rheological, mechanical and durability, and because of environmental concerns (Hallal et al., 2010; Jalal, Mansouri, Sharifipour, & Pouladkhan, 2012). When compared with normal PC type I, SF shows: (i) particle two orders of magnitude finer, (ii) highly pozzolanic reactive chemistry, but (iii) apparent increment in water requirement. Currently, nanostructured SiO_2 is industrially produced for numerous applications that take advantage of the particles' large surface area, binding capacity, and basic pH. Additions of SF/nS in concrete results in lower: porosity, permeability, and bleeding while causing the $\text{SiO}_2\text{-Ca(OH)}_2$ reaction to effect a secondary C-S-H (Kawashima, Hou, Corr, & Shah, 2013; Kontoleontos, Tsakiridis, Marinos, Kaloidas, & Katsioti, 2012), which improves the materials strength. Nevertheless, the use of nS in concrete industry is not yet a common practice because of the associated cost and workability drawbacks (Kontoleontos et al., 2012; Van de Griend, Lazaro, & Brouwers, 2012).

The present research demonstrates how the Marsh cone test of mortar samples can reveal fundamental rheological information and posterior validation was carried out by casting concrete trial

batches containing mineral additions. The global experimental tests were planned in three stages because the experimental processes were designed from fewer components (PC-SP) to several components (concrete = PC-SP-nS/SF-aggregates). That is the reason why the present manuscript is divided into three stages as can be seen in the methodology. The replacement levels of SF and nS commonly used range from 5 to 30 wt% (Aitcin, 1998; American Concrete Institute, Committee 234 (ACI 234R-06), 2006; Mazloom, Ramezani-pour, & Brooks, 2004) and 0.5–5 wt% (Jalal et al., 2012; Senff, Hotza, Repette, Ferreira, & Labrincha, 2010; Stefanidou & Papayianni, 2012), respectively. The SP levels on concrete validations were based on SP trial batches until reaching segregation or excessive bleeding. The saturation dosages from the Marsh’s experiments were not taken into account because the objective was to validate those results by making concrete specimens with the same materials used in the experiments on cement paste carried out using the Marsh cone test. Finally, fresh and hardened states were analyzed to study the effects of employing nS/SF in concrete mixes at the levels studied with the Marsh cone test.

2. Materials and methods

2.1. Portland cement type I

The cement employed in this research is a PC Type I according to ASTM C150 (Table 1). It is well known that an important number of cases of fresh state problems in concrete are related to the levels of tricalcium aluminate (C_3A). Therefore, in the present research from all available cements, we selected one with the highest C_3A amount (Table 1). Our intent was to explore the Marsh cone test effectiveness under extreme conditions.

2.2. Fine and coarse aggregates

The coarse aggregate has 9.5 mm maximum diameter, SG (SSD) = 2.7 and absorption of 4.2%. The fine aggregate has SG (SSD) = 2.6 and absorption of 4.1%. Both materials follow the ASTM C33 standard.

2.3. Chemical admixtures

This study employs five different polymer-based admixtures whereas the SP doses ranged from 0.4 to 2.5%. These are expressed as the weight ratio between the solid SP material and the dry cementitious content (see Table 2).

2.4. Mineral admixtures

Table 3 shows the principal characteristics of nS and SF (ASTM C1240). The X-ray diffraction (XRD) spectra in Figure 1 was obtained from nS and SF specimens; peaks at 2θ angle of 21° and 22° correspond SF and nS, respectively. The diffractograms reveal the mostly amorphous nature of both products.

Table 1. Physical-chemical and mineralogical characteristics of the employed PC

Chemical composition (wt%)		BOGUE composition (wt%)	
SiO ₂	20.29	C ₃ S	55.4
Al ₂ O ₃	6.40	C ₂ S	16.4
Fe ₂ O ₃	3.51	C ₃ A	11.0
CaO	65.13	C ₄ AF	10.7
SO ₃	2.65	Physical properties	
MgO	1.03	Blaine (m ² /kg)	394
K ₂ O	0.48	Specific gravity	2.90
Na ₂ O	0.12	Normal consistency (%)	26.5
LOI	3.13	Compressive strength on cubes (MPa)	
Alkalis	Na ₂ O eq. = 0.44%	1 d	14.2
Free-CaO	1.2	3 d	24.3
Insoluble residue	0.31	7 d	31.5

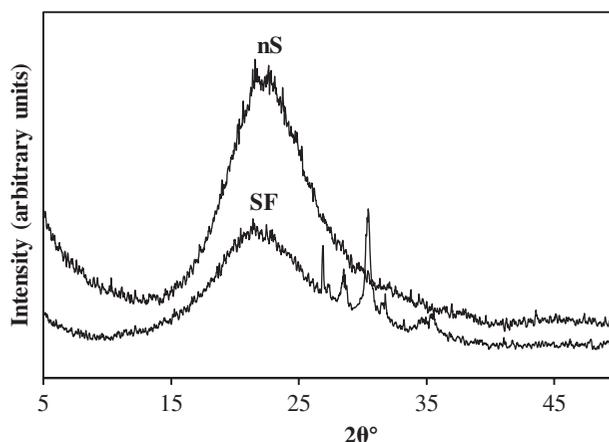
Table 2. Physical and chemical properties of the chemical admixtures

	SP1	SP2	SP3	SP4	SP5
Solid content	35%	40%	30%	35%	35%
Physical state	Liquid	Liquid	Liquid	Liquid	Liquid
Color	Brown	Blue	Brown	Brown	Blue
pH	4.4–4.9	4.8–6.8	8.0–10	8.0–10	3.0–5.0
Specific gravity	1.08	1.08	1.08	1.10	1.08
Chemical family	Carboxylated polyether	Carboxylated polyether	Carboxylated polyether	Carboxylated polyether	Polycarboxylate solution
Chemical ingredient	Polyacrylate aqueous solution	Carboxylated polyether copolymer	Triethanolamine	Triethanolamine	Aqueous polycarboxylate
Standard ASTM	C494 types A and F. C1017 type I	C494 types A and F. C1017 type I	C494 types A and F	C494 types A and F	C494 types A and F

Table 3. Physical and chemical characteristics of the mineral admixtures

Items	Chemical composition (wt%)	
	SF	nS
SiO ₂	91.3	99.9
Carbon	0.4	-
H ₂ O	0.3	-
LOI	-	0.1
pH value	-	9.0
	Physical properties	
Specific gravity	2.2	2.1
Mean size (nm)	200	25
SSA (m ² /kg)	25,000	109,000

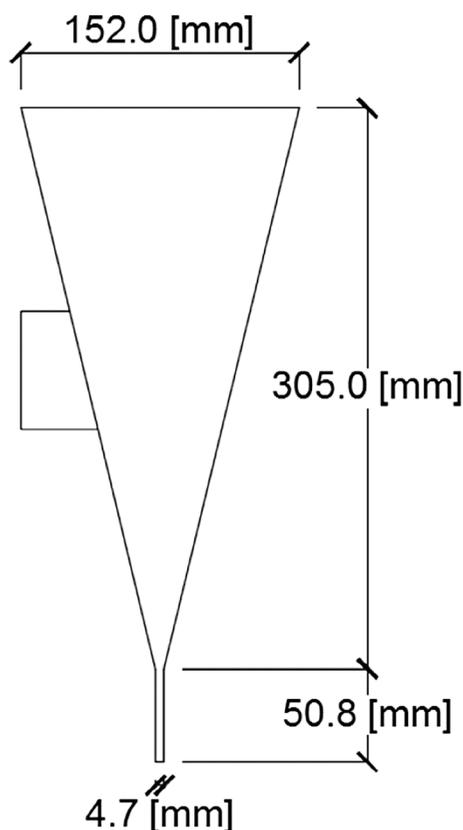
Figure 1. XRD pattern of nS and SF obtained using a CuK α radiation.



2.5. Marsh apparatus and testing procedure

The Marsh device is a funnel viscometer used for routine quick measurements of fluid viscosity by tracking the time it takes to a known volume of liquid to flow from the cone. This conical device has 152 mm in diameter at the top and has 305 mm in high (Figure 2). The fluid runs through a fixed

Figure 2. Scheme of the Marsh cone apparatus.



orifice at the end of the funnel, which is 4.7 mm diameter. In this research a Marsh funnel viscometer with capacity of 1.5 L was used. A volume of 1.2 L of cement paste was employed (Aïtcin, 1998; Sonebi, García-Taengua, Hossain, Khatib, & Lachemi, 2015). The pastes were mixed in a 1.7 L Hamilton-Beach blender with 550 watt peak-power motor 120 V, 60 Hz, and 3.5A. Following literature recommendations the said blender was selected over the Hobart mixer (Aïtcin, 1998; Ferraris, Obla, & Hill, 2001).

Sample preparation comprised the following sequence (Aïtcin, 1998):

- Step 1: Record the water temperature before starting the mixing process, as it must range between 20° and 23°C for normal initial hydration conditions.
- Step 2: Pour the water, SP and nS (if used) into the jar and start the mixing process during 10 s.
- Step 3: Progressively add the amount of cement for a time not exceeding 2 min. In the case of PC-SP-SF systems, the cement and SF were previously manually mixed in dry condition for 3 min.
- Step 4: Suspend the mixing process for 15 s to clean the cement adhered to the jar wall.
- Step 5: Mix the blend for 60 s and then monitor the temperature (20–23°C); if the temperature is not within the range, repeat the experiment from step 1.
- Step 6: Fill the Marsh cone to about 1.4 L, and then proceed to record the time it takes to fill the 1.2 L beaker with cement paste.

2.6. Concrete mix proportions

Concretes were prepared at 0.35 w/b and 1.50 coarse-to-fine aggregate ratios with 468 kg/m³ of cementitious content. The SP dosage for each system was obtained from prior trial batches while the preparation and curing of the samples followed the ASTM C192 standard. The water level in the mixes included the one resulting from the as-provided nS (slurry) and SP. Table 4 shows the amount

Table 4. Mix proportions of the concrete specimens

Mix ID	kg/m ³						
	PC	nS	SF	Fine	Coarse	SP	Water
CO	468.7	–	–	673	1,000	9.1	219
N1	463.9	4.8	–	665	989	9.9	212
N2	459.2	9.6	–	664	989	8.0	213
N3	455.1	14.3	–	662	983	10.8	206
S5	445.1	–	23.4	664	986	4.2	224
S10	421.9	–	46.9	658	980	2.8	226
S15	398.3	–	70.3	659	979	3.3	221

of materials used, where the symbols CO, N and S correspond to control (or plain) samples, nS-containing samples and SF-systems, respectively. The numbers in the symbols of N/S designs are the amount of additive used, i.e. 1, 2, and 3 wt% of nS and 5, 10, and 15 wt% of SF. These amounts of nS and SP are expressed as solid contents by mass of cementitious material, wt%.

2.7. Fresh concrete test

The slump-cone test (ASTM C143) measured the consistency, i.e. property describing how easily fresh cementitious mixes flow (Zongjin, 2011); more specifically, the slump loss was used to bring out the dynamical rheological behavior of each mix through time. Upon the flow table test, we placed the concrete into a standard cylindrical steel mold (ASTM C 230/C1437). After lifting the cylinder the mix was allowed to spread, and the diameter of the resulting material cake was measured. The flow table test is usually employed in cement mortars, but in this study this standard was adopted because the flow test provided an indication of the mix cohesion. Therefore, the test is important to determine if a particular mix is prone to segregation and would produce a non-circular pool of concrete. In general, we consider this test as an adequate indicator of the rheology in a mix design (Chandra & Björnström, 2002). The fresh density (ASTM C138) is a measure of compactness (Chandra & Björnström, 2002); and the entrapped air content (ASTM C138) is a measure of the voids in concretes. In the fresh state the number of specimens consisted of two per each type of test above described.

2.8. Mechanical strength tests

The mechanical tests followed the ASTM C39 standard for compression and the ASTM C496 one for tensile strengths using a 3,000 kN Forney universal testing machine operated with load control. The experimental samples consisted of standard 50 × 100 mm cylinders (ASTM C470) cured in limewater until testing. Three testing ages were used in this research: 3, 7 and 28 days and three specimens were used in each mix design per each age. Thus, since there were seven mix designs (CO, N1, N2, N3, S5, S10, S1) the total number of fractured specimens was 126: 63 in the compression tests (ASTM C39) and 63 in the splitting ones (ASTM C496).

3. Results and discussion

3.1. PC-SPs couples (Stage I)

The rheological analysis in Table 5 revealed that SD, FT and ΔFT present important variations through the studied systems even though we used the same cement and all five SP used were cataloged as modern polymer technology (Rixom & Mailvaganam, 1999). In general, poor compatibility was observed in these PC-SPs couples. An adequate SP in conjunction with a particular cement type should have been selected by conducting experiments before applying these materials in field and/or massive conditions (Aïtcin, 1998).

Table 5. Fresh state results of the PC-SP systems

Rheological parameters	PC-SP1	PC-SP2	PC-SP3	PC-SP4	PC-SP5
T average (°C)	21.0	21.8	20.2	20.0	20.0
SD (wt%)	0.60	0.80	0.60	1.40	-
FT at SD (seconds)	111	83	135	164	-
Δ FT at SD (seconds)	+116	-9.0	∞	∞	∞
Compatibility criterion	No	Yes	No	No	No

Figures 3 and 4 display the FT results from SP1 through SP5 at 5 and 60 min, respectively. Figure 3 shows PC-SP1 system where the SD presents the smallest dosage in the present study (0.6 wt% with FT = 111 s). But in Figure 4 at 60 min FT becomes 227 s. Thereby, this system is an incompatibility case due to low dispersion capability at 1 h of age. PC-SP2 system (see Figure 3) demonstrated the best performance between the SPs tested: SD = 0.8 wt% with FT \approx 83 s and negative Δ FT at the SD (see Figures 3 and 4). Therefore, this system can be classified as compatible following the rules for plain systems. PC-SP3 couple presents SD = 0.6 wt% and FT = 135 s at SD in conjunction with a stable behavior through the experimental range (see Figure 3). However, Figure 4 demonstrates that values of FT at SD as well as FT at $Sp = 0.4$ and $Sp = 0.8$ wt% were not possible to generate; in other words, the cement paste mixes did not flow through the Marsh cone rendering this system as incompatible due to the poor fluidity at the SD.

Figure 3. Flow time as a function of SP-dosage at 5 min.

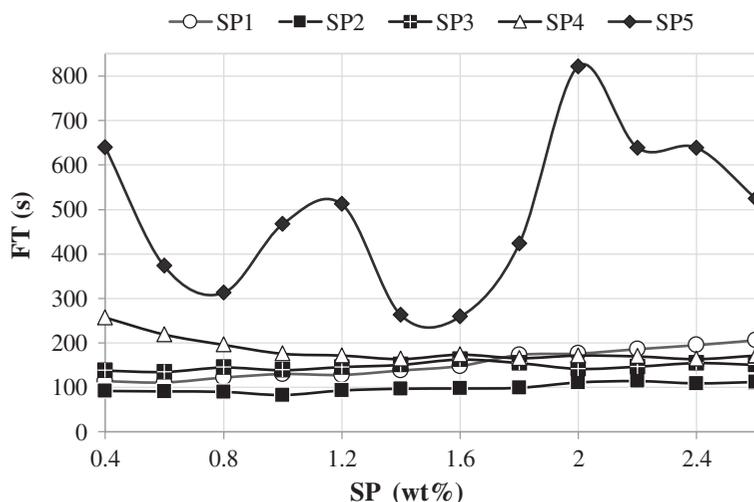
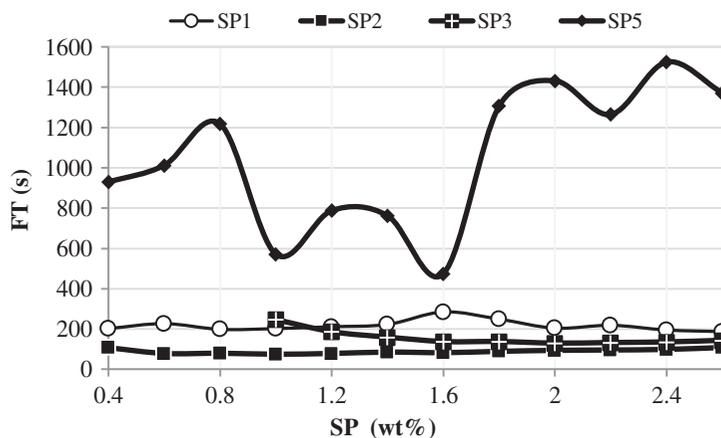


Figure 4. Flow time as a function of SP-dosage at 60 min.



PC-SP4 exhibited $Sp = 1.4$ wt% with $FT = 164$ s at SD, which are values higher than those found in the literature for plain systems (Agulló et al., 1999; Aitcin, 1998; Bahurudeen, Marckson, Kishore, & Santhanam, 2014; Hallal et al., 2010). In addition, due to lack of fluidity this couple did not exhibit experimental points at 60 min (see Figure 4). PC-SP5 did not present a defined SD. Also, at 60 min the behavior is unstable through the experimental range, erratic behavior typical in incompatible systems. As a consequence, both PC-SP4 and PC-SP5 systems are incompatible ones because the conditions imposed for PC-SP couples are not met (Agulló et al., 1999; Aitcin, 1998; Hallal et al., 2010). Finally, the case of PC-SP4 and PC-SP5 systems may be interpreted as a chemical incompatibility, which led us to argue that the cement particles were not efficiently dispersed.

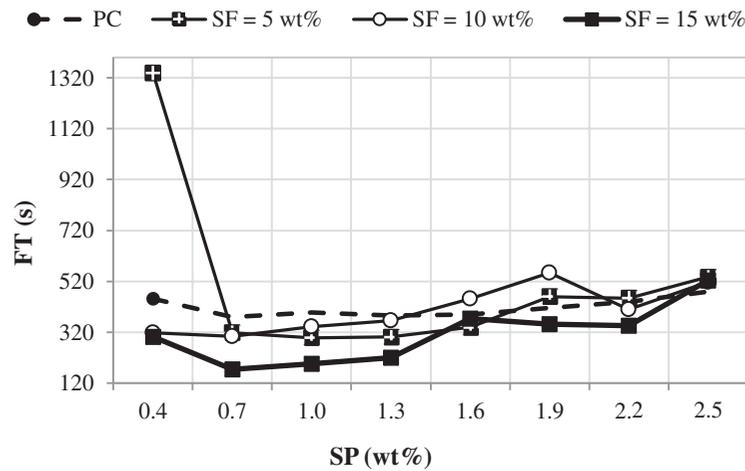
A look at Table 2 permits deduced that this particular cement chemistry was incompatible with the polycarboxylate type SPs where SP5 belongs. It could be attributed to binds up of the Ca^{2+} ions in the pore solution by the SP molecules which inhibited the formation of small calcium-trisulfoaluminate-hydrates; thus, the hydration reaction is not dropped. Another option could be that cement chemistry and SP chemistry inhibited the adsorption of the SP on the cement grains, therefore the steric hindrance mechanism could be altered, which is the main mechanism of polycarboxylates (Li et al., 2014). Nevertheless, more advanced techniques are required in order to understand this complex behavior because it is related of the architecture of the molecular structures, molecular weight, side chain length, degree of sulfonation, and the action of each of the chemical component of the admixture on each individual phase of Portland cement. Techniques such as zeta potential, liquid chromatography, nuclear magnetic resonance, infrared spectrum, mass spectrometry, or molecular dynamic simulations are often used to analyze the PC-SP interactions (Burgos-Montes, Palacios, Rivilla, & Puertas, 2012; Ferrari, Kaufmann, Winnefeld, & Plank, 2010; Mardani-Aghabaglou, Tuyan, Yilmaz, Ariöz, & Ramyar, 2013; Navarro-Blasco et al., 2014; Shu et al., 2016; Zhang & Kong, 2015). Unfortunately, these areas are out of the scope of the authors.

With the exception of the PC-SP2 system, one could argue that the other PC-SP couples are not to be adopted in concrete designs. In these particular cases the SPs could not prevent the cement particles reaction with water causing hydration products to form. We deem also relevant to note the very close behavior between SP1 and SP2 both at 5 and 60 min. Nevertheless, the decision of adopt SP2 as the best SP in this study was made principally taking into account the difference in the percentage at 60 min (see Figure 4) where the rheological state is critical due to age effects. However, in real field conditions other considerations could be playing an important role, such as local price or availability of the product, therefore SP1 could be another good option. There are several possible parameters involved, for example, the SP compositions and physico-chemical properties of the cement grains (see Table 1). Notice that the soluble alkali content of the cement has been identified as an important parameter in the analysis of these couples (Nkinamubanzi, Kim, & Aitcin, 2000; Yamada et al., 2001). However, in the present study this is discarded as a possible source of incompatibility since the present cement has $Na_2O\text{-eq} = 0.44\%$, which is within the theoretical optimal range where FT at 5 min and ΔFT has been found to exhibit better values (Hallal et al., 2010).

The main findings in this section could be summarized as follows:

- With the exception of the PC-SP2 system, PC-SP1/SP3/SP4/SP5 couples are not to be adopted in concrete designs because they could not prevent the cement hydration.
- There are several possible parameters involved, e.g. the SP compositions and the physico-chemical properties of the cement.
- Even though the soluble alkali content ($Na_2O\text{-eq}$) of the cement has been identified as an important parameter in the fresh state behavior of cementitious materials, in the present study this is discarded as a possible source of incompatibility since the $Na_2O\text{-eq}$ of the cement is within the theoretical optimal safety range for flowability.

Figure 5. Flow time as a function of SP2-dosage at 5 min ($w/b = 0.35$).

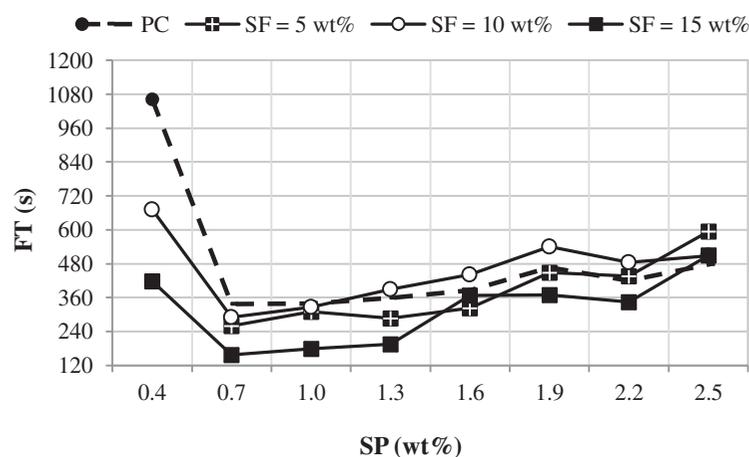


3.2. PC-SP2-SF-0.35 system (Stage II)

Once the most satisfactory PC-SP couple had been identified ($SP = SP2$), we carried out an analysis at 0.35 w/b by using SF-SP2. Figures 5 and 6 display the rheological behavior of the system at 5 and 60 min, respectively. Hereupon, this system is designated as PC-SP2-SF-0.35. Figure 5 reveals high $FT = 1,340$ s at $Sp = 0.4$ wt%, which was developed by the system with SF = 5 wt%. The rheological behavior in this particular point (SF = 5 wt%) has been found troubling by several investigators (Hallal et al., 2010; Nehdi & Mindess, 1998) since high SP dosage is required. In this study this may be explained as follows: (i) the packing density of the materials, particularly at SF nearing 5 wt%, in which the granular particles presented the worst packing between them (increasing the SP demand), (ii) it is known that the aluminates phases are highly reactive (Dalas et al., 2015) and at that low w/b working with cementitious materials is more challenging. However, the presence of gypsum is expected to suppress the reactivity of these phases. The relatively low mineral admixture concentrations tended to accelerate the solubility of the aluminates, which permitted that the anionic SP molecules be more likely adsorbed on these phases. In addition, the vacancy gypsum molecules tend to accelerate the C_3S hydration. In this particular research the cement used has a high value of $C_3A + C_4AF$, which could worsen the situation. At 60 min (see Figure 6), as at 5 min in Figure 5, the same troubling point ($Sp = 0.4$, SF = 5 wt%) displayed an extreme FT value of 1,998 s, not shown in Figure 6 as it fall off scale.

In general, at $w/b = 0.35$ and at the saturation dosage, the presence of the mineral additions improved the FT of the PC-SP2 couple, with respect to the value obtained with plain conditions. Nevertheless, the following considerations must be noted as the main findings in this section:

Figure 6. Flow time as a function of SP2-dosage at 60 min ($w/b = 0.35$).



- Although 10 and 15 wt% SF additions appear to improve the FT at 5 min, the ΔFT increased with respect to the plain system. Yet, the ΔFT is not an absolute amount but a relative one and, therefore, these SF additions are still better than the control-case.
- At SF = 5.0 wt% the SD increased from 0.7 to 1.0 (wt%) with respect to the plain case and the ΔFT reached the most critical “relative” value (+12.0) between the PC-SP2-SF-0.35 systems.

3.3. PC-SP2-SF-0.40 system

Figures 7 and 8 display the rheological behavior of the PC-SP2-SF-0.40 systems at 5 and 60 min, respectively. In general, contrary to PC-SP2-SF-0.35 systems, these couples managed to have the SD improved by the SF at all replacement levels. As in PC-SP2-SF-0.35, the FT is very long in the PC-SP2-SF5 system at 5 and 60 min (see Figures 5, 6 and 8). With regard to FT, note that there is no established numerical criterion for the Marsh test when mineral admixtures are added. Then, the criterion employed was based on the times established for plain systems (Aitcin, 1998; Hallal et al., 2010). All eight systems analyzed presented acceptable values of SD ranging from 0.40 to 1.0 wt%. Also, the PC-SP2-SF5-0.35 system showed high $\Delta FT = +12$ s, and the PC-SP2-SF15-0.40 system showed the highest ΔFT of +35 s.

Thus, the compatibility criterion at $w/b = 0.40$ for the eight systems was only successful for three of them, namely: SF = 0.0, 5.0 and 10.0 wt%. The other systems were found incompatible applying the conventional criteria from the Marsh test without mineral admixtures. With the exception of data point SF = 5 wt% at $w/b = 0.35$, note that SF additions allowed smaller both FT at 5 min and SD values. This behavior contradicts other works (Agulló et al., 1999; Zenati, Arroudj, Lanez, & Oudjit, 2009), where the addition of SF led to FT increments. In that literature, the results were attributed to the high fineness of the mineral addition, which caused an increment of the required water. In the present study, the improvement in FT as the SF content raises is attributed to the gradation in the packing density of the granular phase even though the use of the finest SF particles, as long as the SP is present to avoid earlier PC-SF chemical reactions. Nevertheless, the results here are in agreement with Erdoğan, Arslantürk, and Kurbetci (2011) which found that melamine-type superplasticizer needed the same dose as that required by cement type I to induce the same rheological behavior. As can be seen this is a complex phenomenon, and the improvements in rheological properties depends in several factors including on the type of the SP employed.

3.4. Fresh concrete properties (Stage III)

Table 6 lists the test results performed on fresh experimental samples. The purpose of these concrete rheological measurements was to validate the conclusions previously obtained from the Marsh's experiments. The initial slump of all mixtures was in the range of 108–130 mm, except the SF = 15 wt%, which reported 83 mm. The air content of all mixtures was in the range of 3.6–5.2%, the unit weight in the 2,352–2,392 kg/m³ range, and the flow area, within the 103–150% range.

Figure 7. Flow time as a function of SP2-dosage at 5 min ($w/b = 0.40$).

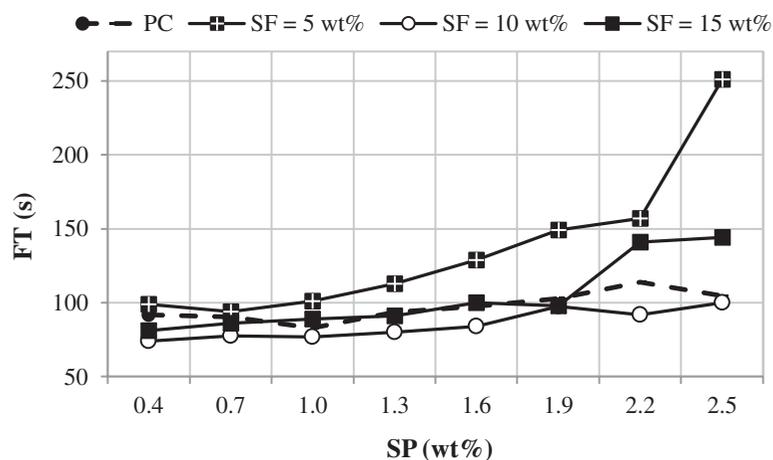
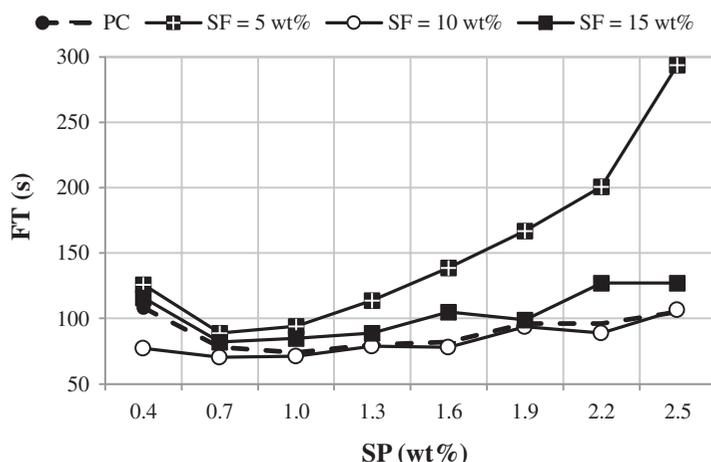


Figure 8. Flow time as a function of SP2-dosage at 60 min (w/b = 0.40).



The unit weight for all nS concretes showed steady values very similar to the control-samples. The unit weight for SF-concretes varied from 2,392 kg/m³ at SF = 5 wt% to 2,352 kg/m³ at SF = 15 wt%. This behavior is expected because of the relative high replacement level of PC, i.e. 15%, and the different specific gravities (SG) of both materials, i.e. SG (SF) = 2.1 (see Table 3) < SG (PC) = 2.9 (see Table 1). In all concrete designs the quantities of fine/coarse aggregates were kept constant (see Table 4). Nevertheless, the unit weight in control-concretes was smaller than those in nS-concretes; this indicates that nS-concretes acquired a better cohesion when compared to plain-concretes (see Table 6).

3.4.1. Fresh concrete results for silica fume additions

The incorporation of amorphous silica of different size induced very different rheological results (see Table 6). The SF-systems presented SP dosages lower than both control- and nS-specimens. Nonetheless, SF-samples exhibited slump loss higher than them. In particular, the effect of SF additions in the present concretes can be described as follows:

- (1) Maintaining the same initial slump, the replacement of PC by SF reduced the amount of SP from 54% (SF = 5 wt%) to 64% (SF = 15wt%) when compared to control samples. This result using SF agrees with the literature (Ferraris et al., 2001; Khatib, 2008; Swamy, Sakai, & Mokamura, 1994) where it was reported that replacements of ultrafine fly ash, slag, and fly ash as mineral additions in concretes could reduce the SP amount without drawbacks in workability. Nevertheless, the SF results in Table 6 disagree with the behavior found by some authors (Ferraris et al., 2001) where the replacement of SF (12 wt%) induced a 50% increase in the SP dosage to maintain the rheological properties of the control concretes. It can be concluded from this survey of the literature that the concrete rheological behavior with fine

Table 6. Fresh properties of concrete binary mixtures (w/b = 0.35) with time t in minutes

Mix code	Unit weight (kg/m ³)	Flow area (%)	SP (wt%)	Air (%)	Slump (mm)					
					t = 0 (min)	t = 10 (min)	t = 30 (min)	t = 60 (min)	t = 90 (min)	t = 120 (min)
CO	2,382	138	1.94	4.7	114	111	98	89	44	22
N1	2,386	125	2.11	3.8	108	108	102	95	95	89
N2	2,382	142	1.71	4.3	114	114	114	105	102	95
N3	2,391	108	2.30	4.3	108	108	89	89	32	13
S5	2,392	150	0.90	3.6	114	102	83	32	13	0
S10	2,370	119	0.60	4.8	130	89	25	0	0	0
S15	2,352	103	0.70	5.2	83	32	0	0	0	0

mineral additions is a rather complex problem, and moreover the simultaneous use of mineral additions and chemical additives (Peng, Deng, Huang, Yuan, & Peng, 2015). In this sense, Burgos-Montes et al. (2012) by using adsorption isotherms demonstrated that higher consumptions of SP in SF-cements could be related to the high specific area rather than its affinity for the admixtures. This former situation does not favor any adsorption affinity; therefore, the fluidity is not enhanced.

- (2) In laboratory tests the problem present in the SF-concretes at medium and high levels ($SF \geq 10$ wt%) was related to the extreme susceptibility to bleeding and segregation associated with high SP levels. Therefore, the SP amount cannot be large, but a low SP dosage could have induced a premature slump loss at early time (see Table 6). At lower levels of replacement, e.g. $SF = 5$ wt%, the SD corresponded to the point with better initial slump, because higher dosages of SP tended to decrease the slump even at $t = 0$ min. This latter fact confirms the trends predicted from the Marsh's analysis (see Figures 5–8) in which SP increments also increased the FT.

The S5 sample was the SF system with the best behavior in slump loss (see Table 6), because it admitted the highest SP dosage before the initial slump, segregation, or excess bleeding (as side effects) were observed. Note that this particular point ($SF = 5$ wt%) presented the highest SP requirement in the Marsh's experiments (see Figures 5 and 7). This is in agreement with Nehdi and Mindess (1998), who found increments in the SP dosage at 5% SF. This fact can easily be correlated with our laboratory experiments because this particular SF addition supported higher SP amounts before exhibiting side effects as explained earlier. In summary, in Table 6 for SF-concretes the experimental SP-values were 0.90 (S5), 0.60 (S10), and 0.70 (S15) and the predicted SP-values for the SD from the Marsh's analysis ($w/b = 0.35$) were 1.0 (S5), 0.70 (S10) and 0.70 (S15). These results proved the accuracy of the Marsh's method to predict SD in SF-concretes.

In a similar fashion, SF systems with replacements higher than 5 wt% displayed poor slump values in the beginning ($t = 0$ min), as the SP was increased and segregation was observed simultaneously in the flow table test. This agrees with the results from the Marsh' analysis (see Figures 5 and 6) where an increase in SP dosage induced an increase in FT at both 5 and 60 min. Finally, with respect to SF, one should note that the general graphical behavior from Marsh' analysis at $w/b = 0.40$ also adequately relates to the experimental results found hereby. Nevertheless, the numerical results registered during the Marsh's analysis (Stage II) were obtained by selecting only minimum values from the graphical behavior, hence this fact affected the good global performance registered in the figures (see Figures 7–8). As a consequence, in systems with mineral additions the use of Marsh's methodology seems to be an appropriate alternative to predict the behavior of field SF-SP mixes, as long as the w/b employed is the same in both cases, i.e. laboratory and field concrete conditions.

3.4.2. Fresh concrete results for nano-silica additions

Additions of nS appeared to maintain the same SP dosage requirement as in the control samples. This was unexpected because the specific surface area of both materials are extremely different, with the nS particles bearing almost 300 times the value of SSA for the cement particles (see Tables 1 and 3). This results contrast with three recent works carried out employing SP (polycarboxylate) and nS: the first one was using nS and metakaolin where the large specific surface area of ns particles led to a large SP consumption as compared with metakaolin with lower surface area (Navarro-Blasco et al., 2014). In the second and third ones, the side effect in the fresh state due to the increase in the amount of nS could be overcome by using the SP at dosages higher than the SD (Sonebi et al., 2015; Zapata, Portela, Suárez, & Carrasquillo, 2013); nevertheless, these latter works were carried out in mortar samples not in concrete ones. In fact, the slump loss at 1 and 2 wt% was better than in control and SF concretes. We attribute this effect to the synergy between both enhancements in the packing density and effective SP adsorption. Nevertheless, the highest SP dosage was in the highest nS level (N3), but this particular level seems out of the optimal range of enhancements in the packing density, i.e. up to 2 wt% nS (following our experiments). These results indicate

that for the chemistry/physics of the PC-SP-nS herein, there exists an optimum (2 wt%) and a worst (3 wt%) nS content. One possible cause is the tendency to flocculation associated with large amounts of nS. This adverse effect controlled over the beneficial fluidification effect imparted by the nanoparticles' morphology (filler effect). As a consequence, for the present study higher SP dosages in nS concretes not necessarily guaranteed slump loss delay (see Table 6).

Studies conducted on calorimeter curves at early age of the hydration reaction demonstrated that nS can reduce the calcium and hydroxyl ion concentrations (Zhang & Islam, 2012). Therefore, a reduction in calcium and hydroxyl-ions induces crystallization of the calcium-aluminate-trisulfate hydrate as large crystals structures, and then the hydration reaction of the PC is not slowed down (Chandra & Björnström, 2002). Nevertheless, in the present study at 2 wt% nS the amount of SP required was less than in the control samples, and the slump loss at 120 min was the best reported here, with 332%, which is even better than in control concretes (see Table 6). A varying effect on the SP dosage came forth as we varied the nS amount; this is attributed to the physico-chemical properties of the materials employed and the fluidification effect in the packing density for this particular cement and the nS content at 2 wt%. Fresh concrete tests indicate an SP of 2.1 wt% (see Table 6) for N1 samples. From the Marsh's analysis at both w/b ratios the minimum value registered was $Sp = 1.6$ wt%. One can conclude that the Marsh's-nS analysis and field concrete trials do not agree in terms of their numerical outcomes. Nevertheless, the general graphical behavior could effectively reflect the experimental trend found in field concrete investigations.

3.4.3. Summary of fresh concrete experiments

Based on the aforementioned results one can conclude that the Marsh's methodology is an effective (yet preliminary) test to understand the *global or overall* behavior of PC-SP-nS/SF systems. However, the tabulated Marsh's values must be interpreted cautiously because they can easily lead to erroneous conclusions when mineral admixtures are presence in conjunction with SP. On the other hand, we found that the Marsh's-graphical global behavior at 5 min is a better indicator of the field and/or laboratory experiments on actual concretes. Nonetheless, the Marsh's method at 60 min and w/b = 0.40 did not mirror the findings in concrete specimens carried out at w/b = 0.35. However, for nS-concretes the graphical behavior at w/b = 0.35 and 60 min was almost representative of the concretes. Ferraris et al. (2001) stated that cement pastes and concretes present different rheological exposure conditions because the aggregates in the latter act as both heat sinks and shear sources during the mixing process. In addition, in order to reduce cement content or minimize the final cost of concrete, cement industry is increasing the use of mineral admixtures, but the incorporation of these materials make the interaction between the cementitious materials and superplasticizers more complex (Hallal et al., 2010; Shu et al., 2016). Finally, one must note that results for nS/SF concretes from laboratory experiments at w/b = 0.35 concurred more adequate when the Marsh's analysis where developed also at w/b = 0.35. This disagrees with the available literature (Aitcin, 1998) on plain systems where Marsh's experiments carried out with any value of w/b ratio within the 0.35–0.45 range can be representative for the majority of the concrete cast within that range.

3.5. Mechanical strength tests

Table 7 summarizes the average mechanical strength of three specimens at different ages. The analyses were performed using the Fisher least significant difference method at 5% level of error type I. By using this methodology the null hypotheses to be tested is, according to the literature (Montgomery, 2001), Equation (1):

$$H_0: \mu_i = \mu_j \text{ for all } i \neq j \quad (1)$$

where the letter μ is indicating the value of the mean. Assuming a two-sided alternative, the pair of means μ_i and μ_j is declared significantly different (from a statistical viewpoint) if the relation in Equation (2) is possible:

$$|\bar{y}_i - \bar{y}_j| > t_{\alpha/2, N-a} \sqrt{MS_E \left(\frac{1}{n_i} + \frac{1}{n_j} \right)} = \text{Least Significant Difference} \quad (2)$$

Table 7. Mechanical tests analyzed using Fisher’s methodology

Mixture type	Compressive strength (MPa)			Splitting tensile strength (MPa)		
	3 days	7 days	28 days	3 days	7 days	28 days
CO	28.8 (A)	31.9 (A)	50.3 (A)	4.3 (A)	5.3 (A)	5.2 (A)
N1	27.9 (A)	37.1 (B)	49.7 (A)	3.3 (B)	6.1 (A)	7.0 (B)
N2	30.6 (A)	43.5 (C)	53.3 (B)	3.6 (B)	6.8 (A)	6.7 (B)
N3	36.7 (B)	54.1 (D)	67.8 (C)	5.2 (A)	6.5 (A)	6.8 (B)
S5	37.9 (B)	47.9 (E)	65.2 (D)	5.8 (A)	5.8 (A)	6.6 (B)
S10	26.3 (A)	40.8 (C)	56.2 (E)	4.4 (A)	6.3 (A)	6.4 (B)
S15	28.3 (A)	45.1 (C)	60.6 (F)	5.1(A)	5.4 (A)	6.2 (B)

The term $N-a$ refers to the degrees-of-freedom, n_i and n_j are the sample sizes and MS_e is the error mean square. Then, the observed difference between each pair of averages is compared to corresponding *least significant difference value*. If Equation (2) is satisfied then, the conclusion is that population means differ. In Table 7 the letters from “A” to “F” are related to statistically homogeneous groups within the same age of testing (columns).

Figures 9 and 10 for compression and tension analysis, respectively, show the behavior in the hardened state of the concretes through time and for the different mixes. As expected the compressive strength increased with age in all concretes (see Figure 9). At 3 days the compressive strength of N3 and S5 specimens was 27 and 32% higher than in control concretes, respectively. The remaining samples were at the same compressive level than control concretes. At 3 days note that even the large replacement of S15 of cement, these samples exhibit similar compression values as the control concretes, even though at this early age of 3 days the production of $Ca(OH)_2$ is still limited. This behavior is attributed to the SF filler effect rather than to its pozzolanic reaction. At the same age in the tensile test analysis S15, N3, and S5 showed an increase of 19, 21 and 35% compared to control concretes, respectively. Also, the tensile strength of S10 remained unchanged with respect to control concretes and N1 and N2 decreased by 23 and 16% respect to control concretes, respectively.

At 7 days all the samples had higher compressive strength than the control concretes (see Figure 9). The best performances were reached for N3 (70% higher) and S5 (50% higher) samples with respect to control concretes. At the same age, splitting tensile strength results showed that S15 remained unchanged with respect to control concretes (see Figure 10). N2 and N3 specimens showed higher

Figure 9. Compressive strength as a function of age ($w/b = 0.35$).

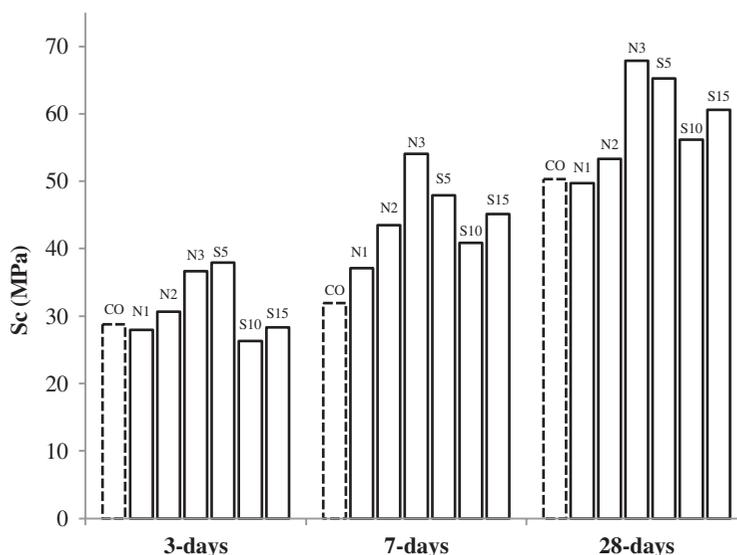
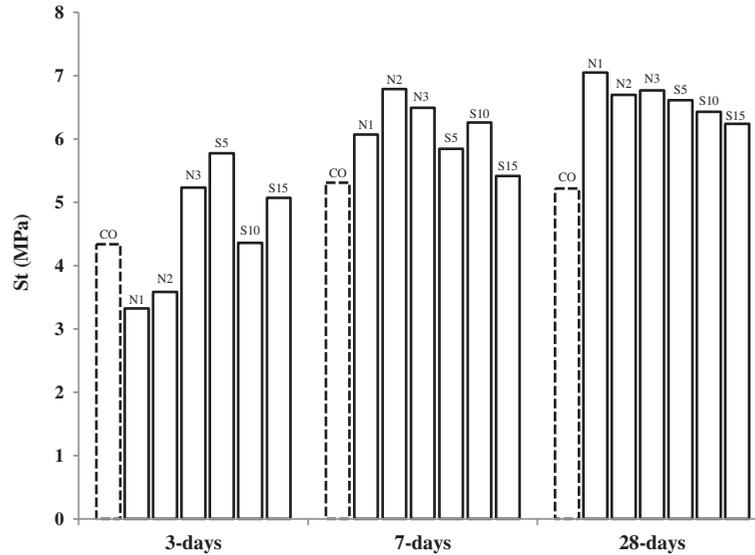


Figure 10. Tensile strength as a function of age ($w/b = 0.35$).



strength, i.e. 28 and 23% respectively, than control concretes, and the N2 samples reached the highest strength level at 7 days. This fact is attributed to the development of the pozzolanic reaction: nS (SiO_2)- $Ca(OH)_2$. At 28 days the compressive strength results showed that N3 and S5 samples were the systems bearing the best behavior, with 35% and 30% values higher than the control concretes, respectively (see Figure 10). This agrees with the report by Senff et al. (2010) who found an optimum content of $nS = 3.3$ wt% in mortars at $w/b = 0.35$. The strength gained at early ages for SF concretes was slightly higher than in nS -concretes. This means that the strength ratio of 3–7 days for nS -concretes ranged from 0.68 to 0.75 whereas for SF-systems it was between 0.63 and 0.79.

Similarly, the 7-to-28 days strength ratio for nS systems ranged from 0.75 to 0.82 whereas for SF systems it was between 0.73 and 0.74. This latter result is in agreement with those of Almusallam, Beshr, Maslehuddin, and Al-Amoudi (2004) who reported that ratio to be from 0.74 to 0.80 for concretes with SF = 10 and 15 wt% at $w/b = 0.35$. In that same research (Almusallam et al., 2004) a strength ratio of 7-to-28 days between 0.60 and 0.65 was reported for plain concrete, which encompassed perfectly the ratio found here for control concretes of 0.63. In general, at 28 days the splitting tensile strength and the compressive strength increased for all mixtures as compared to control concretes. These results agree with published literature on the effect of nS and SF on the tensile strength (Almusallam et al., 2004; Burgos-Montes et al., 2012; Senff et al., 2010).

4. Conclusions

- Among the five chemical admixtures employed, only the couple formed between the cement and superplasticizer called 2 (PC-SP2) presents compatibility with acceptable saturation dosage, low flow time at 5 min and negative fluidity loss. All these rheological characteristics suggest that this couple may be employed in concrete trial batches to study the performance with added aggregates and confirm the results obtained by using the Marsh cone test on cement pastes.
- The PC-SP1, PC-SP2 and PC-SP5 systems showed that high SP dosages can reduce the paste fluidity. These results corroborate that some systems are prone to detrimental effects resulting from excessive SP dosage. We attribute such behavior to nonlinearities in the plastic viscosity rather than improvements in the yield shear stress of the systems when the SP is excessive.
- Addition of amorphous silica in different size particle has very different rheological results. The SF-concretes used SP dosages lower than control samples and nS -concretes. Nevertheless, SF-concretes exhibited slump loss higher than both control and nS -concretes. Particularly, in SF-concretes, the samples exhibited higher susceptibility to bleeding and segregation for higher SF

amounts. This limited the application of high SP dosages, but this fact induced a premature slump loss even at the early age.

- Despite the high surface energy of the nanosilica particles, compared to the cement particles, concretes with silica nanoparticles tended to maintain the same SP dosage requirement as the control specimens. This is attributed to the filler effect of the nS particles, which tend to prevent bleeding, increase packing density and enhance cohesiveness of the cement matrix. Therefore, higher SP dosages are possible without the side effects of segregation or excess bleeding. These qualities were not observed in SF-concretes.
- Based on our results, we can conclude that when mineral additions are applied in concrete mixes the Marsh cone method on cement pastes must be interpreted carefully. In this study, the global graphical trend observed for the cement paste using the Marsh's methodology effectively predicted the behavior found in the fresh concrete tests, as long as the *w/b* in the cement pastes using the Marsh's methodology and the concrete trials are the same. In addition, for SF-concretes the numerical results between cement pastes and concretes were effectively anticipated. Nevertheless, in nS-concretes the numerical results did not reflect the amounts of SP anticipated from the Marsh's experiments. This disagreement is related to deviations from the Bingham model induced by nonlinearities on the plastic viscosity, which violates assumptions of the Marsh's methodology. An abnormal dilution effect (effects of the plastic viscosity) was not observed in SF-cement pastes.
- Compressive and splitting tensile strength improved rather significantly in all mixtures containing amorphous silica. In particular, the compressive strength improvement was higher in the samples containing SF = 5 wt%. On the other hand, the mixture with nS = 3 wt% had the highest compressive strength (35% higher than the control concretes). Also, statistical results showed that the highest splitting tensile strength was measured at 28 days in all the SF/nS- concretes; this again represented an increase of 35% with respect to control samples.

List of notation

<i>w/b</i>	Water-binder-ratio
wt%	Weight by mass in percent
PC	Portland cement
SP	Superplasticizer
SF	Silica fume
nS	Nanosilica
SD	Saturation dosage
FT	Flow time
Δ FT	FT at 60 min minus FT at 5 min

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