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Synthesis of silica nanoparticles to enhance the fire resistance of cement mortars

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Abstract

Silica nanoparticles are known to enhance the strength and durability of cementitious materials, due to their nano-filling effect and their high pozzolanic reactivity. They also have the potential to improve their thermal properties and fire resistance. However, these improvements are highly dependent on the nanoparticles' characteristics. In this work, silica nanoparticles were prepared by sol-gel reaction and a design of experiments with four factors was used to conclude about the parameters that have more influence in the synthesis of these nanoparticles and, thus, optimize this process and the particles' properties. Using a lower ethanol/water, higher hydrolysis and condensation time and higher volume of catalyst, the smallest particle size was obtained (118 nm). The effect of the incorporation of these silica nanoparticles into cement mortars was studied in terms of density and thermal conductivity of these mortars, after curing at room temperature. The presence of silica nanoparticles led to an increase in density and decrease of thermal conductivity. The mortars were also exposed to high temperature, which originated a significant reduction (~50%) in their thermal conductivity.

Introduction

Cement-based materials are of high importance for the construction industry and are used in very large scale. Therefore, continuous research is being done in order to enhance the properties of these materials, such as better mechanical properties, higher durability, better resistance to corrosion and better fire resistance.[1,2] Nanomaterials appear as an emerging approach to improve the characteristics of cement, with the incorporation of nano silica being the most common.[3]

Silica nanoparticles are known to enhance the characteristics of cementitious materials, even in very small quantities, such as 0.5% (wt.) of cement.[4,5] They act as fillers, occupying the empty voids between cement grains. Furthermore, due to their high surface area and, thus, high reactivity, they have high pozzolanic activity, which leads to the increase of the amount of calcium silicate hydrate (C-S-H) gel. These two effects lead to a densification of the matrix, resulting in higher strength and durability of the materials.[1,2] Commercially available silica nanoparticles, both in powder and colloidal form and with sizes ranging from 15 nm to 150 nm, have been incorporated in the matrix of cementitious materials, multiple times.[6-8] Silica nanoparticles are typically produced by sol-gel technology and the cost and production volume of these nanomaterials are two deciding factors that prompt the development of new processes,[9] so that these nanoparticles can be available in the needed quantities for this industry.

The potential of nano silica in the enhancement of thermal resistance of cement has also been object of study, with its presence leading to an increase in the stability of these materials at high temperatures.[2,7] Most of these studies focus on their mechanical properties after being exposed to high temperature, showing significant improvements in compressive and flexural strength with the presence of nano silica in the matrix.[3] However, little attention is given to other properties such as thermal conductivity.[8] The assessment of the influence of nano silica on thermal conductivity of cement mortars is important for certain applications, particularly when these materials are protecting other structures, such as steel structures, that are very sensitive to high temperatures.

In this work, silica nanoparticles were synthesized by sol-gel reaction to be incorporated in cement mortars. Before the addition of these nanoparticles to the mortars' matrix, it is important to understand which parameters of the synthesis have the most influence in the nanoparticles' properties, so that these can be optimized to improve the characteristics of cement mortars. Therefore, a design of experiments (DOE) was used to study the influence of different factors of the nanoparticles' synthesis, which is the focus of this paper.

Materials and Methods

For the synthesis of silica nanoparticles, tetraethyl orthosilicate (TEOS, $Si(OC_2H_5)_4$, 98%, Acros Organics) was used as silica precursor, ammonium hydroxide (NH_4OH (aq), 25%, Fluka) as base catalyst and ultra-pure water and ethanol (C_2H_6O, 99%, Fisher Scientific), as co-solvents.

In the DOE, four factors were chosen for the screening (the time of hydrolysis, the

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Key words: Silica nanoparticles; Nanomaterials; Nano-cement; Fire protection.

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time of condensation, the volume of NH_4OH and the ethanol/water volumetric ratio) and a full factorial design with two levels for each factor was planned. The average size and zeta potential (ZP) were chosen as responses for the DOE and the levels for the factors were established based on preliminary tests: (A) Time of hydrolysis: 0.5 h (-) and 3.0 h (+); (B) Time of condensation: 1.0 h (-) and 3.0 h (+); (C) Volume of NH_4OH: 1.25 mL (-) and 1.65 mL (+); (D) Ethanol/water volumetric ratio: 2/3 (-) and 3/2 (+).

In the synthesis, ethanol and water were mixed together (D), making up a total volume of 30 mL, and then 5 mL of TEOS were added and the mixture was stirred at room temperature for a certain period of time (A). The pre-established volume of NH_4OH (C) was then added and the reaction took place for a certain time (B). The nanoparticles were then centrifuged at 7000 rpm for 20 min and washed with ethanol multiple times, before being redispersed in water.

The size and stability of the nanoparticles were evaluated by Dynamic Light Scattering (DLS) and ZP measurements using a *Zetasizer Nano ZS* (Malvern Instruments, United Kingdom) and taking suspensions of the nanoparticles in water with a concentration of 0.1 mg/mL. These suspensions were sonicated for 30 minutes before the measurements. To analyze the DOE results, *JMP Pro* from *SAS* was used.

For the preparation of cement mortars, nano silica (NS) was used in colloidal form, because its handling is easier and safer and there is less agglomeration, which is characteristic of the redispersion of nano silica powder in water. Reference mortars (without nano silica) and mortars with nano silica (1% wt. of binder) were prepared (Table 1). First, siliceous sand with a granulometry of <2 mm was mixed with a part of the total water for 1 minute; then Portland cement CEM I 42.5 R was added and mixed for another minute; the suspension of nano silica in water, which was previously sonicated for 30 min, was added (when needed), and finally, the remaining water was added and the mixture was stirred until a mixture with the desired consistency was obtained.

The mortar specimens were prepared at 19.5ºC and casted into 4×4×1.5 cm^3 moulds. After that, the specimens were cured in the laboratory environment with a temperature of 25ºC (±5ºC) and R.H. ≥60% (±10%) until they were tested.

The density of the mortar specimens was determined by measuring their mass and dimensions. Thermal conductivity measurements were performed in a *Thermal Constants Analyzer TPS 2500S* (Hot Disk, Sweden), using the transient plane source method with two samples stabilized at 20ºC. Finally, in order to simulate the fire temperature condition, the specimens were heated to 700ºC at a heating rate of 3ºC/min and held at this temperature for 120 min. The density and thermal conductivity of the specimens were measured again after this test.

Results and Discussion

Design of experiments

The design of experiments consisted in 2^4 runs, considering only the low and high levels presented in the *Materials and Methods* section and no central points. The planned experiments of the DOE, as well as the results obtained by DLS and ZP measurements, are presented in Table 2. Besides the average diameter of the particles (*d*), DLS also provides a value for the polydispersity index, which is an indication of size dispersity of the sample.

As seen in Table 2, the diameter of the

Table 1. Composition of the mortars.

Mortar composition	Cement (kg/m³)	Water (kg/m³)	Sand (kg/m³)	NS (kg/m³)
Reference	350	175	1829	-
With NS	346.5	175	1829	3.5

NS, nano silica.

Table 2. Results of the design of experiments.

Experiment	A	B	C	D	*d* (nm)	PDI	ZP (mV)
1	-	-	-	-	198.6±1.3	0.300±0.016	-38.4±0.3
2	+	-	-	-	171.7±1.6	0.233±0.012	-32.8±0.6
3	-	+	-	-	224.1±5.4	0.311±0.010	-30.6±0.6
4	+	+	-	-	313.4±4.2	0.379±0.016	-38.1±1.0
5	-	-	+	-	130.2±0.9	0.091±0.010	-43.6±4.7
6	+	-	+	-	172.3±2.4	0.133±0.010	-45.2±1.1
7	-	+	+	-	125.7±2.9	0.094±0.014	-48.1±2.0
8	+	+	+	-	118.0±1.4	0.090±0.026	-44.4±0.8
9	-	-	-	+	1209.3±26.3	0.346±0.033	-54.3±1.7
10	+	-	-	+	507.6±4.2	0.025±0.027	-53.1±0.1
11	-	+	-	+	1436.7±18.0	0.453±0.046	-56.1±0.8
12	+	+	-	+	673.9±12.5	0.202±0.037	-55.0±0.3
13	-	-	+	+	1328.7±50.5	0.077±0.038	-54.7±1.1
14	+	-	+	+	508.3±1.4	0.031±0.023	-52.1±0.6
15	-	+	+	+	1081.7±10.3	0.217±0.100	-48.7±0.6
16	+	+	+	+	569.3±9.7	0.117±0.017	-52.3±0.5

d, average diameter of the particles; PDI, polydispersity index; ZP, zeta potential.

particles ranged from 118.0 nm to 1436.7 nm, confirming that the values of the parameter levels were well chosen. It is important to note that this average diameter given by DLS is based on the intensity size distribution, but size peaks as low as 80 nm were seen when observing the number size distributions. ZP showed less variation, with all particles presenting values below -30 mV, indicating that they form stable suspensions in water.

With the DOE results, the influence of the main effects, as well as first order interactions, on the two responses was studied, using the standard least squares fit to obtain the models. The predicted expressions for the two responses are presented in Eqs. 1 and 2.

With the model estimates obtained in the DOE, the predicted and actual responses can be compared (Figure 1a and c), in order to confirm the efficacy of the model. In Figure 1a and c, the red line indicates that the predicted and actual values are equal.

Looking at the data points in Figure 1a, it can be seen that the actual and predicted values for the diameter are very close to each other, confirming that the model fits to the data (R^2=0.9902). In terms of ZP, the predicted and actual values differ slightly for some data points, but the model obtained still fits relatively well to the data (R^2=0.9341).

With the *JMP Pro* Software, the Pareto plots of the estimates obtained for the two responses can also be represented (Figure 1b and d). It can be seen that the ethanol/water volumetric ratio (D) is the parameter that has the most influence in both the average size and ZP. For the diameter response, the interaction between time of hydrolysis and ethanol/water ratio (A*D), and the time of hydrolysis (A) also have a strong influence on this response, followed by the interaction between condensation time and volume of NH_4OH (B*C), and the volume of NH_4OH (C). On the other hand, for ZP, besides the solvents' volumetric ratio (D), the interaction

$$\begin{aligned}d\ (nm) = {} & 548.09 + (-168.78)\cdot\left(\frac{A-1.75}{1.25}\right) + 19.76\cdot\left(\frac{B-1.50}{0.50}\right) + (-43.82)\cdot\left(\frac{C-1.45}{0.20}\right) \\ & + 366.34\cdot\left(\frac{D-1.08}{0.42}\right) + \left(\frac{A-1.75}{1.25}\right)\cdot\left(\frac{B-1.50}{0.50}\right)\cdot 19.58 + \left(\frac{A-1.75}{1.25}\right)\cdot\left(\frac{C-1.45}{0.20}\right)\cdot 6.48 \\ & + \left(\frac{B-1.50}{0.50}\right)\cdot\left(\frac{C-1.45}{0.20}\right)\cdot(-50.36) + \left(\frac{A-1.75}{1.25}\right)\cdot\left(\frac{D-1.08}{0.42}\right)\cdot(-180.88) \\ & + \left(\frac{B-1.50}{0.50}\right)\cdot\left(\frac{D-1.08}{0.42}\right)\cdot 6.21 + \left(\frac{C-1.45}{0.20}\right)\cdot\left(\frac{D-1.08}{0.42}\right)\cdot 1.38\end{aligned}$$

Eq. 1

$$\begin{aligned}ZP\ (mV) = {} & -46.72 + 0.094\cdot\left(\frac{A-1.75}{1.25}\right) + 0.06\cdot\left(\frac{B-1.50}{0.50}\right) + (-1.92)\cdot\left(\frac{C-1.45}{0.20}\right) \\ & + (-6.57)\cdot\left(\frac{D-1.08}{0.42}\right) + \left(\frac{A-1.75}{1.25}\right)\cdot\left(\frac{B-1.50}{0.50}\right)\cdot(-0.88) + \left(\frac{A-1.75}{1.25}\right)\cdot\left(\frac{C-1.45}{0.20}\right)\cdot 0.04 \\ & + \left(\frac{B-1.5}{0.5}\right)\cdot\left(\frac{C-1.45}{0.20}\right)\cdot 0.21 + \left(\frac{A-1.75}{1.25}\right)\cdot\left(\frac{D-1.08}{0.42}\right)\cdot 0.07 \\ & + \left(\frac{B-1.50}{0.50}\right)\cdot\left(\frac{D-1.08}{0.42}\right)\cdot 0.21 + \left(\frac{C-1.45}{0.20}\right)\cdot\left(\frac{D-1.08}{0.42}\right)\cdot 3.26\end{aligned}$$

Eq. 2

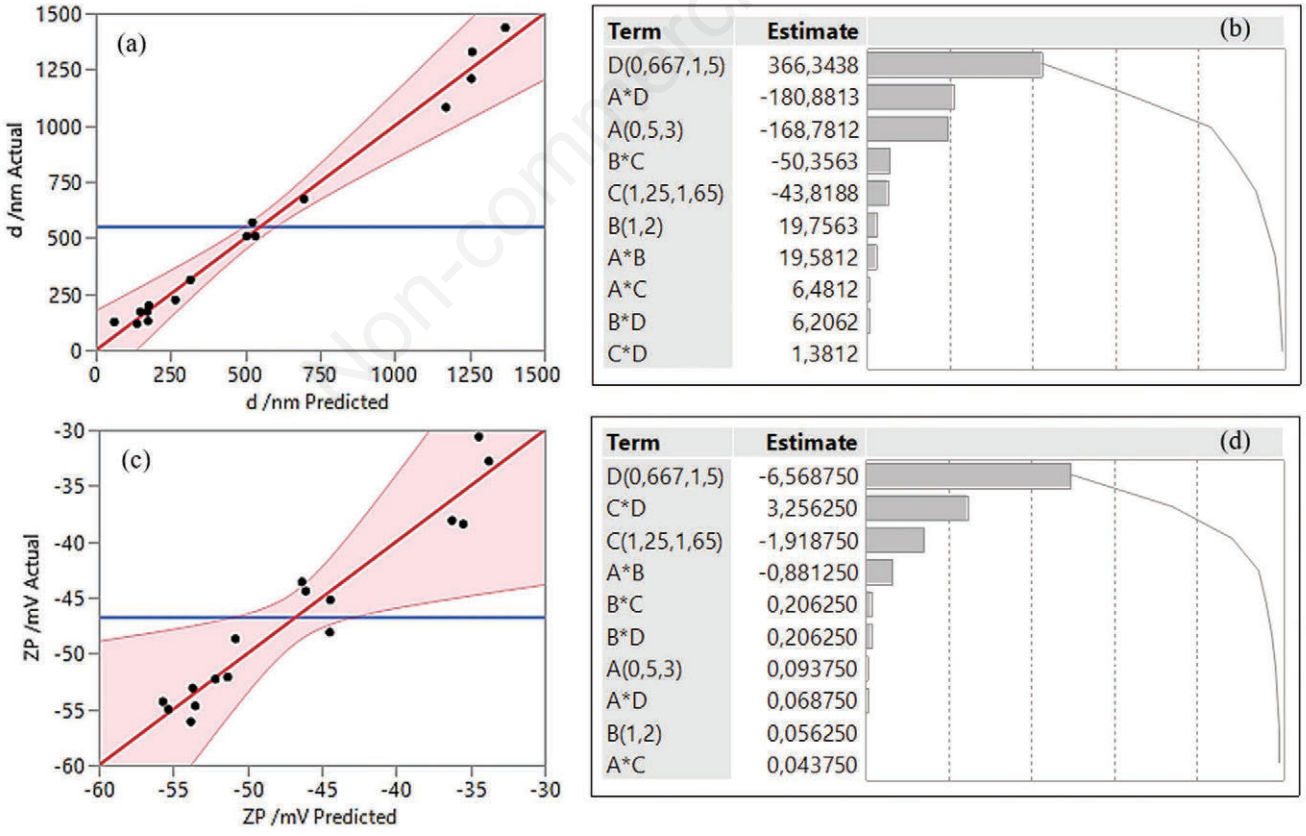

Figure 1. Actual by predicted plots obtained for the (a) diameter and (c) zeta potential, and Pareto plots of the estimates for the two responses: (b) average diameter, (d) zeta potential (A, time of hydrolysis; B, time of condensation; C, volume of NH_4OH; D, ethanol/water volumetric ratio).

between the volume of NH_4OH and the ethanol/water ratio (C*D), the volume of NH_4OH (C) and the interaction between hydrolysis time and condensation time (A*B) are also important parameters for this response.

Comparing the results presented in Table 2 with the Pareto plots, the influence of the ethanol/water ratio in the responses can be confirmed: using the lower value for this ratio, diameters between 100 and 350 nm were obtained, while, with the higher value of this ratio, the average diameter was above 500 nm for all experiments. On the other hand, with a higher ethanol/water ratio, ZP values lower than -50 mV could be obtained, while for the lower ratio these values were only as low as -48 mV.

For the incorporation of nano silica in the mortars, only one type of nano silica was used. Since all experiments led to ZP lower than -30 mV and, thus, all samples formed stable suspensions in water, only the average diameter was studied in more detail, to choose one experiment for the incorporation. Looking at the results obtained in Table 2, it was observed that the use of a higher ethanol/water ratio led to larger particles, which agrees with results found in literature where sodium silicate was used as silica precursor.[10] On the other hand, generally, a higher amount of NH_4OH led to smaller particles, which might be due to the fact that, with more base, a higher number of smaller nuclei are formed initially, which grow into smaller particles. On the contrary, less base leads to slower condensation and, thus, formation of less nuclei that then grow into larger particles.

In order to synthesize particles of small size, the lower value of the ethanol/water ratio was chosen, as well as the higher amount of NH_4OH. The higher amount of NH_4OH was chosen not only because smaller particle sizes were obtained, but also because the reaction yield was higher. For the lower ethanol/water ratio, it can be seen that the diameter response does not vary much with hydrolysis time. Therefore, a smaller hydrolysis time was chosen, in order to produce the nanoparticles in less time and thus, the particles of experiment 7 were chosen to be incorporated in the cement mortars. This experiment also led to a more negative ZP, when compared to experiment 8, and thus, more stability of the suspensions.

Cement mortars

As previously stated, the cement mortars were prepared with the nanoparticles from experiment 7 (Figure 2). While making the cement mortars, it was noticeable that with the addition of NS, the mixture became visually more cohesive and thicker, even while it was being stirred. Additionally, while handling both types of mortars, after they were removed from the cast and cured, it was perceptible that reference specimens released more dust than the mortars with NS. Both observations are related to the fact that, as a consequence of the high pozzolanic reactivity, silica nanoparticles act as nucleating sites for the hydration products, leading to a higher interaction between the nanoparticles and the binder, and creating a network that is more connected.[11] Therefore, mortars with nano silica appear thicker while fresh, and release less dust in hardened form.

It is also visible in Figure 2 that the specimens with NS seem to have a denser structure, as expected,[1] which is due to the pore filling effect of NS. This was confirmed by the obtained values of the density (Table 3), which were higher for the specimens with nano silica.

The presence of silica nanoparticles led to a decrease of thermal conductivity after curing at room temperature (Table 3), as expected according to the literature.[8] In the specimens with NS, the nanoparticles fill the pores, which means there is less avail-

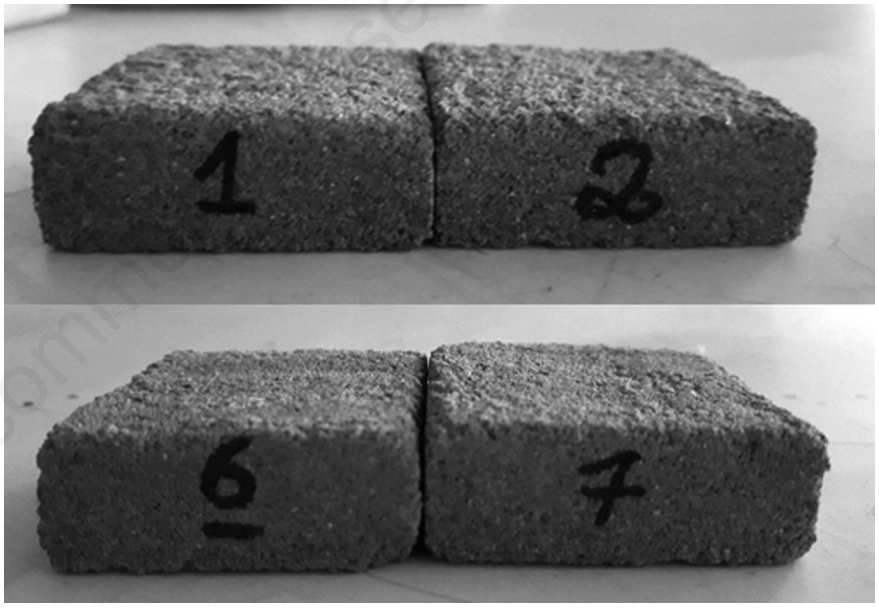

Figure 2. Reference cement mortars (1-2) and cement mortars with 1% of nano silica (6-7).

Table 3. Obtained properties of cement mortars.

After curing at room temperature Mortar	Density (g/cm^3)	Thermal conductivity (W/m.K)
Reference	1.963±0.005	1.644±0.002
With NS	2.038±0.022	1.609±0.004
After exposure to 700°C Mortar	**Density (g/cm^3)**	**Thermal conductivity (W/m.K)**
Reference	1.907±0.026	0.777±0.002
With NS	1.956±0.026	0.802±0.001

NS, nano silica.

able space for free water in the specimens, and thus, this leads to the observed decrease in thermal conductivity.[12]

After being exposed to high temperature, spalling was not observed in any of the samples, but it was again noticeable that the reference mortars released more dust than the mortars with NS.

The measured properties after this test are also presented in Table 3.

The density of cement mortars, both reference and with NS, decreased after the exposure to 700ºC, which is mainly due to the evaporation of free water, decomposition of calcium hydroxide and other components of the cement mortars.[12] Thermal conductivity decreased significantly in both cases (53% and 50% for reference and NS mortars, respectively), mainly as a result of the decrease in water content.[12] This reduction was slightly higher for the reference samples, which is in agreement with results found in literature.[13] The mortars with NS have a higher amount of the C-S-H gel and might be able to retain chemically bonded water for longer when exposed to high temperatures, thus leading to a smaller decrease in thermal conductivity, when compared to the reference samples.

Conclusions

The design of experiments allowed the identification of the variables of the synthesis that had more influence on the two studied responses: the average diameter and ZP of the silica nanoparticles. For both of these properties, it was seen that the ethanol/water ratio had the most relevant effect. The smallest nanoparticles (average size of 118 nm) were obtained with the higher hydrolysis time, higher condensation time, higher volume of NH_4OH and lower ethanol/water ratio.

The incorporation of silica nanoparticles (average size of 126 nm) in cement mortars was successful and led to the increase of bulk density and also to the decrease of thermal conductivity at room temperature. The differences in these properties were not very high but showed the potential of NS. An increase in the percentage of NS in the mortars should be studied in the future, in order to obtain a higher decrease in thermal conductivity.

After being exposed to high temperatures, bulk density and thermal conductivity decreased significantly, as expected. These properties and others should be assessed after exposition to direct fire, but the incorporation of nano silica shows potential to increase the fire resistance of cement mortars.

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