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# **Effect of nanosilica addition on the fresh properties and shrinkage of mortars with fly ash and superplasticizer**

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## **ABSTRACT**

The ongoing use of various mineral additions along with chemical admixtures such as superplasticizers justifies the need for further research. Understanding and quantifying their effects and possible synergies on the fresh and hardened properties of cement-based materials is necessary, especially if some of these components are known to have a pozzolanic effect. This paper describes and models the fresh and hardened properties of cement mortars including nanosilica and fly ash, and relates their properties to the proportioning of these materials and the superplasticizer dosage. Mini-slump, Marsh cone and Lombardi cone tests were used to examine the properties of the fresh mortars, and to assess density, plastic shrinkage, and drying shrinkage up to 20 days. The equations presented in this paper make it possible to optimize mortar proportionings to the required levels of performance in both fresh and hardened states.

## **KEYWORDS:**

fly ash, mortar, nanosilica, superplasticizer

## 1. INTRODUCTION

### *1.1 Nanosilica as a supplementary cementitious material*

The use of active and inert powders as materials for concrete production has been prompted by two main factors: 1) an increasing interest in high-performance cement-based materials such as high-performance grouts, self-compacting concrete, or ultra-high strength concretes that typically include significant amounts of powders other than cement [1-4], and 2) the demand for sustainable construction and for the reduction of energy consumption associated with cement production [5].

As a response to these two factors, cement replacement materials, also known as supplementary cementitious materials, have attracted much interest from researchers and industry. These terms refer to raw materials such as fly ash (FA), silica fume (SF), ground granulated blast-furnace slag (GGBS) and limestone powder (LSP) that are generated as by-products of other industries and added to concrete.

Nanosilica (nano-SiO<sub>2</sub> or simply nS) can be considered as one of these supplementary cementitious materials [6] but it also falls into the category of nanomaterials or nanoparticles. The nanoparticles most commonly used in cement-based materials are nS, TiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> and carbon nanotubes [7]. Most of the research published to date has dealt with nS [8], and it is reportedly the most widely used variety of nanoparticles nowadays [9]. Nanoparticles in general have attracted considerable interest as a result of their ability to improve concrete properties by modifying the structure of the cementitious matrix at the micro and nano levels [10,11], despite the fact that their market price is still higher than that of fly ash or silica fume [6].

Nanosilica consists of ultra-fine particles of amorphous silica, which is usually distributed and used in aqueous solution, in the form of a slurry or hydrosol [12]. It can be produced via several methods, and the production method affects its properties by determining the degree of dispersion in the slurry or gel [13]. This variable, along with the impact of fineness and particle size on nanosilica performance as a supplementary material, highlights the convenience of referring to “types” of nS when comparing different results [10].

### *1.2 Mechanisms of action*

The reactivity of nS is attributed to two main factors: its high purity in terms of SiO<sub>2</sub> content and its high specific surface area [11]. The effect of nS on the

enhancement of fresh and hardened properties of cement-based materials is exerted through a variety of simultaneous mechanisms:

- Filler effect or pore-filling effect. As a result of the extremely reduced size of nS particles, they function as a filler in the cementitious matrix, improving its microstructure [11]. As nS particles fill the voids between cement grains, they potentially increase the packing density when correctly dosed and dispersed [9].
- Acceleration of cement hydration through nucleation effect. Nanosilica particles, when dispersed in the pore solution during cement hydration, act as highly efficient nucleation sites for the silica units released from cement particles [14] and also for the first C-S-H seeds [8,11]. The hydration products accumulate not only on the surface of cement grains but also around these additional nucleation sites dispersed in the pore solution. As a result, upon good dispersion of nS particles, the production of the C-S-H phase also takes place in voids between grains, producing a potentially more compact matrix [9].
- Pozzolanic effect. Calcium hydroxide in the pore solution forms as a by-product of cement hydration and eventually forms portlandite, a crystalline phase that has no relevant contribution to strength [9]. The maximum concentration of calcium hydroxide in the liquid phase is reached during the dormant period of cement hydration [15]. Nanosilica particles react very quickly with the calcium hydroxide, which is a product of cement hydration, to form additional C-S-H. This was confirmed by monitoring the evolution of the free portlandite content through time in cement pastes, which was significantly decreased in mixes with nS.
- Synergy between the acceleration of cement hydration and the pozzolanic effect. Calcium hydroxide in the pore solution results from the hydration of  $C_3S$  and  $C_2S$ . Besides, since cement hydration is accelerated by the nS particles as a result of the nucleation effect, the rate of  $C_3S$  consumption is accelerated [11,14]. As a result, the rate of calcium hydroxide release is also accelerated. This means that the nucleation effect and the consequent acceleration of cement hydration provoked by nS particles makes the calcium hydroxide more readily available, thus favoring the pozzolanic effect of nS. In consequence, the induction period of cement hydration is shortened when nS is present, as a result of this

accelerated release of calcium ions and their rapid consumption by the pozzolanic action of nS [13].

### ***1.3 Influence of nanosilica on the properties of cement-based materials.***

Nanosilica has been extensively reported to be a material that potentially enhances density, strength development and the mechanical properties of cement-based materials in general [9,16-19]. However, contradictory results are found in literature in relation to the following two key concerns: whether or not the use of nS implies substantial improvement, and the advisable range for the nS contents.

Two main factors contribute to these discrepancies. One is the fact that the nanosilicas used in different studies are of different types, have a different particle size, a different specific surface, or have been produced by different methods [13]. The second is the difficulty of dispersing nS particles in the fresh cement grout, paste, mortar or concrete [6].

The dispersion of nS particles cannot be completely explained on mechanistic grounds. It is true that varying the mixing energy can affect the initial aggregation or dispersion state of these particles in a pure water solution [20]. However, even if nS particles are stable and well dispersed in their original slurry or hydrosol form, once they come in contact with the pore solution of a cement-based material they tend to aggregate as a result of the presence of ions such as  $\text{Ca}^{2+}$ ,  $\text{Na}^+$  and  $\text{K}^+$  released into the pore solution by cement upon contact with water. The high concentration of these ions in the liquid phase compresses the double layer [21] surrounding the nS particles, and the adsorption of  $\text{Ca}^{2+}$  ions onto the surface of nS particles causes a reduction in their negative electrostatic charge. Furthermore, these ions have a bridging effect, agglomerating silica units according to the pattern  $(\text{SiO}^-)-(\text{Ca}^{2+})-(\text{SiO}^-)$  [13]. All of these mechanisms tend to destabilize the distribution of nS particles in the pore fluid and prevent their homogeneous dispersion.

The rheology of cement pastes and mortars with nS presents another issue: the introduction of nS potentially affects the compatibility between the cement and superplasticizers or any other chemical admixture or mineral additions [6,22]. In these systems, increasing nS contents results in significantly higher yield stress values [22], and using superplasticizers at dosages higher than the saturation point has been reported as a convenient way of obtaining better performance in the fresh state [18].

Different conclusions concerning the effect of nS have been reported with respect to the compressive strength of mortars. Some studies have found that it has a limited or negligible impact on compressive strength [12]. In other cases, increasing nS contents increased compressive strength values up to a certain dosage, with further increases causing a reduction in compressive strength, leading to the determination of an intermediate optimum dosage for nS [18,23]. There is no consensus regarding this optimum nS dosage, as the values reported are not congruent. However, even though nS contents of 10% over cement weight or even higher have been considered in some studies, it appears that a rule-of-thumb maximum dosage acceptable for nS has been established as 5% over cement weight [6].

## **2. OBJECTIVES AND RESEARCH SIGNIFICANCE**

The aim of this study was to evaluate the effects of different contents of nS, FA and different SP dosages on the fresh properties and plastic and drying shrinkage of cement mortars. A series of cement mortars was produced and tested, and the experimental results were analyzed and modelled in a semi-empirical manner following a statistical approach. Key parameters and synergies with a statistically significant impact on the rheology and shrinkage of the mortars were detected, and their effect quantified. The equations obtained can be used to evaluate the potential influence of the proportioning of the different components, and to adjust their dosages to ensure the stability of mortar proportionings that include nS and FA. These tools can facilitate the protocol needed to optimize mortar with a given set of performance criteria.

## **3. EXPERIMENTAL PROGRAMME**

### ***3.1 Factors and levels considered***

The factors considered in this research were:

- Nanosilica added to the mortar. Its solid weight, expressed as percentage of the cement weight in the mortar, was varied between 0.5% and 3.0%.
- Fly ash as partial replacement of cement. It was used in amounts between 5% and 20% over the weight of cement.
- Superplasticizer dosage, varying between 0.3% and 0.9% over total binder weight, or over total weight of cement and fly ash.

Three different values were considered for each one of these factors, as summarized in Table 1.

### **3.2 Materials**

The materials used to produce the mortars were tap water, cement, FA, nS, a PCE-based SP, and sand. Table 2 presents the equivalent oxide composition of cement and FA and the composition of the solid fraction of the colloidal nS. All values are expressed as percentage relative to total mass.

The cement used was Portland cement type CEM I 42.5N, as specified by the standard EN 197-1:2000 [24]. The FA used conforms with the standard EN 450-1:2005 [25]. Nanosilica was used in a commercially available colloidal form: an aqueous solution with a SiO<sub>2</sub> content of 50% by mass. The SP used was a modified polycarboxylate. The same well-graded siliceous sand was used for all mortars, with a density of 2.7 Mg/m<sup>3</sup>, a water absorption capacity of 1%, and a maximum particle size of 1.18 mm.

### **3.3 Design of the experimental program**

A total of eleven mortar proportionings were considered, as summarized in Table 4. Mortars 1 to 8 corresponded to all possible combinations of the maximum and minimum values of the factors considered, as shown in Table 1. Mortars 9 to 11 were selected as center points in this experiment and were all proportioned identically: the value for each factor is the central or average value shown in Table 1. The introduction of the center points in the experimental program makes it possible to detect quadratic trends, if any.

Two batches of each of the mortars in Table 4 were prepared and tested according to the details and procedures described in the following section.

### **3.4 Experimental methods**

A water-to-binder ratio (*w/b*) of 0.35 was kept constant throughout the experiment. All mortars were prepared in seven minutes using a planar-action high-shear mixer with a maximum capacity of 4.5 litres.

The sequence and timing of operations was exactly the same in all cases. Water, nS and SP were first poured into the mixer and mixed for one minute at low speed (140 rpm). After that, cement and FA were added to the mixer and mixing went on for two

more minutes. Then, the mixer was stopped and any lumps were crushed and any solids adhered to the surfaces of the mixer were rehomogenized. The time for these operations was less than one minute. Subsequently, the mortar was mixed for two more minutes at high speed (285 rpm), then for one more minute at low speed (140 rpm).

Given the number of tests to be performed for each mortar proportioning, it was decided to prepare two batches of each. First, one 2 litre batch of mortar was produced to carry out the following tests: mini-slump, Marsh cone, and Lombardi plate. A second 1.8 litre batch of mortar was produced for the cone shrinkage test (to evaluate plastic shrinkage) and the drying shrinkage test.

The mini-slump flow test was carried out immediately after mixing, using a truncated cone with an upper diameter of 19 mm, a lower diameter of 38 mm, and a height of 57 mm [26]. The value of spread measured was the average of two perpendicular measurements.

The Marsh cone test was carried out after the slump-flow test, measuring the time it took for the mortar to flow out of its 10-mm orifice. One litre of mortar was poured into the Marsh cone, and the time it took for 700 ml of mortar to flow out of the cone was measured.

The density of the fresh mortar was determined by measuring the grout with a mud balancer. Cohesion was measured 30 minutes after mixing using a Lombardi plate cohesion meter. A thin galvanized steel plate (100×100×1 mm) was immersed in the grout and hung on a stand placed on an electronic balance. The weight of the grout still adsorbed to the plate when the mortar stopped dripping was retained, and with this value, along with the density of the mortar, the average thickness of the mortar adhered to the plate was obtained.

The plastic shrinkage of the mortar up to 20 hours after mixing was determined using the shrinkage cone, shown in Figure 1. It is based on the measurement of the distance between a laser emitter and a reflector placed on the surface of the mortar sample and the variation of this distance with time was monitored over a period of 20 hours. The sample of mortar was put in a thin cone-shaped plastic bag, which was then placed in a clean and a dry conical stainless steel mould. The plastic bag minimized the friction between the sample and the mould surface so that when the sample shrank, a downward movement of the upper surface was registered. The reflector (a plastic plate of 20×20 mm) was placed on the top surface of the sample. The reflector displacement over the measurement time was converted to volume change.



## 4. RESULTS AND DISCUSSION

Several outputs from the tests carried out to characterize the behavior and performance of fresh and hardened mortar were obtained. All results are given in Tables 5 to 8. Each one of these parameters was related to the values of the factors considered in this research by means of Multiple Linear Regression (MLR). The threshold p-value for selecting statistically significant effects was 0.05. The equations obtained are presented and discussed in the following subsections.

### 4.1 Flowability: Marsh cone test results

Experimental results obtained from the Marsh cone test are given in Table 5. To model the flow time in the Marsh cone test  $t_{700}$  in relation to the mortar components, the inverse of this time was considered instead,  $1/t_{700}$ , in order to include those cases when the mortar was too thick to flow (in such cases,  $1/t_{700} = 0$ ). The following relationship was obtained (R-squared = 0.97):

$$\frac{1000}{t_{700}} = -8.75 + 30.4 SP + 1.49 nS - 4.96 nS SP \quad (1)$$

Where:  $t_{700}$  is the flow time for 700 ml of mortar coming out of the Marsh cone,  $SP$  is the dosage of superplasticizer expressed in percentage over binder weight, and  $nS$  is the amount of nanosilica added, expressed in percentage over cement weight. As the equation reflects, the Marsh cone flow time is significantly affected by  $nS$  content and  $SP$  dosage.  $FA$  content is not included in the equation because it did not have a statistically significant effect on  $1/t_{700}$ .

Figure 2 plots the modelled response surface as given by equation (1). It was assumed, in agreement with the experimental results, that  $t_{700}$  values higher than 140 seconds as predicted by equation (1) correspond to mortars that are too thick to flow through the Marsh cone. Only the part of the response surface corresponding to mortars with this level of acceptable flowability is presented in Figure 2. It is observed that increasing  $nS$  contents make the mortar less flowable, that is: higher amounts of  $nS$  require higher  $SP$  dosages to maintain a certain degree of flowability. This is a consequence of the high specific surface of  $nS$  particles, giving an increase in water demand and/or  $SP$  dosage to maintain a certain flowability. If the  $w/c$  ratio of the mortar

is maintained, as was the case in this research, the minimum SP dosage required for the mortar to be able to flow through the Marsh cone is 0.54% o/b when nS is used at 0.5% o/c. This minimum SP dosage is raised to 0.82% o/b when nS is used at 3.5% o/c.

If the aforementioned limitation ( $t_{700} < 140$  seconds) is introduced in equation (1), the following criterion is obtained to ensure that the fresh mortar is flowable enough to flow through the Marsh cone:

$$-8.75 + 30.4 SP + 1.49 nS - 4.96 nS SP < 7.14 \quad (2)$$

Equation (2) is a useful tool for estimating the minimum SP dosage required to assure an acceptable degree of flowability depending on nS content. More conservative versions of equation (2) can be obtained if the threshold value 7.14 (which is the ratio  $1000/t_{700}$  when  $t_{700} = 140$  seconds) is modified. Figure 3 shows different curves relating the minimum SP dosage required, as a function of the nS content, when the target value of  $t_{700}$  is set to 100, 120, and 140 seconds.

#### 4.2 Mini-slump results

Experimental results obtained from the mini-slump test are shown in Table 5. The mini-slump test completes the information obtained through the Marsh cone test concerning the rheology of fresh mortar. The Marsh cone test results are informative in regards to the mix viscosity, while the mini-slump test results provide information on yield stress [27-29].

For the spread obtained in the mini-slump test,  $sf$  (expressed in mm), the following equation was obtained (R-squared = 0.99):

$$sf = -8.167 + 49 nS - 14.33 nS^2 + 175.83 SP \quad (3)$$

Nanosilica content and SP dosage are the parameters affecting  $sf$ , while the addition of FA was not found to have a statistically significant effect. Figure 4 plots the response surface given by equation (3). It is observed that the effect of varying the SP content is more important in magnitude than varying the nS content, although both factors have a statistically significant effect on  $sf$ . The increase in  $sf$  with higher SP dosages may be attributed to the enhanced adsorption mechanisms of SP when nS

particles are present in the mix: the lubrication and deflocculation effects of SP are more efficient and the steric and electrostatic repulsion between cement particles and between cement and nS particles are enhanced, resulting in better deflocculation of the particles in the mortar [30,31].

Since the effect of nS on  $sf$  follows a quadratic trend, using equation (3) it is obtained that its impact on this parameter is maximized when the content is 1.71% o/c:

$$\frac{\partial sf}{\partial (nS)} = 0 \rightarrow 49 - 14.33 \times 2 \times nS = 0 \rightarrow nS = 1.71\% \text{ o/c} \quad (4)$$

#### 4.3 Cohesiveness: Lombardi plate test results

Experimental results obtained from the Lombardi plate test are given in Table 5. For thickness values resulting from the Lombardi plate,  $h$  (expressed in mm), the following equation was obtained (R-squared = 0.88):

$$h = 0.0257 + 0.0567 FA + SP(0.131nS - 0.0487FA) - 0.00681 nS FA \quad (5)$$

In terms of mortar cohesion, the three factors considered not only have a statistically significant effect but each one of them interacts with the others, revealing important synergies between them. This relationship, modelled by equation (5), is plotted in Figure 5, in which the two horizontal axes correspond to the two powders (nS and FA), and the vertical dimension plots cohesion values. The figure plots two response surfaces, corresponding to the two extreme values considered for the SP dosage in this research. The effect of varying nS contents on cohesion is altered by the FA content, as shown in Figure 5. When FA is used at 5% o/c, the effect of variations in nS content is not very important in magnitude, regardless of the SP dosage. However, variations in the nS content become more important when the FA content is increased. Therefore, increasing the nS content appears to be effective at improving mortar cohesiveness, thus reducing the tendency to segregation. Increasing the SP dosage reduces the impact that either FA and/or nS contents have on cohesion: Figure 5 shows that the thickness obtained from the Lombardi plate is practically constant when SP is used at 0.9% o/c.

#### 4.4 Density of the fresh mortars

Experimental results for the density of the fresh mortars are given in Table 6. For the density of fresh mortars,  $\rho$  expressed in  $\text{g/cm}^3$ , the following relationship was obtained (R-squared = 0.95):

$$\rho = 2.1056 + 0.0329 nS - 0.00965 nS^2 + 0.0982 SP - 0.00383 FA \quad (6)$$

Figure 6 shows the response surface for the mortar density as given by equation (6), plotted for the two extreme values considered for the FA content in this research. The effect of increasing nS contents on mortar density follows a quadratic trend. It is worth noting that the density of fresh mortar, with respect to the factors considered, was highly consistent with the factors affecting mini-slump spread values, as the trends observed in Figure 6 are very similar to those in Figure 4. In fact, the nS content that maximizes the mini-slump spread, which is 1.71% o/c based on equation (4), is very close to the nS content that maximizes the density of fresh mortar, which is 1.7% o/c:

$$\frac{\partial \rho}{\partial (nS)} = 0 \rightarrow 0.0329 - 0.00965 \times 2 \times nS = 0 \rightarrow nS = 1.7\% \text{ o/c} \quad (7)$$

#### 4.5 Volume change due to plastic shrinkage

The cone test was used to measure the volume change of the mortar due to plastic shrinkage during the first day after mixing. Experimental results for the plastic shrinkage are provided in Table 7. For the volume change of the mortar due to plastic shrinkage as measured by means of the cone test,  $\Delta v$ , the following equation was obtained (R-squared = 0.84):

$$\ln(\Delta v) = 0.0649 - 0.0334 t + 0.396 \ln(t) + 0.612 SP - 0.17 nS + 0.00958 FA \quad (8)$$

Where:  $\Delta v$  is the volume change expressed in percentage, and  $t$  is the time since the completion of mixing, expressed in hours.

Equation (8) is plotted assuming different scenarios in Figures 7 and 8. It is generally observed that increasing the nS content significantly reduces plastic shrinkage.

Plastic shrinkage increases with time, as expected, although it clearly tends to stabilisation with time.

Figure 7 compares the evolution of plastic shrinkage with time for the two FA contents considered in this research. It is observed that plastic shrinkage at any age is only slightly affected by varying the FA content between 5% and 20% o/c. Contrarily, plastic shrinkage is more sensitive to variations in the SP dosage: Figure 8 shows that increasing the SP dosage from 0.3% to 0.9% o/b gives increases shrinkage at 20 hours from 2.08% to 2.99%.

Therefore, only variations in nS content or the SP dosage have an important influence on plastic shrinkage: the effect of FA is less relevant in magnitude, as shown in Figures 7 and 8. Increasing the SP dosage results in an increase of plastic shrinkage. On the other hand, increasing the nS content gives a reduction in plastic shrinkage. This effect can be linked to the filler effect of nS particles and their impact on cement hydration kinetics. As the cementitious matrix is densified by nS particles, they contribute to restrain volume changes due to plastic shrinkage. In addition to that, the presence of nS tends to decrease the rates of sedimentation and bleeding.

#### ***4.6 Volume change due to drying shrinkage***

Volume changes caused by drying shrinkage of the mortar were monitored for 20 days after mixing. Experimental results are shown in Table 8. For the volume change due to the drying shrinkage,  $\Delta V$ , the following relationship was obtained (R-squared = 0.88):

$$\ln(\Delta V) = -4.789 - 0.00797 t + 0.553 \ln(t) + 0.294 nS - 0.061 nS^2 + 0.035 FA \quad (9)$$

Where  $\Delta V$  is the volume change due to drying shrinkage, expressed in percentage, and  $t$  is the time since the conclusion of mixing, expressed in days.

Nanosilica and FA contents have been found to have a statistically significant effect on drying shrinkage, while the SP dosage does not have a significant influence.

Figure 9 plots the relationship given by equation (9), where the drying shrinkage is related to nS content and age for the two extreme values considered for FA content in this research. Increasing FA contents give slightly higher drying shrinkage at all ages. With respect to the effect of nS contents, a quadratic trend has been detected, giving that

the highest value for drying shrinkage is obtained for an intermediate nS content. However, the effect of variations in nS or FA, though statistically significant, is not comparable in magnitude to the effect of the age of mortars, which is clearly the most relevant parameter.

## 5. CONCLUSIONS

- Mortar flowability, measured with the Marsh cone, was significantly affected by nS content and SP dosage, but not by FA content. Increasing the amount of added nS required higher SP dosages to maintain mortar flowability at acceptable levels. An equation has been provided to estimate the minimum SP dosage required depending on nS content.
- The spread obtained from the mini-slump test has been analyzed as informative of the yield stress of the mortars. The amount of nS and SP had a significant effect on this parameter, while variations in FA content had no impact. The effect of SP dosage was more important in magnitude than that of nS content, which can be attributed to the increased efficiency of SP in terms of lubrication and deflocculation when nS particles are present.
- Cohesion of the mortar, evaluated with the Lombardi plate, was affected by nS and FA contents as well as by the SP dosage. Important synergies between these factors were detected; increasing the nS content improved mortar cohesiveness, and this effect was more important with high FA content. On the other hand, increasing SP dosage reduced the impact of both nS and FA on cohesiveness.
- Plastic shrinkage was evaluated by means of the cone shrinkage test. Plastic shrinkage was shown to be relatively sensitive to nS content and SP dosage, while FA had less of an effect. Increasing nS content significantly reduced plastic shrinkage. In terms of drying shrinkage, however, the influence of these factors was less evident.
- In terms of the density of fresh mortars, the trends detected were very similar to those observed in the mini-slump test results. Increasing SP dosage resulted in higher mortar density, while higher FA content tended to decrease it. The optimum nS content in terms of the mini-slump test and the density of the fresh mortars was 1.7% over cement weight.

- It is inferred from the above conclusions that nS has only a moderate effect on most of the parameters analyzed compared to the effect of FA and SP, when these are varied between the ranges considered in this research. However, variations in nS content have a more prominent effect on flowability (Marsh cone flow times), and on plastic shrinkage, which is significantly reduced when nS content is increased.

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## FIGURES

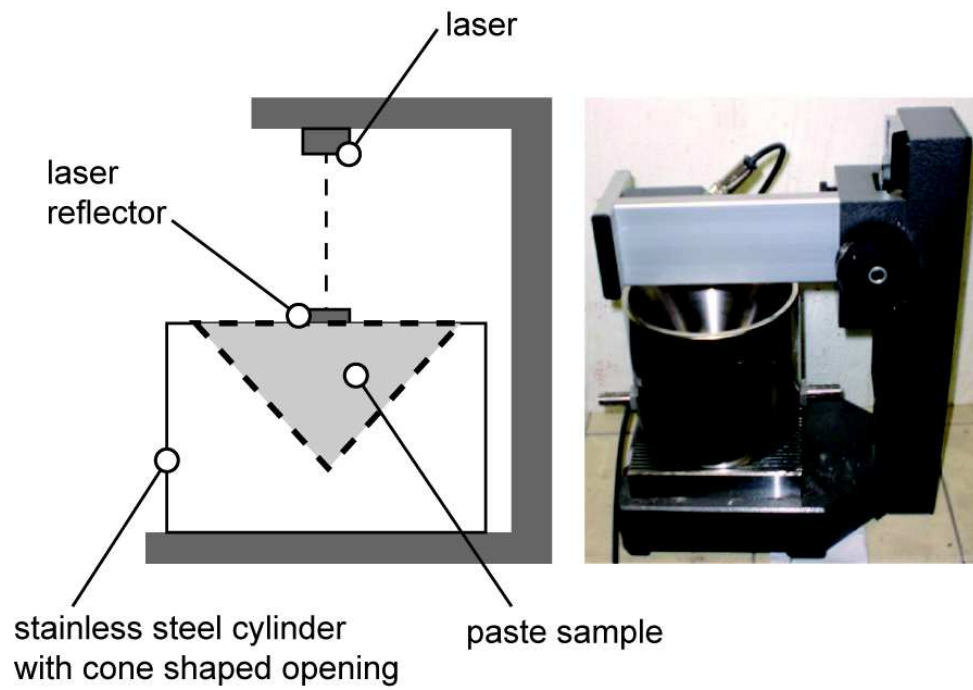


Figure 1. Diagram and picture of the “shrinkage cone” apparatus.

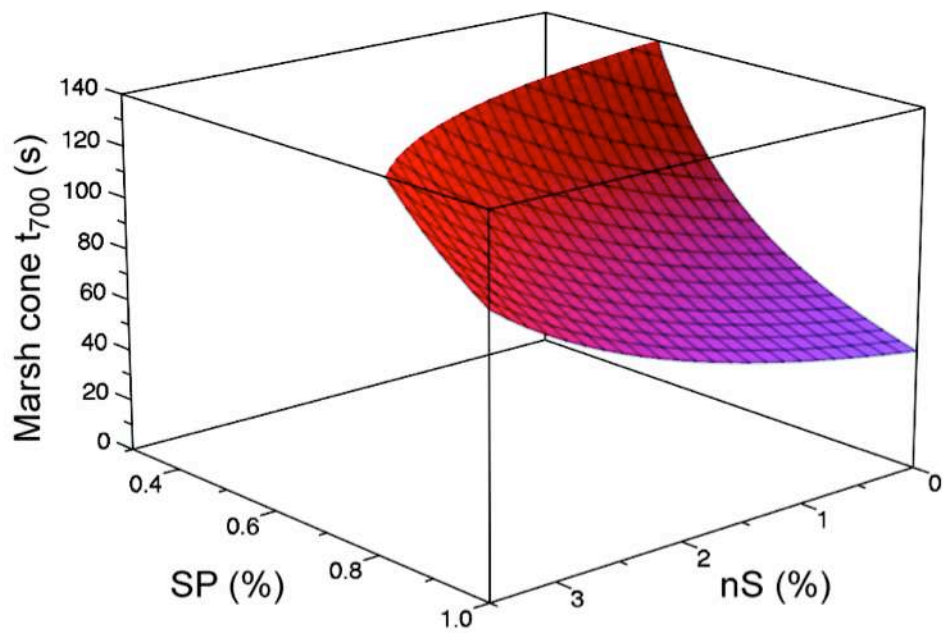


Figure 2. Marsh cone results.



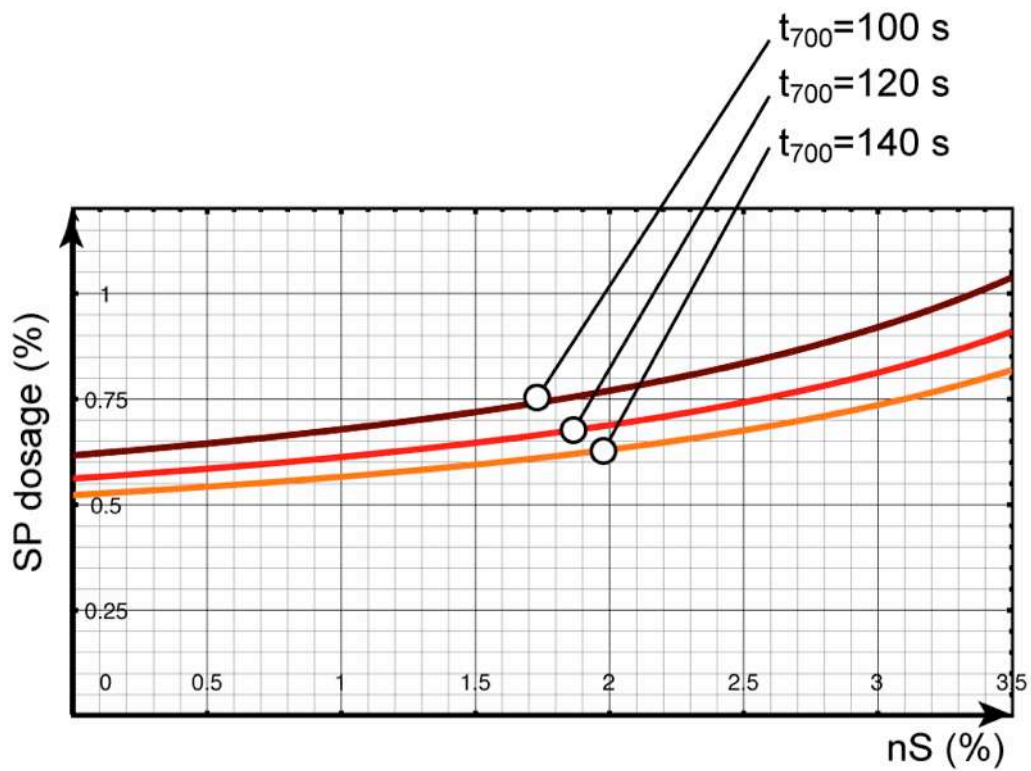


Figure 3. SP dosages depending on nanosilica content for different targeted levels of flowability in the Marsh cone test.

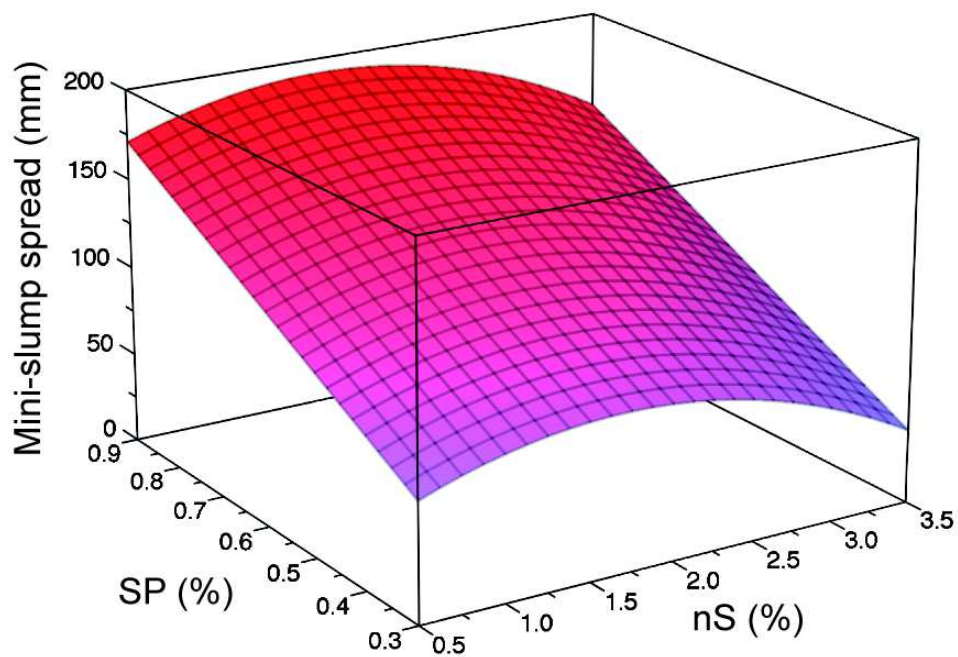


Figure 4. Mini-slump results.

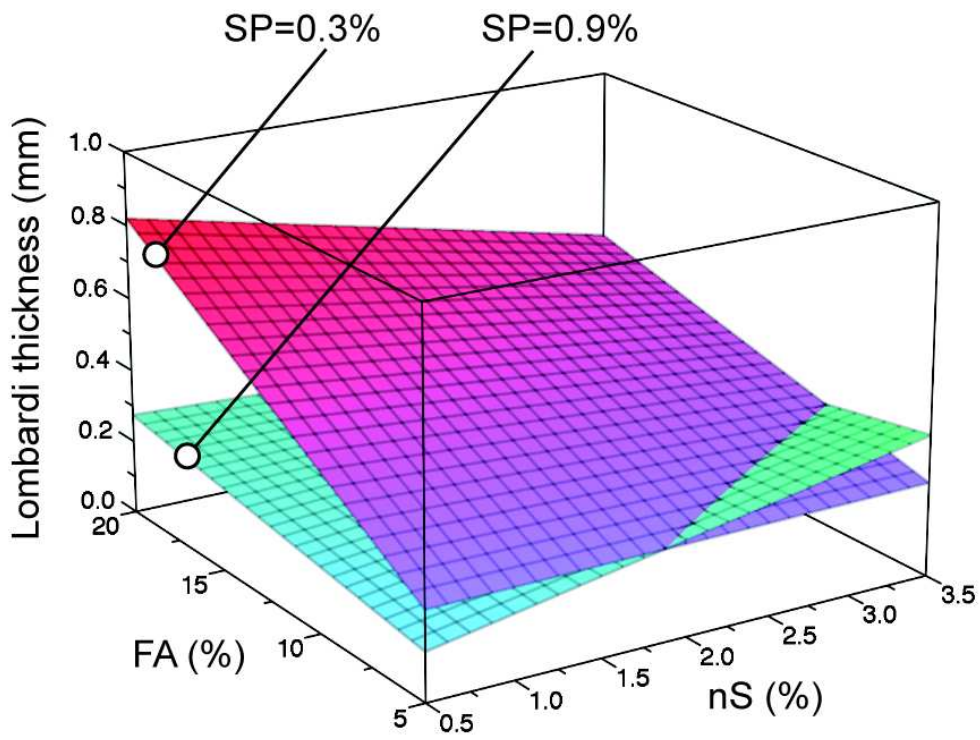


Figure 5. Cohesion results (Lombardi).

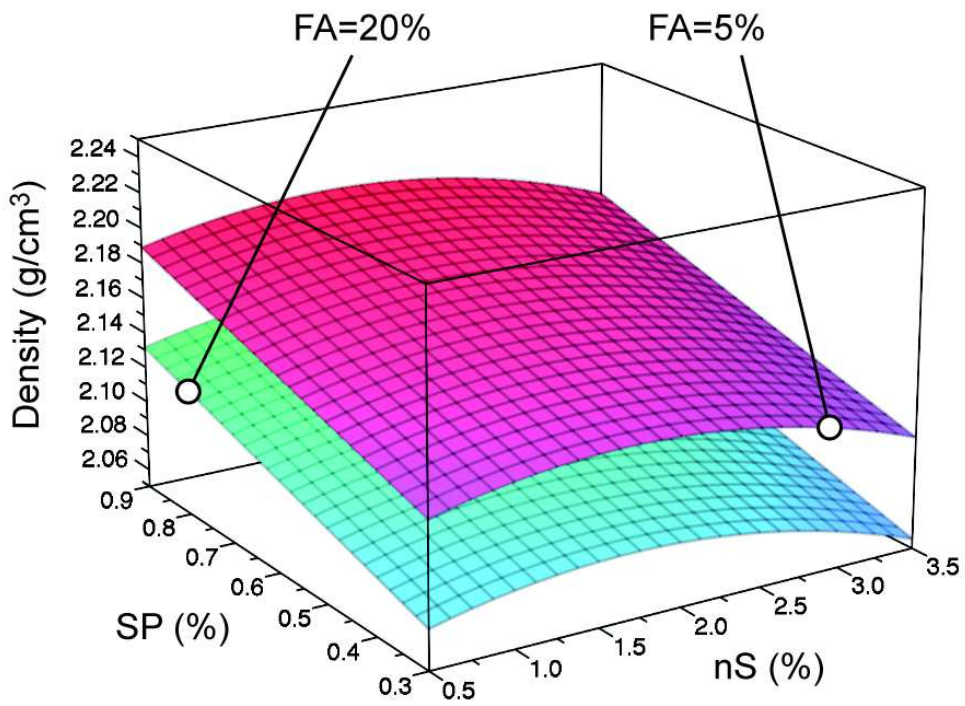


Figure 6. Density of the fresh mortars.

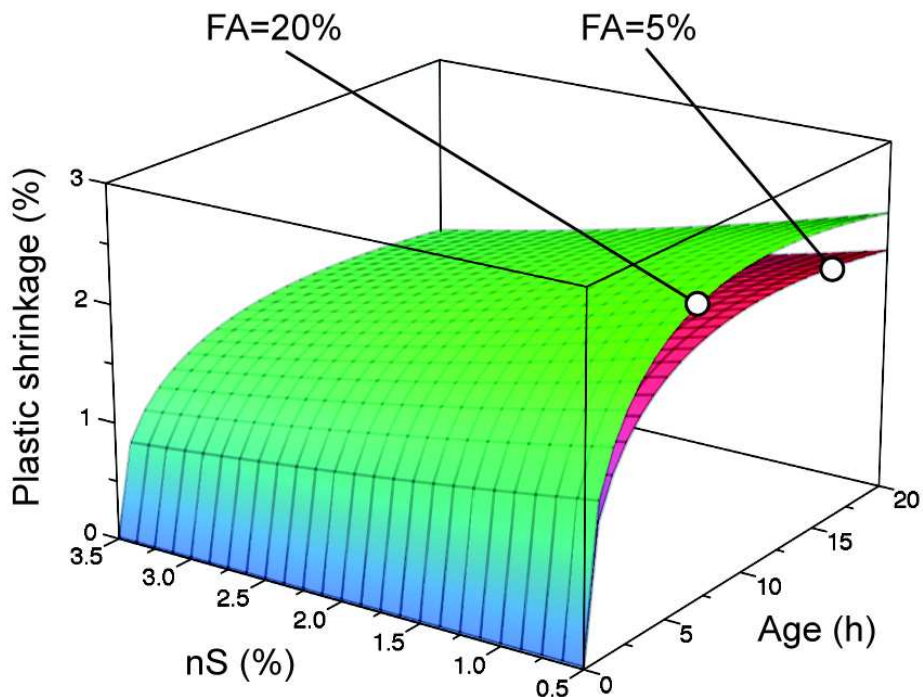


Figure 7. Plastic shrinkage, assuming constant SP dosage of 0.3% o/b.

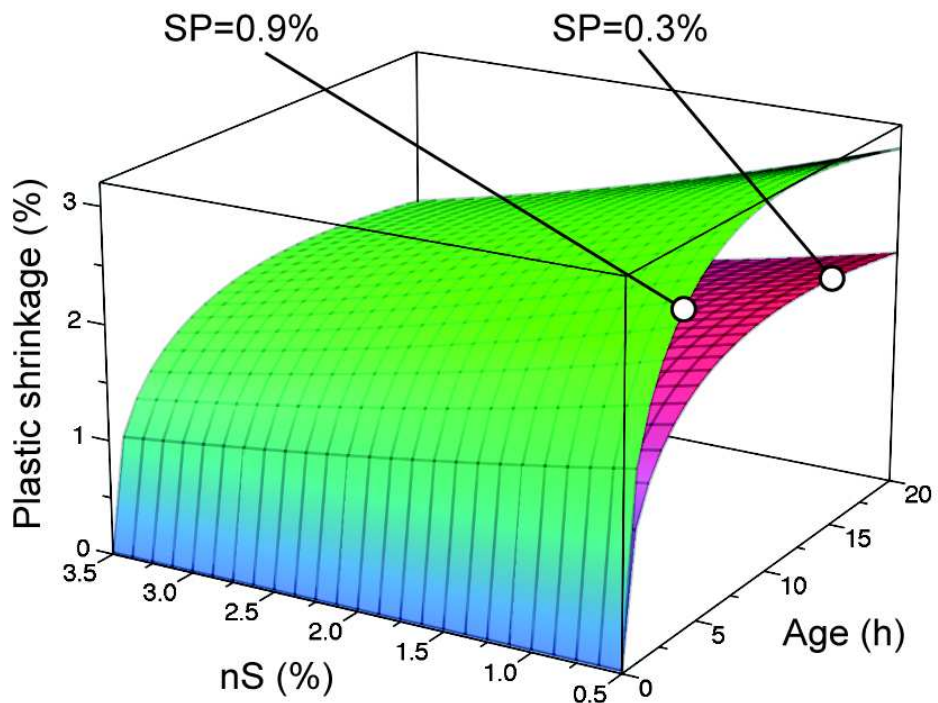


Figure 8. Plastic shrinkage, assuming constant FA replacement of 5% o/c.

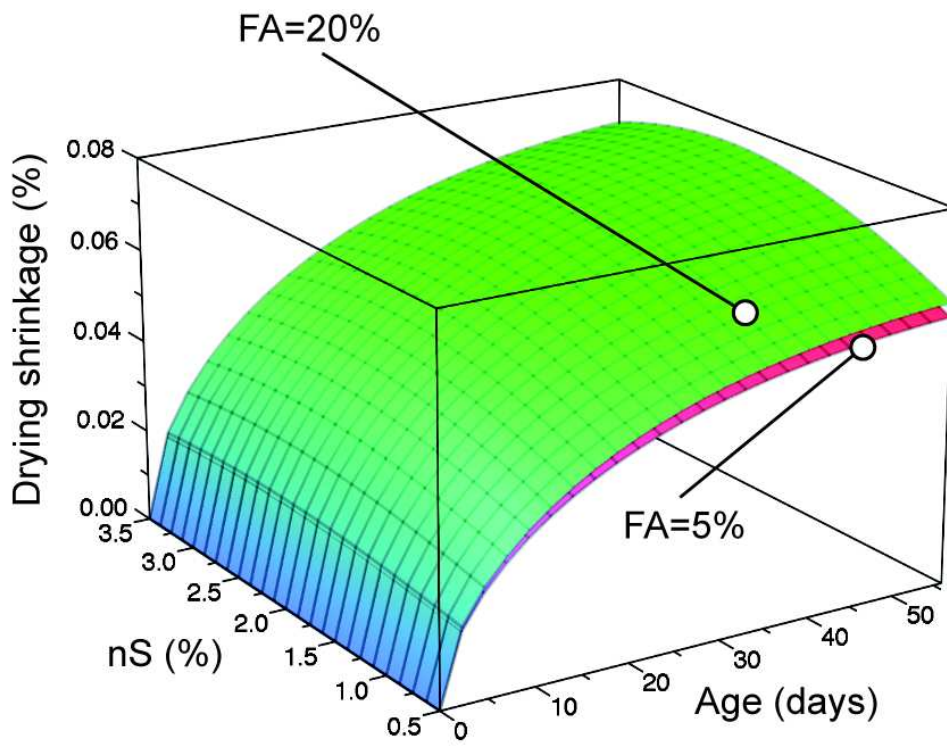


Figure 9. Drying shrinkage.

## TABLES

Table 1. Factors and levels considered.

Factor	Levels (*)
Nanosilica addition, nS (solid content)	0.5% o/c
	2.0% o/c
	3.5% o/c
Fly ash, FA (cement replacement)	5.0% o/c
	12.5% o/c
	20.0% o/c
Superplasticizer, SP	0.3% o/b
	0.6% o/b
	0.9% o/b
(*) o/c: over cement weight	
(*) o/b: over binder weight (cement+FA)	

Table 2. Chemical composition of the materials used.

	Cement	Fly ash	Nanosilica
SiO <sub>2</sub> (%)	21.01	55.95	99.40
Al <sub>2</sub> O <sub>3</sub> (%)	4.92	23.3	0.08
Fe <sub>2</sub> O <sub>3</sub> (%)	2.84	4.84	--
MgO(%)	2.20	1.85	--
CaO (%)	64.52	4.76	--
Na <sub>2</sub> O (%)	0.20	0.91	0.45
K <sub>2</sub> O (%)	0.71	1.82	--
SO <sub>3</sub> (%)	2.53	0.65	--
P <sub>2</sub> O <sub>5</sub> (%)	0.11	0.73	--
LOI (%)	1.26	3.47	0.10

Table 3. Physical properties of nS, FA and cement.

	Cement	Fly ash	Nanosilica
Specific gravity	3.08	2.21	1.40
% passing 45 µm sieve	85%	85%	--
Mean particle size	22 µm	--	50-60 nm
Specific surface area [m <sup>2</sup> /kg]	360	--	--
Specific surface area (BET)	--	--	80 m <sup>2</sup> /g
Solid content (SiO <sub>2</sub> -content)	--	--	50 wt %
pH	--	--	9.5
Viscosity	--	--	<15 cPas

Table 4. Proportionings of the mortars tested.

	Ref.	w/b	Nanosilica (%)	Fly ash (%)	SP (%)
Selected mixes	1	0.35	0.5	5.0	0.3
	2	0.35	3.5	5.0	0.3
	3	0.35	0.5	5.0	0.9
	4	0.35	3.5	5.0	0.9
	5	0.35	0.5	20.0	0.3
	6	0.35	3.5	20.0	0.3
	7	0.35	0.5	20.0	0.9
	8	0.35	3.5	20.0	0.9
Center points	9	0.35	2.0	12.5	0.6
	10	0.35	2.0	12.5	0.6
	11	0.35	2.0	12.5	0.6

Table 5. Fresh properties of mortars.

	Ref.	Marsh cone		Mini-slump (mm)	Cohesion, thickness (mm)
		Flow time $t_{700}$ (s)	Inverse $1/t_{700}$ ( $s^{-1}$ )		
Selected mixes	1	n/a (*)	0	76	0.19090
	2	n/a (*)	0	38 (**)	0.33946
	3	68	0.014706	171	0.18295
	4	118	0.008475	148	0.30265
	5	n/a (*)	0	60	0.89920
	6	n/a (*)	0	38 (**)	0.44311
	7	53	0.018811	166	0.19707
	8	139	0.007194	149	0.30758
Center points	9	129	0.007752	137	0.38624
	10	136	0.007353	140	0.33369
	11	134	0.007463	137	0.33423

(\*) Grouts did not flow through the Marsh cone.  
(\*\*) Grouts did not spread.

Table 6. Density of the fresh mortars.

	Ref.	Density (g/cm <sup>3</sup> )
Selected mixes	1	2.14249
	2	2.11218
	3	2.18638
	4	2.16257
	5	2.06239
	6	2.05367
	7	2.13127
	8	2.12627
Center points	9	2.15412
	10	2.14718
	11	2.13029

Table 7. Plastic shrinkage results (volume change, in percentage).

	Ref.	2 hours	5 hours	20 hours
Selected mixes	1	1.70	2.01	2.13
	2	0.81	0.93	0.98
	3	2.68	2.75	2.74
	4	1.36	1.77	2.00
	5	1.88	2.48	2.52
	6	1.12	1.37	1.41
	7	2.44	2.52	2.49
	8	1.37	2.27	2.42
Center points	9	1.27	1.93	2.04
	10	1.44	2.23	2.41
	11	1.56	2.38	2.55

Table 8. Drying shrinkage results (volume change, in percentage).

	Ref.	14 days	21 days	28 days	42 days	56 days
Selected mixes	1	0.037586	0.050524	0.053576	0.059407	0.063921
	2	0.041558	0.052244	0.055041	0.060721	0.067038
	3	0.031343	0.042595	0.044260	0.052044	0.054594
	4	0.046980	0.049886	0.056886	0.063767	0.065731
	5	0.039369	0.049842	0.053544	0.059724	0.064179
	6	0.041099	0.054154	0.055297	0.063907	0.067971
	7	0.035770	0.046639	0.048287	0.054095	0.058524
	8	0.049690	0.056568	0.062439	0.070663	0.074299
Center points	9	0.048530	0.054466	0.058016	0.065473	0.069765
	10	0.054677	0.061000	0.067863	0.072816	0.078127
	11	0.045320	0.051912	0.060731	0.064860	0.067379



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