ALCONPAT Journal, Volume 6, Issue 1, january - april 2016, Pages 1 – 14

ALCONPAT Journal

http://www.revistaalconpat.org

eISSN 2007-6835

Journal of the Latin-American Association of Quality Control, Pathology and Recovery of Construction

Rheological and mechanical properties of self-compacting concrete with the addition of nano-silica and microsilica

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Article information
DOI:
http://dx.doi.org/10.21041/ra.v6i1.111
Article received on September 22, 2015, reviewed under publishing policies of ALCONPAT journal and accepted on December 15, 2015. Any discussion, including authors reply, will be published on the third number of 2016 if received before closing the second number of 2016.

Legal Information
ALCONPAT Journal, year 6, No. 1, January-April 2016, is a quarterly publication of the Latinamerican Association of quality control, pathology and recovery of construction-International, A.C.; Km. 6, Antigua carretera a Progreso, Mérida, Yucatán, C.P. 97310, Tel.5219997385893, alconpat.int@gmail.com, Website: Revista ALCONPAT.
Editor: Dr. Pedro Castro Borges.
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Responsible for the latest update on this number, ALCONPAT Informatics Unit, Eng. Elizabeth Maldonado Sabido, Km. 6, Antigua carretera a Progreso, Mérida Yucatán, C.P. 97310, last updated: March 30, 2016.

ABSTRACT

Self-compacting concrete is the result of the redesign of quality mixtures with the ability to ensure its correct placement in strongly assembled structures, where the vibration process is too complicated and where there is the risk of altering the position of the reinforcement bars. Along with the advantages of this concrete and due to the greater demand for high performance concrete, silica fume is used, and more recently, nanomaterials with nano-silica as well; mainly, nano-silica. The objective of this work is to obtain self-compacting concretes with nano-silica, silica fume and binary mixtures of both, which satisfy the demands for high mechanical resistance and durability, determining that the dosage with the best features contains: 2.5% of nano and 2.5% of silica fume.

Keywords: Self-compacting; nano-silica; silica fume; rheology; mechanical properties.

RESUMEN

El hormigón autocompactante es el resultado de diseñar mezclas de calidad con capacidad para asegurar su correcta colocación en estructuras fuertemente armadas en las cuales el proceso del vibrado resulta muy complicado y con riesgo de alterar la posición de las armaduras. Unido a las ventajas de este hormigón y debido a la mayor demanda de hormigones de altas prestaciones, se utiliza humo de sílice y, más recientemente, nanomateriales como adiciones. Principalmente nano-sílice. El objetivo de este trabajo es obtener hormigones autocompactantes con nano-sílice, humo de sílice y mezclas binarias de ambas adiciones que satisfagan la demanda de altas resistencias mecánicas y durables, determinando que la dosificación con mejores prestaciones es la que contiene 2.5% de nano y 2.5%.de humo de sílice.

Palabras clave: Autocompactante; nanosílice; humo de sílice; reología; propiedades mecánicas.

RESUMO

O Concreto Auto-adensável é o resultado da concepção de um concreto de qualidade com a capacidade para assegurar a colocação de reforço em estruturas fortemente armados em que o processo de vibração é muito complicado e arriscado por alterar a posição da armadura . Juntamente com as vantagens deste concreto e devido ao aumento da procura de concretos de alto desempenho , o fumo de sílica e mais recentemente , os nano-materiais são usados como adições . Principalmente a nano- sílica. O objetivo deste trabalho é a obtenção de concreto auto- adensável com nano- sílica , sílica ativa e misturas binárias das duas adições para atender a demanda de alta resistência mecânica e durável. A mistura com melhores desempenhos é aquela que contém 2,5 % de nano - sílica e 2,5% de pó de sílica.

Palavras-chave: Auto-compactável; nano-sílica; sílica activa; reologia; propriedades mecánicas.

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1. INTRODUCTION

Self-compacting concrete is the result of the design of quality concrete with the ability to ensure its correct placement in the strongly assembled structures, where the vibration process is too complicated and where there is the risk of altering the position of the reinforcement bars. Professor Okamura and Ozawa (1996) began the development of said concrete at the University of Tokyo during the mid-1990s, improving it in the following years (Okamura, 1997; Okamura and Ouchi, 1999; Okamura, Ozawa, and Ouchi, 2000; Okamura, Maekawa, and Mishima, 2005). This concrete is characterized by a diminished water/cement ratio and a high content of fines, for which chalky filler is added to the mixture, as well as having a reduced content in coarse aggregate and the inclusion of superplasticizers. All of this allows obtaining a concrete with very high fluidity, that due to its own weight is able to achieve a good consolidation without exudation or segregation (De la Peña, 2001, EHE-08, 2010). In the industry of prefabs, the advantages of using this cement are even greater, as they increase the useful life of the molds due to the fact that the absence of vibration allows these to be lighter and, therefore, the maintenance costs are reduced.

Combined with the advantages of the self-compacting cement and as consequence of the increase in the demand for high resistance cement, nano-materials are starting to be used as additives. The aim of this is to provide the material with special characteristics, be it in terms of resistance or in their durability. Therefore, the cement that is sought is considered a high-performance cement, as it should not only satisfy the demand for high mechanical resistance, but also comply with the high demands regarding its durability.

There are several nano-particles that are being researched, the most commonly used are silica, titanium, alumina, and iron (Sanchez and Sobolev, 2010). The nature of the type of the additive to be selected depends on the properties that are required to be improved or conferred to the material, according to the functionality intended. The highest concentration of studies regarding the incorporation of nano-particles in the field of civil engineering are the ones related to nano-SiO_2 (Kawashima, Hou, Corr, Shah, 2013). The majority of studies coincide in stating that the incorporation of said nano-particles produces microstructural changes as it is a catalyst for the pozzolanic additives (Bjornstrom, Martinelli, Matic, Borjesson, Panas, 2004). Similar to the already known fumed silica or micro-silica, the nano-SiO_2 reacts with the calcium hydroxide ($Ca(OH)_2$), producing a larger amount of CSH gel that densifies the material with the consequent reduction of its permeability (Said, Zreidan, Bassuoni, Tian, 2012) and control of the leaching Ca^{2+} (Nazari and Riahi, 2010). The size of the silica that is added produces changes in the mean number and size of the portlandite crystals. These microstructural changes are associated to the changes in the macrostructural properties of mortars and concrete such as resistance to compression, elastic module (Yu, Spiesz, Brouwers, 2014; Zyganitidis, Stefanidou, Kalfagiannis, Logothetidis, 2011), and durability (León, Massana, Alonso, Moragues, Sánchez-Espinosa, 2014), among others.

There are several studies on the influence of nano and micro silica on concrete in which they compare different parameters (Mondal, Shah, Marks, Gaitero, 2010; Borralleras, 2012; Craeye, Van Itterbeeck, Desnerck, Boel, De Schutter, 2014; Rong, Sun, Xiao, Jiang, 2015), but there are few works where binary mixtures of both additives are included in self-compacting concrete with high performance. Thus, this work intends to study the influence of nano-silica, micro-silica or fumed silica, as well as that of the additives of ternary mixtures on the rheological and mechanical properties of self-compacting concrete, in order to establish the differences between the different dosages and to be able to determine the mixture with the best behavior in light of these properties, both in fresh and hardened concrete.

2. PROCEDURE

For the manufacture of the mixtures, Portland cement CEM I 52,5 R (PC) was used according to EN 197-1, the properties of which can be seen in table 1.

Table 1. Physical-chemical properties of Portland cement (PC), nanoSi (nSi), and microSi (mSi).

	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	K_2O	Na_2O	Lost fire (%)	Density (g/cm^3)	Specific surface (m^2/g)
CP	19.20	6.07	1.70	63.41	2.56	3.38	0.2	0,33	2,09	3,5	0,42
nSi	99.90	-	-	-	-	-	-	-	0,10	1,29	200
mSi	94	-	-	-	-	-	-	-			

The nanosilica (nSi) used is Levasil 200/40% in aqueous dispersion form with 40% richness, a specific surface of 200 m^2/g and a particle size of 15 nm (approx.) (see Table 1). The micro silica or silica fume (mSi) used is Elkem Microsilica MS 940 U, composed of non-porous, submicron size, amorphous spheres of SiO_2 and small agglomerates of these, with a specific surface of 15-30 m^2/g and a mean sphere particle size of approximately 0.15 microns. Even though some of the spheres may be found individually, the majority of them form agglomerates of primary particles with a typical range of 0.1-1 micron (see Table 1). The additives used were: SIKA Viscocrete 5720 (SP) (polycarboxylate polymer) superplasticizer and a viscosity modifier (VM) additive SIKA Stabilizer 4R. The coarse aggregates used in the mixtures were: river sand smaller than 4 mm, 6 to 12 mm gravel, and limestone filler whose granulometry complies with the UNE standards 12620:2003+A1:2009, with a maximum diameter of 63 μm.

Ten dosages were designed (see Table 2). All samples maintained a water/cementing material relation of 0.36. The dosages were: three with 2.5%, 5%, and 7.5% of nano-SiO_2 ([nSi]-2.5; [nSi]-5; [nSi]-7.5), three with 2.5%, 5%, and 7.5% of micro-SiO_2 ([mSi]-2.5; [mSi]-5; [mSi]-7.5), and three with mixtures of both with the percentages of each additive being of 2.5%/2.5%, 5%/2.5%, and 2.5%/5% of nano-SiO_2 and micro-SiO_2, respectively ([nmSi]-2.5/2.5; [nmSi]-5/2.5; [nmSi]-2.5/5), with regard to the weight of the cement. A tenth mixture without any type of additives was designed, which will be considered the reference concrete.

In order to evaluate the self-compacting characteristics of the designed concretes, the standardized tests were done in fresh material with the EHE-08 (2010) instruction. The aforementioned tests are: slump-flow or the extension of flow tests (UNE-EN 12350-8), the V funnel test (UNE-EN 12350-9), the L Shape Box Test (UNE-EN 12350-10), and the slump flow combined with Japanese ring test (UNE-EN 12350-12).

Once the self-compactness of the mixture was confirmed, the manufacture of 12 test tubes of 100 mm in diameter and 200 mm tall, and of 2 standardized test tubes of 150 mm of diameter and 300 mm tall, was carried out. These test tubes were kept in the laboratory for 24 hours. Once this time had elapsed, they were demolded and cured for 28 days inside a chamber at a temperature of 20±2 °C and a humidity greater than 95%, according to the UNE-EN 12390-2 standard.

Table 2. Dosage of the concretes studied

Component (kg/m^3)	HAC	[nSi]-2,5	[nSi]-5	[nSi]-7,5	[mSi]-2,5	[mSi]-5	[mSi]-7,5	[nmSi]-2,5/2,5	[nmSi]-5/2,5	[nmSi]-2,5/5
Cement	450	450	450	450	450	450	450	450	450	450
Nano-silica	-	11,25	22,5	33,75	-	-	-	11,25	22,5	11,25
		2,5%	5%	7,50%				2,5%	5%	2,5%
Micro silica	-	-	-	-	11,25	22,5	33,75	11,25	11,25	22,5
					2,5%	5%	7,50%	2,5%	2,5%	5%
Water	162	166,0	170,1	174,1	166,0	170,1	174,1	170,1	174,1	174,1
Filler calizo	100	100	100	100	100	100	100	100	100	100
Sand	1160	1160	1160	1160	1160	1160	1160	1160	1160	1160
Gravel 6/12	585	585	585	585	585	585	585	585	585	585
SP (%)*	2	3,30	4	6	2,30	2,50	2,70	3,60	4,80	3,90
MV (%)*	0,15	0,15	0,15	0,15	0,15	0,15	0,15	0,15	0,15	0,15

(*) Percentage in cement weight.

In order to characterize the concretes according to their mechanical properties, 3 test tubes were evaluated in terms of resistance to compression at 7, 28, and 90 days since their manufacture, according to the UNE-EN 12390-3 standard. The maximum size of the coarse aggregates, inferior to 12 mm, is what enabled their use for said test (Fernandez, 2013). After 28 days of being cured, the resistance to indirect traction was also determined through the testing of two 100x200 mm test tubes in accordance with the UNE-EN 12390-6:2001 standard. The two 150x300 mm test tubes were tested at the same age to determine the elasticity module according to the UNE-EN 83316:1996 standard. The aforementioned tests were carried out in an IBERTEST press with a maximum capacity of 1,500 kN. In order to determine the elasticity module, the deformities in the standardized test tubes were measured through a differential transformer of lineal variation from the IBERTEST house with a computer controlled data acquisition system. The loads were increased evenly to the velocity of 0.2 MPa/s during 3 successive load and unload cycles, up to a 40% of the compression resistance. The resistance values to compression, indirect traction, and the elasticity module are the mean value of the results obtained in their corresponding test.

The remaining test tube is used for the microstructural characterization of the mixtures. For this, a thermogravimetric analysis (TGA) at 7, 28, and 90 days was done for all ages and mixtures designed, in accordance with the ASTM E1131:(2008) standard.

For this test, a powder sample was used with a particle size inferior to 0.5 mm. In order to obtain these characteristics, a sample of 20 mm obtained from the test tube after having eliminated the outermost 20 mm was used. The sample obtained went through a grinder in order to obtain particles smaller to 8 mm. These particles were placed in a desiccator connected to a vacuum pump that guaranteed a vacuum pressure between 1 and 5 kPa. The desiccator was left running for 45 minutes. Subsequently, it was submerged for 24 hours in 95% isopropanol in order to stop the hydration processes in concrete. Afterward, it was dried on a stove at 40°C during a minimum period of 72 hours to guarantee the complete drying of the sample.

Prior to the completion of the test, the particles were grinded in a manual steel mortar, finishing the refining of the grain in a Retsch RM 200 agate mortar. The process finalizes through the sieving of the powder through a 0.5 mm sieve. The grinded mass, of a weight of approximately 300 g, was

stirred in an air-tight seal bag in order to homogenize it. The total sample was then divided into 8 parts and a portion of each part was then taken in order to complete two samples of 2 g each, which were placed on a stove at 40°C during 7 days in order to stabilize the mass. The equipment used for the thermogravimetric analysis was a simultaneous thermal analyzer of the SETARAM brand, model LABSYS EVO, with a precision balance of 0.1 µg. For the test, a sample of approximately 55 mg was used, having been subjected to a dynamic heating ramp rate that varied between 40°C and 1,100°C with a heating rate of 10°C/minute. Alumina crucibles were used as reference material, α-alumina (α–Al_2O_3), previously burnt out at 1,200ºC, and a nitrogen test atmosphere (N_2). This analysis allowed determining the quantity of CSH gel and portlandite ($Ca(OH)_2$ that is present in each concrete. For this, the gel water loss values were determined, which were obtained subjecting the sample to temperatures between 105ºC and 400ºC approximately. The water losses of free portlandite were obtained within a temperature range of approximately 400°C and 600°C.

3. RESULTS AND DISCUSSION

3.1 Rheological properties

In the 0 we can observe the visual inspection of the 10 mixtures, where in no case did segregation or exudation of the grout present itself. This result is contrary to the one obtained by Dubey and Kumar (2012) who state that with amounts larger than 2% of a SP of carboxylate type, similar to the one used in this study, a segregation of the mixture can be observed.

Nevertheless, the visual evaluation of the mixtures showed a great amount of bubbling in those that contained nSi. This phenomenon is attributed to the amount of SP that is used to obtain the necessary workability, as indicated by Borrelleras Mas (2012).

In the case of this study, no air occlusion test was carried out on the mixtures. However, Yu *et al*. (2014) carried out tests in high performance concrete with nano-silica contents between 1% and up to 5% of additive with a steady amount of SP, and they obtain an exponential increase of the content of occluded air as the amount of nSi rose, which leads us to conclude that both the amount of SP as well as that that of nSi result in an increase in the amount of occluded air.

On the other hand, in order to evaluate whether this amount of air could be eliminated from the mixtures, those created with the nSi additive were repeated and a table-top vibration was carried out; there, it was observed that the air bubbles did not reached the surface and that the mixture moved from a homogenous form within the molds, forming one mass that moved uniformly. Furthermore, the superficial layer had a plastic appearance that did not allow the expulsion of said bubbles. Subsequently, resistance to compression and PIM tests were done on these vibrated mixtures, and in no case, were there significant differences, therefore the values of the same are not shown in this study.

The proposal of the authors in this study to mitigate the amount of bubbles is to increase the mixing energy for the concrete and to increase the mixing time in the mixer, thereby making it possible for this amount of bubbles to escape due to the mechanical movements of the mixer—thus obtaining a greater workability in the mixtures. The use of condensed polyethylene, along with polycarboxylate, acting as a defoamer, is also recommended.

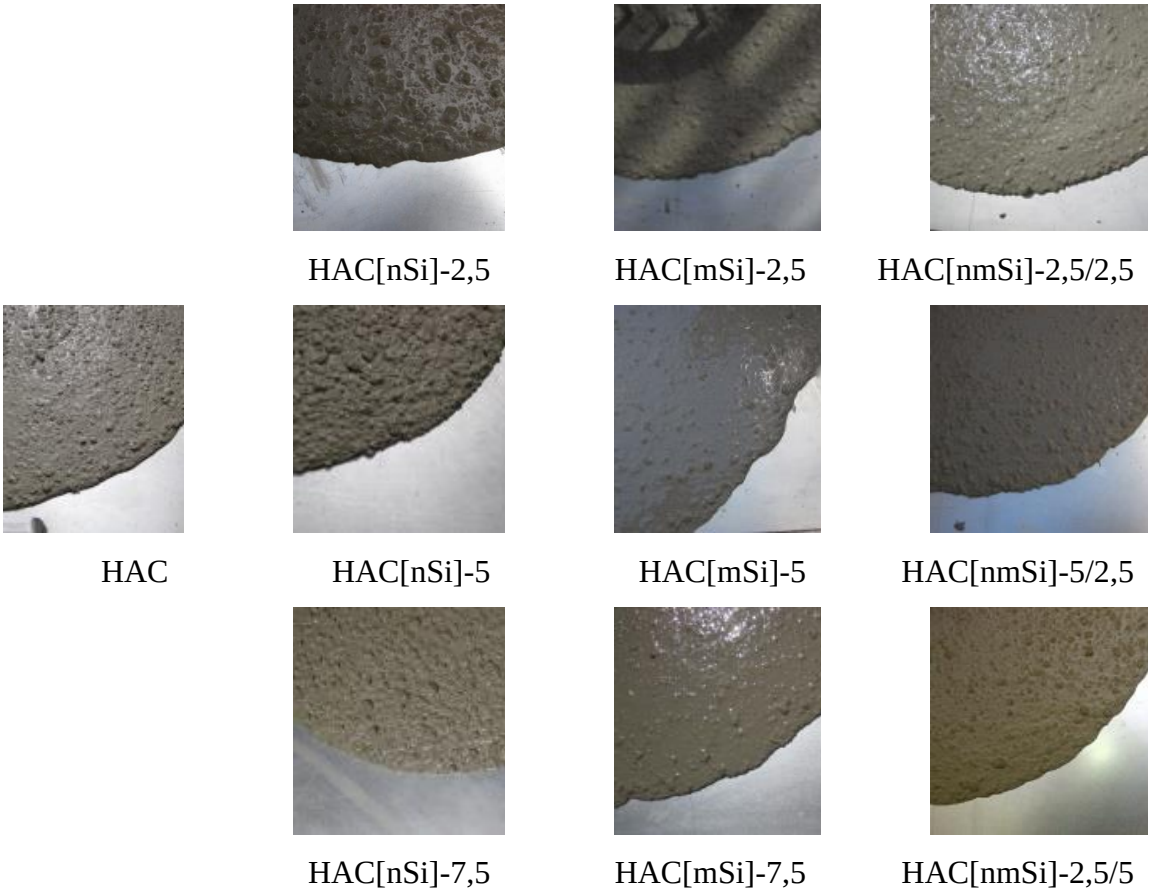

Figure 1. Border aspect of the different mixtures designed, fresh, after the slump-flow test

The values obtained in the different tests for the verification of the self-compacting characteristic of the mixtures, according to the EHE-08 (2010), are collected in Figures 2, 3, 4, and 5. These show the slump-flow diameter of the mixtures (d_f) and the SP used for their manufacture (Figure 2), the Tb time of passage through the V funnel (Figure 3), the capacity of passage through the L shaped box (C_{bl}) (Figure 4), and the slump-flow diameter combined with Japanese ring (d_{jf}) (Figure 5).
In figure 2 and in a general manner, it can be observed that the slump-flow diameter can be found between 550 mm and 850 mm, thus all mixtures comply with said parameter. Furthermore, they do not present segregation or exudation despite the fact that they possess high amounts of SP and even, for the mixture [nSi]-7.5, superior to the 5% that is allowed by the *Instrucción Española del Hormigón Estructural* (EHE-08). These results contradict Dubey and Kumar (2012) who state that with amounts greater than 2% of a SP of the carboxylate type, similar to the one used in this study, segregation of the mixture can be observed. Furthermore, there are authors (Borralleras, 2012) that defend that the maximum amount of SP is determined when the additive stops producing rheological improvements in the fresh material.

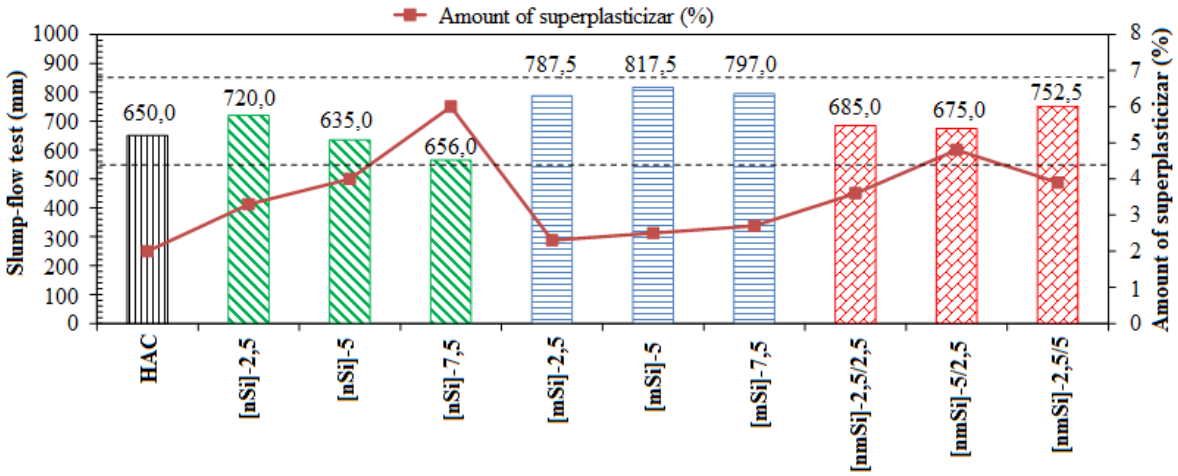

Figure 2. Slump-flow test (d_f) (mm) and amount of superplasticizer.

The existence of a clear influence of the type of additive can also be observed. Therefore, the mixtures with addition of nSi show a decrease in the slump-flow diameter as said addition increases. This can be translated into a lesser workability of the mixture, even when there is an increase of up to 6% in the amount of SP, superior to the recommended amount by the EHE. This phenomenon does not appear when mSi is used as the additive. In this case, there is very little variability in the diameter, which is around 800 mm. Lastly, regarding the binary mixtures, it can be observed how the nSi compromises the workability of the material, making it necessary to increase the amount of SP when increasing the amount of nSi incorporated. Jalal *et al.* (2012) state that both the nSi and the mSi improve the consistence of the self-compacting concrete, but they do not have part in the valuation of the increase of said consistency regarding the content or the type of these. Nevertheless, they determine what quantities of the nSi of the 2% regarding the weight of the cement do not significantly cause a variation in the slump-flow diameter, and if they do, then they are mixed with a 10% of mSi and 2% of nSi. On the other hand, this quantity of additive produces an important amount of bubbling that is directly proportional to the amount added (Nazari and Riahi, 2010). These bubbles may cause the formation of pores that are not interconnected in the hardened material and which could compromise the resistance characteristics of this concrete so that the use of a condensed polyethylene, along with polycarboxylate, acting as defoamer, is recommended (Jalal *et al.*, 2012).

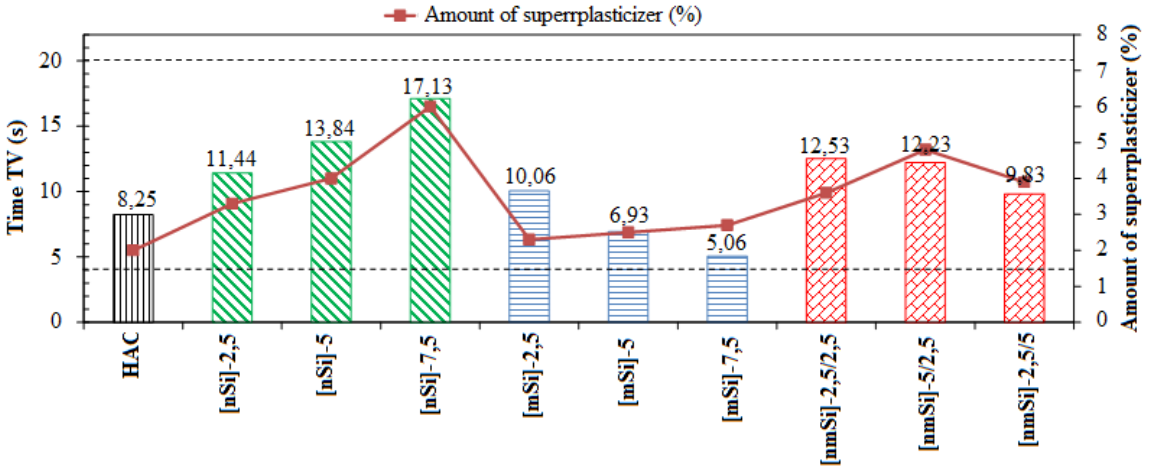

Figure 3. Time (TV) of passage (s) through the V funnel and amount of superplasticizer.

In figure 3, the passage time TV through the V funnel is shown. Also, for this parameter, the requirements of the EHE-08 are fulfilled with regard to the self-compacting characteristic, as the values vary between 4 s and 20 s.

In it, it can be observed that the behavior of the mixtures is clearly different. Those that contain only nSi increase TV as the content in nSi is increased, meaning, they densify, whereas in the mSi mixtures the effect is the opposite, reducing the TV down to 5.06 seconds when the content of mSi is of 7.5% with regard to the amount of cement. In both cases, an increase in SP is necessary—the quantity of it being rather superior in the dosages with nSi. Therefore, it can be confirmed that in the mixtures with nSi, with a similar amount of SP, similar d_f are achieved, though the mixture becomes more liquid due to the action of the higher amount of SP in them. The binary mixtures present a behavior that is somewhat inconclusive, as with a higher content of nSi there is a greater demand for SP even though its TV is similar, making the mixture more viscous when increasing the amount of mSi even though the demand of SP is lower. These results are inconsistent with the ones obtained by Jalal *et al*. (2012), who obtained a minimum passage time through the V funnel of 4 s for the mixture with 500 kg/m^3 and a 2% of nSi, and maximum (12 s) for the binary mixture of 10%mSi+2%nSi and 400 kg/m^3. The differences in the contents of the cement could be the reason for these significant differences in the results, as an increase in the amount of cement improves all rheological properties due to an increase in the volume of the paste (Jalal *et al.*, 2012).

In figure 4, the measure of the capacity of passage C_{bl} can be observed, with all the concretes having values that remain within the limit values of 0.75 and 1. Despite this fact, a different behavior can be observed according to the type of addition. Thus, the capacity of passage for mixtures with nSi experiences a decrease when increasing the amount of nSi.

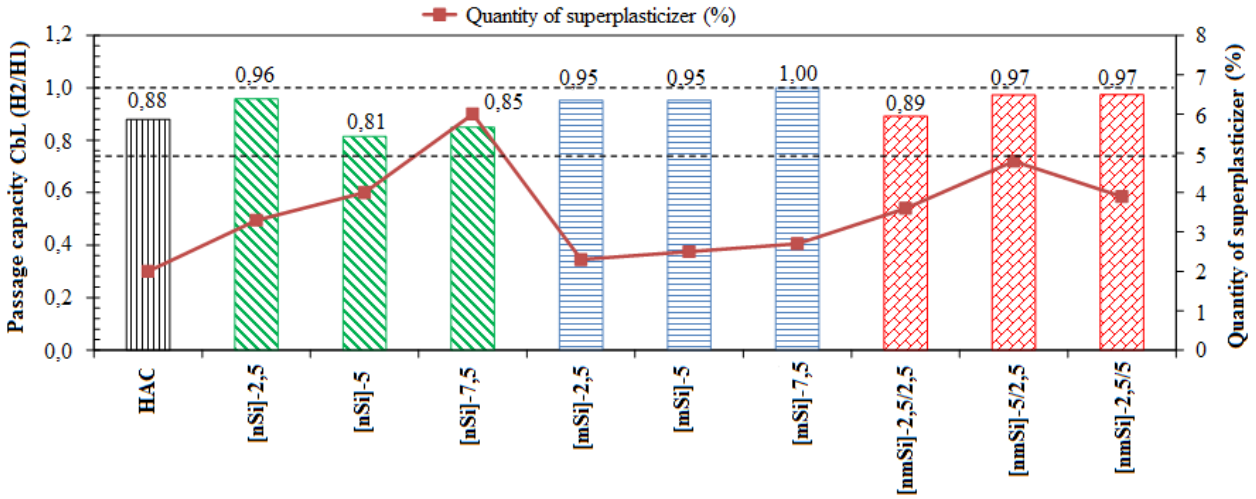

Figure 4. Passage capacity through the L shaped box and quantity of superplasticizer.

Furthermore, this parameter provides information on the capacity of self-leveling of the concrete (EHE-08, 2010), being less self-leveling when the content of nSi is higher. However, the values remain practically constant for both the dosages with nSi as well as for the mixtures with binary additions. It is worth noting the great self-leveling capacity of the concrete that contains a total of 7.5% of mSi with a value of the unit. This good behavior can be due to the fact that this mixture is the one that presents the minimum velocity of PV passage, i.e., it is the most liquid mixture of all the ones that were studied.

In figure 5, the value of the slump-flow diameter combined with Japanese ring (d_{jf}) is shown. The EHE-08 limits the value of this parameter regarding the slump-flow diameter (d_f) obtained in the

same mixture, having to comply in that its difference be inferior to 50 mm, which is fulfilled for the entirety of the designed mixtures.

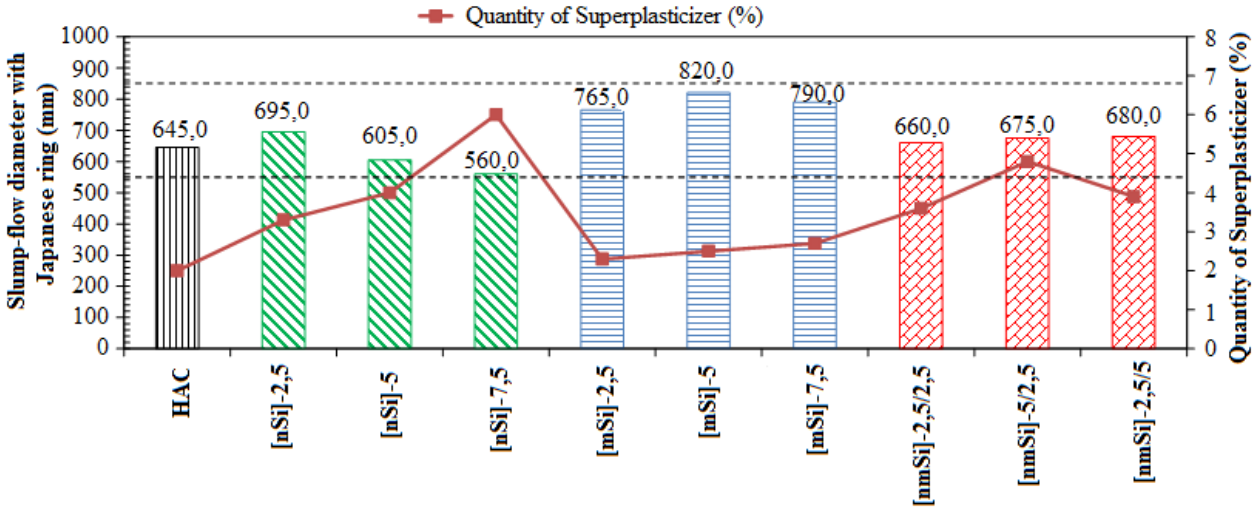

Figure 5. Slump-flow diameter with Japanese ring (cm) and quantity of superplasticizer.

When observing figure 5, it stands out that the concretes with the addition of nSi have a similar behavior to that of the slump-flow test (d_f), though with inferior values, given that with this it is possible to determine the difficulty that the concrete could have when passing through obstacles. Therefore, the greater quantity of nSi the lower the value of this parameter. The highest values are seen in concrete with mSi. In the mixtures with binary additions, the values do not show significant differences among them, not even with the one obtained in [nSi]-2.5. This indicates that it is the content of nSi that governs these mixtures, having to increase the content of SP when the content of nSi increases. An important observation in the manufacture of the mixtures was that the concretes with additions of nSi obtained a significant increase in setting speed where, no matter the amount of SP added, the start of the setting was produced a few minutes after the manufacture. This would make it difficult to manipulate the mixture and, therefore, its implementation. However, this phenomenon could be an advantage in the industry of prefabs, wherein a quick setting could be beneficial due to the possibility of demolding in shorter periods of time. This fact coincides with the studies by Bjornstrom *et al*. (2004), who state that the nSi is a catalyst for the pozzolanic reactions.

3.2 Mechanical properties

3.2.1. Resistance to compression

The resistance to compression of the different dosages is presented in Figure 6. There, it can be observed that the concretes with nSi have higher resistance to that obtained in the reference concrete. Furthermore, said resistance increases as the amount of additive increases.

In the case of concretes with mSi, the resistance to compression is slightly higher for the reference concrete, with notable increases in 7 days and moderate for the rest of the ages. Lastly, and in the case of the mixtures with binary additives, there is no consistent behavior that suggests the preponderance of one of the types of additives. However, the highest resistances were obtained with the [mmSi]-2.5/2.5 mixture, and so the authors consider that the resistance to compression not only depends on the size of the particle and on the amount of additive, but also on the granulometric distribution of all the components of the mixture. Therefore, when there is a higher continuity in

the granulometry of the components of the mixture, the higher their compression will be and thus the greater their resistance.

In these mixtures, the resistance values for compression are of 82.17 MPa at 28 days of being cured and of 86.87 MPa at 90 days. This implies an 36% increase with regard to the values obtained for the reference concrete at the curing times of 28 and 90 days, respectively.

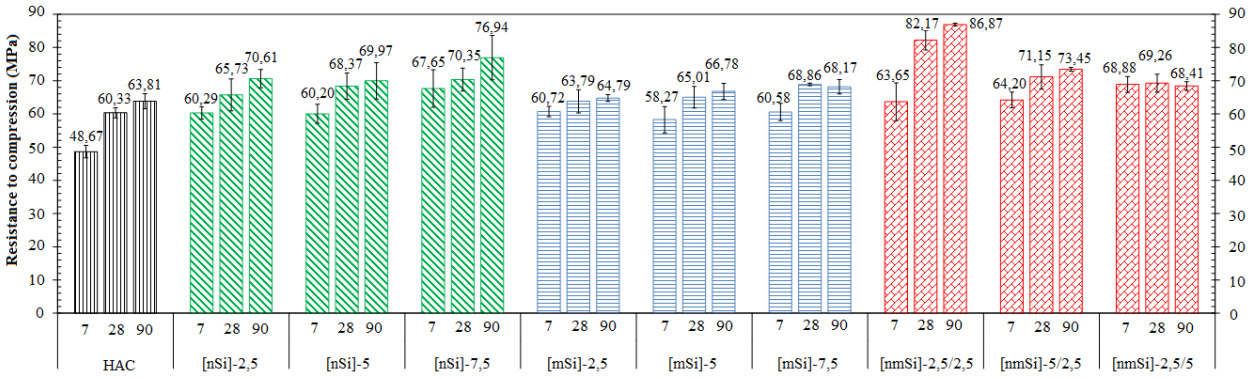

Figure 6. Resistance to compression (MPa)

3.2.2. Resistance to indirect traction and modulus of elasticity

In figures 7 and 8, we present the results to indirect traction resistance as well as the results of the modulus of elasticity.

The value of indirect traction in concretes with additives is significantly higher to the value of the reference concrete, even if these are small differences. However, there are no significant differences between the mixtures with additives. This means that the size and the content of the different additives contained in the different mixtures does not change this property significantly.

Regarding the modulus of elasticity, it can be observed that there are significantly lower values for the mixtures that contain nSi. In the rest of the concretes, the values obtained are similar without them being significant among them or with regard to the reference concrete.

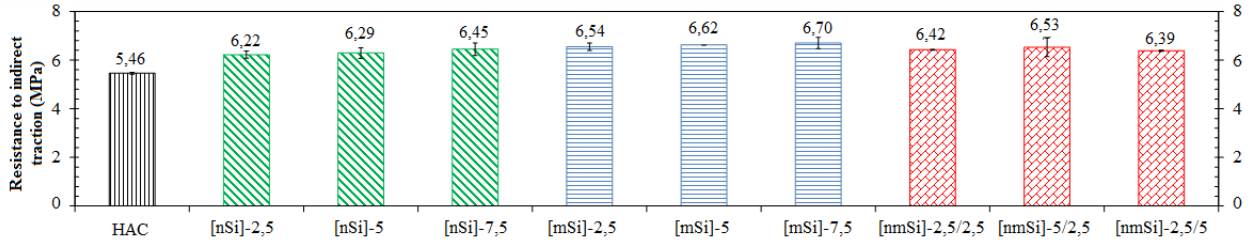

Figure 7**.** Resistance to indirect traction (MPa)

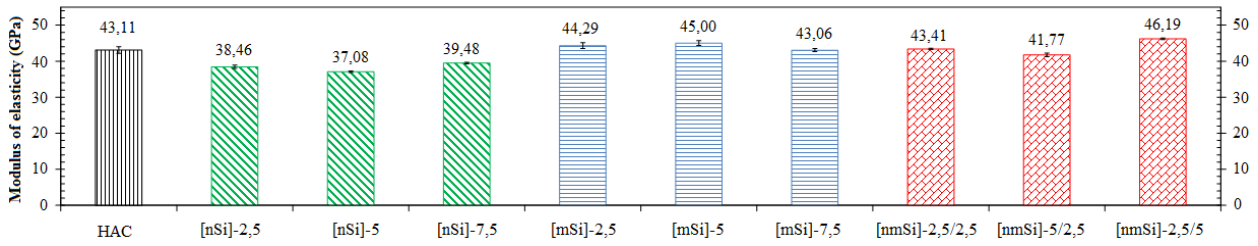

Figure 8. Modulus of elasticity (GPa)

3.3 Microstructural characterization. Thermogravimetric analysis

The results of the thermogravimetric analysis of the ten dosages are shown in Figures 9, 10, and 11 in which the relation between the losses of gel water and of free portlandite water are shown at 7, 28, and 90 days after curing, respectively.

In general, the values obtained allow us to state that, at all ages, the highest values of said relation are the ones obtained in concretes with nSi. This brings to light the fact that the formation of secondary gel or tobermorite gel is higher, which implies a lesser presence of portlandite.

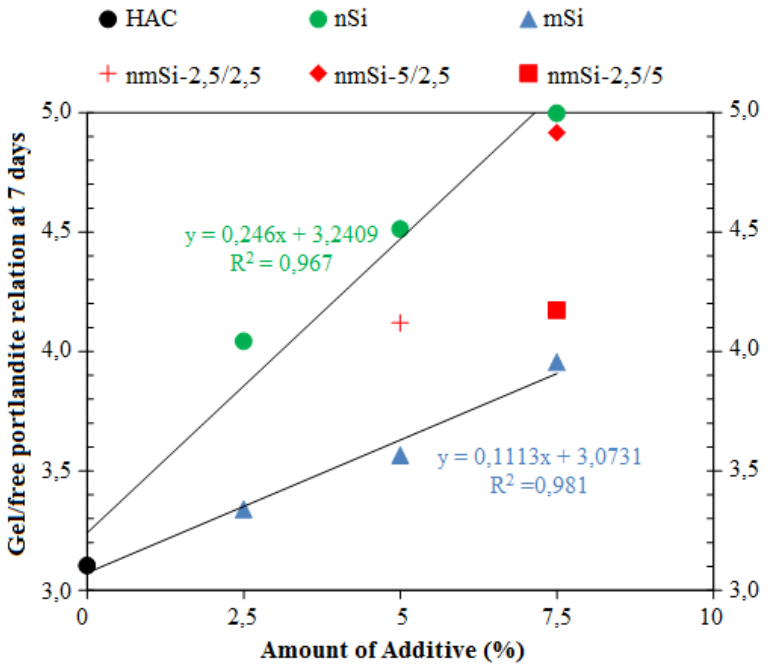

Figure 9. Gel/free portlandite relation at 7 days after curing

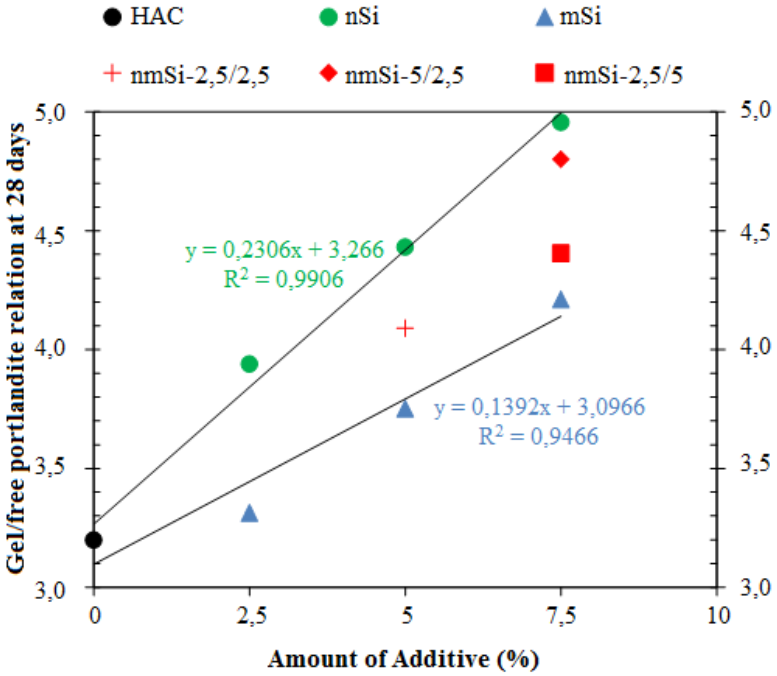

Figure 10. Gel/free portlandite relation at 28 days after curing

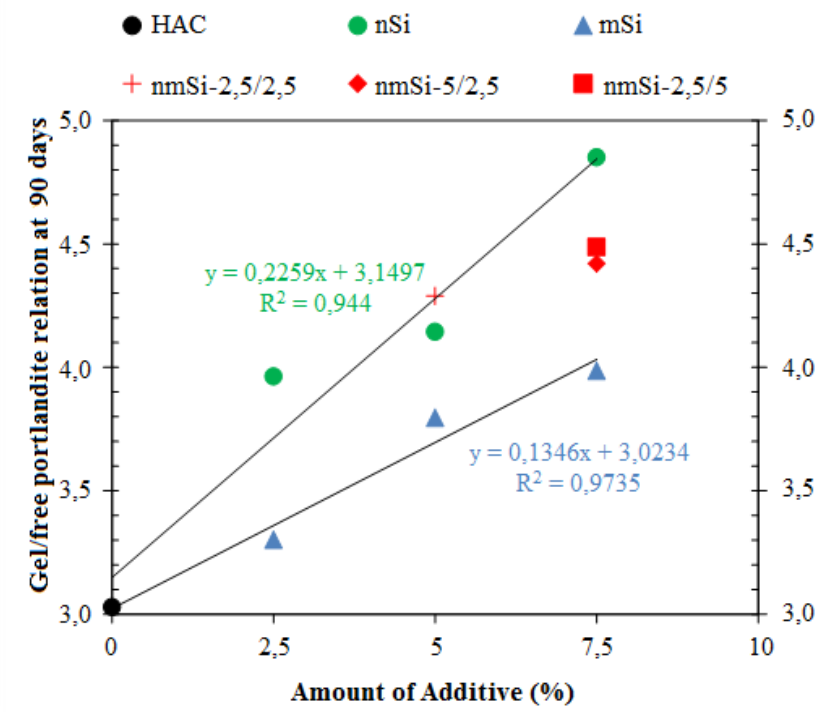

Figure 11. Gel/free portlandite relation at 90 days after curing

Similarly, in the case of concretes with mSi, the relations show lower values, which are consistent with the results obtained by Mondal *et. al.* (2010), Zyganitidis *et al.* (2011), Jalal *et al.* (2012), and León *et al.* (2014). In both cases, the relation increases with the content of the additive. As previously stated, the concretes with a combination of additives do not present a conclusive behavior. The behavior seems to be defined by the higher content of each one of the additives.

On the other hand, it is important to highlight that as curing time passes, the mixtures with nSi show a decrease in the values of the gel/free portlandite relation, a phenomenon that is evidenced by the reduction in the slopes of the lines. This phenomenon can be observed in a progressive manner in Figures 9, 10, and 11. This suggests that the formation of gels is slowed down with the age of curing, being during the early ages when a greater pozzolanic activity can be observed (Jalal *et al.*, 2012). This is consistent with the resistance values to compression at 7 days after curing. However, in concretes with mSi, the values of the gel/free portlandite relation increase as the curing time increases. A smaller particle size accelerates the activation of the pozzolanic reaction.

When analyzing the concretes that comprise binary mixtures, it stands out that in the first ages, the composite mixtures behave in a similar manner to the mixtures that contain a similar additive percentage to the combination of the two, but in each case, they are close to the additive with the higher percentage. When the percentage of both additives is the same, the behavior is practically intermediate. Given that the evolution in time of the micro and nano additive is different, the mixtures that contain both begin matching their behavior, resulting in an intermediate behavior at 90 days to the one that is obtained for the same percentage of each additive. The mixture with 2.5 of nano and micro silica has a differential behavior at longer ages. In this case, their gel/portlandite relation is superior to the one obtained using 5% of nano silica. This result is consistent with the mechanical and durability behavior of the mixture. This behavior could indicate that in this dosage, the relation between the surface of the additive and the free water has been optimal.

4. CONCLUSIONS

The incorporation of nSi generates a loss of workability of the material associated to an increase in the setting speed; a phenomenon that complicates its placement. The viscosity and adaptation to the mold is significantly hindered when nSi is incorporated to the mass. The concretes with a content of 7.5% of mSi or with binary mixtures [nmSi]-5/2.5; [nmSi]-2.5/5 may be considered concretes with a self-leveling capacity. However, the addition of nSi as the only additive implies the loss of this property. The difficulty that the concrete may have due to obstacles increases with a higher amount of nSi. Nevertheless, in concretes with mSi or with binary additives, this property can be considered independent from the content of said additives, even though it is important to note that it is the mixtures with mSi that present a better behavior.

The incorporation of nSi generates a significant increase in the resistance to compression when compared to the concretes with mSi and to the one used as reference. It is the [nmSi]-2.5/2.5 mixture that represents the highest values. Considering all the components of the concrete, this could be due to a more continuous granulometric distribution, being that there is less formation of holes, therefore obtaining a more compact concrete. The incorporation of nSi, mSi, or binary mixtures of both additives cause a slight increase in the value of indirect traction in the designed concretes. The concretes with only nSi show a decrease in their modulus of elasticity, which entails having mixtures with less ductility.

The concretes with mSi show the highest values in the relations between the loss of gel water and that of portlandite during the first stages, which confirms that the formation of secondary gel or tobermorite is higher when nano additives are used. Similarly, in the case of the concretes with mSi, the relations show lower values, which is consistent with the lower resistance that they present. In binary mixtures with the same total amount of additives and with longer ages, the values of the relation come close to the intermediate values of the two additives in the same ratio. The uniquely good behavior of the [nmSi]-2.5/2.5 mixture could suggest that there is an optimal surface / free water relation that could improve the behavior of any of the two individually studied additives.

5. ACKNOWLEDGEMENTS

The authors appreciate the financial support of the *M° de Economía y Competitividad* (Spain), Research project MAT2013-48009-C04-04-P.

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