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Study of durability of Portland cement mortars blended with silica nanoparticles

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HIGHLIGHTS

- There are few studies on mortars of OPC/NS exposed to aggressive agents.
- NS diminished the total volume of pores, especially capillary pores.
- NS helped in the formation of pores with diameter below 10 nm.
- NS improved compressive strength significantly in samples with 10 wt.% of NS.
- NS controlled the expansion under $MgSO_4$ attack.

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ABSTRACT

In this paper the effects of nanosilica (NS) on porosity, capillary suction (UNE 8398:2008), compressive strength (ASTM C 349), and sulfate resistance (ASTM C 1012) were evaluated for mortars made with Portland cement (control) and partially replaced with a commercial NS suspension, in percentages by weight of 0%, 1%, 3%, 5%, and 10%. Mortars with a water/binder (w/b) ratio of 0.55 and addition of superplasticizer, for flow correction, were prepared. NS showed that, it has an important role in pore refining, decreasing the total volume of pores and their diameters. Samples containing NS showed an important positive effect on the capillary suction and sulfate resistance. In the case of expansion due to sulfate attack, mortars with 5% and 10% of NS decreased expansion by 90% and 95% respectively after 2 years of immersion.

1. Introduction

Nanosilica (NS) has been demonstrated to have a high pozzolanic reactivity, with important implications for the behavior of cement-based composites in fresh and hardened states. In the fresh state, it has been found that, NS reduces setting times, increases the release of hydration heat, and modifies the rheological behavior of cement pastes and mortars [1–11]. In the hardened state, researchers have reported that, NS increases the compressive strength [1–4,6,12,13], decreases the porosity and improves some aspects of durability [4,5,8,11,14–18]. Some works have found that, NS produces important mineralogical changes, mainly on C-S-H and portlandite (CH). For C-S-H, NS accelerates its formation, the samples blended with NS have a higher content of C-S-H, and it allows formation of longer C-S-H chains in comparison to the control samples [16–20].

In the evaluation of the incidence of NS on durability, most researchers have argued that, because this material has such good pozzolanic activity; it is possible to expect that, NS will have a major impact on the durability of the mixtures made with. There are few studies published to date where researchers make a real assessment of the performance of cement blended with NS and that, the mortars are exposed to aggressive agents. Among the papers found those by Gaitero et al. [21] and Deyu Kong et al. [22] stand out, they evaluate the reduction of the calcium-leaching rate of cement paste by addition of silica nanoparticles. Other interesting investigations include those by Min-Hong et al. [1], Deyu Kong et al. [22], Said et al. [8], and Mostafa et al. [23], which analyze the resistance to chloride-ion penetration made on concrete of Portland cement blended with NS, and the work of Berra et al. [24], which studied the use of NS for preventing expansive

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alkali-silica reaction in concrete. Quercia et al. [25], which found that, some durability indicators like conductivity, chlorine migration and diffusion coefficients, and freeze–thaw resistance were significantly improved in self-compacting concrete (SCC) with addition of NS. Ibrahim et al. [26], which have researched the effect of the nanosilica on fire resistance of cement mortars.

This work aims to discuss the results of the experimental evaluation of the effects of NS on porosity, water absorption, compressive strength, and sulfate resistance of Portland cement mortars. Regarding sulfate resistance, we show the evaluation of long term (more than 2 years) volumetric stability of mortars containing different percentages of NS immersed in a solution of magnesium sulfate (5% by weight). Magnesium sulfate ($MgSO_4$) is considered the most aggressive agent for the Portland cement [27]. The attack of the $MgSO_4$ on C-S-H produces its decomposition to gypsum, brucite, and silica gel; this process is not directly related to ettringite formation [28]. There is a loss of strength and an adhesion into the cement paste, due to decalcification of C-S-H [28]. Hekal et al. [29] say that, the decalcification of C-S-H, by the attack of magnesium sulfate, produces non-cohesive magnesium sulfate hydrate (M–S–H), as well as the expansion caused by the formation of expansive salts.

2. Materials and methods

In this work mortars of Colombian Ordinary Portland Cement (OPC), produced by Cementos Argos, were prepared, with dry weight percentages of 0%, 1%, 3%, 5%, and 10% of commercial NS produced by BASF Chemicals Company. The nanosilica was presented as an aqueous suspension, with a suspended solids concentration of 40% on average and a pH of 10 ± 1 at 20 °C.

The durability (sulfate resistance and capillary suction) on mortars of cement with different percentages of substitutions of cement by NS was evaluated. Sulfate resistance was determined by measuring the longitudinal change in mortar bars with 0%, 1%, 3%, 5%, and 10% NS; mortar bars were immersed in a solution of $MgSO_4$ with a concentration of 5%, for 154 weeks, according to ASTM C1012 [30]. Capillary suction was evaluated on mortars, after 3 days of normal curing, with replacement of 0%, 5%, and 10% of cement by NS, according to UNE 8398:2008 [31]. Compressive strength was evaluated on mortars with 0, 5, and 10 wt.% of substitution of cement by NS after 1, 3, 7, and 28 normal curing days, according to ASTM C349-02 [32].

To evaluate durability and compressive strength mortars were prepared in accordance with the procedure in ASTM C305 [33]. Binder-to-Ottawa-sand (b/s) ratio used was 1/2.75, being binder (b) the sum of cement plus nanosilica. A constant water-to-binder (w/b) ratio of 0.55 was used. The w/b ratio was corrected for the amount of water incorporated by the suspension. To achieve a flow between 105% and 115% corresponding amount of superplasticizer (SP) required was incorporated (Table 1), according to ASTM C109 [34]. The superplasticizer (460 Pozzolith BASF Chemicals) was homogenized with the mixing water in order to achieve the optimum dispersion of the NS-particles in the mixes.

In order to evaluate the effect of NS on porosity, pastes with 0, 5, and 10 wt.% of substitutions of cement by NS were prepared and evaluated by a Micromeritics Autopore IV Mercury Porosimeter. Samples were mixed manually with a w/b ratio of 0.4 and they were cured for 28 days at 20 °C and 98% relative humidity (RH). Seeking to improve the dispersion, the NS-particles suspension was pre-mixed with the mixing water.

2.1. Characterization of materials

The chemical composition of the materials used, cement and NS, are presented in Table 2. These analyses were carried out in an X-ray Fluorescence ARL 8680s Total Cement Analyzer using the wave dispersion method under standard ASTM C114-03 [35]. These results allowed conclude that, NS is high purity silica (Table 2).

The NS has mean particle size of 98.65 nm, measurements were carried out in a Zetasizer of Malvern Instruments Ltd. The specific surface area (SSA) was determined in a Micromeritics Gemini 2380 by N_2-physic-adsorption using BET method. Values of SSA found were 1.14 and 51.4 m^2/g for the cement and the NS respectively.

Table 2
Chemical composition of materials.

Parameters	Cement	Nanosilica (NS)
SiO_2	20.13	93.56
Al_2O_3	4.37	0.00
Fe_2O_3	3.71	0.39
CaO	64.30	0.22
MgO	2.27	0.13
Na_2O	2.27	0.62
K_2O	0.31	0.02
SO_3	1.99	0.30
Loss on ignition (LOI)	2.44	4.46
Free lime (FL)	0.33	

The X-ray diffraction (XRD) of the mineral addition (Fig. 1) was performed in a PANalytical X'Pert PRO MPD, using a 2θ range of 2–70° with a step of 0.02° and an accumulation time of 30 s. It can be established that, NS has very low crystallinity and high purity. A broad peak was centered at $2\theta = 21.60°$ and appeared as baseline deviation in the 2θ ranges 20.06° and 26.50°.

Zeta potential was measured to different values of pH in order to evaluate the behavior of the NS dispersion when mixed with Portland cement (Fig. 2); the suspension pH was modified using ammonium hydroxide (NH_4OH). It can be seen that, NS suspension for pH between 7 and 14 is in the stable zone; potential values are lower than −30 mV [36–37], whereby, it is possible to conclude that, the NS will not agglomerate into the paste of Portland cement.

3. Results and discussion

3.1. Capillary suction

This property controls the transport of fluid in the unsaturated concrete and depends on the concrete pore structure and type of fluid used [38]. Results of the tests of capillary suction (absorption of water with time) of the mortars prepared with cement (control) and blended cements (5 and 10 wt.% of NS), after three curing days are presented in Fig. 3.

There is a significant decrease in absorption rate and noteworthy differences in the quantity of absorbed water at the end of the test with the increase of substitution of the cement by NS (Fig. 3). This fact is evidenced because the slope the first part of the curves of capillary suctions (between 0 and 300 $s^{1/2}$), which is associated to the water absorption rate, decreases with the increase of NS percentage in mixes (control = 0.026 $kg/m^2\,s^{1/2}$, 5NS = 0.018 $kg/m^2\,s^{1/2}$, and 10NS = 0.012 $kg/m^2\,s^{1/2}$), showing that, the mortar with 10 wt.% of NS has less than half the water absorption rate in comparison with the control sample. Additionally, total water absorption also decreases with the content of NS as shown by the values after 500 $s^{1/2}$, 5NS shows a reduction of 11.1% and 10NS of 33.3% in comparison with the control sample.

This behavior of the NS shows as this mineral addition has a significant effect on refinement of pores, i.e., NS decreased mortars permeability, due to the rupture of the pore interconnections. Furthermore, NS seems to produce a decrease of total volume of pores. These effects of NS are due to its high specific surface area, their small particle size and good particle dispersion within cement pastes. Thus facilitating chemical reactions necessary to produce a high bulk density cementitious matrix with more C-S-H and less calcium hydroxide (CH), as was suggested by Ozyildirim and Zegetosky [39]. This must be added to a physical effect of filler as

Table 1
Mixture proportions of mortars.

Sample	Cement (g)	NS (g)	b/s ratio	w/b ratio	superplasticizer		Flow (%)
					(g)	(%)	
Control	500	0	1:2.75	0.55	1	0.2	114.8
5% NS	475	25	1:2.75	0.55	3	0.6	106.0
10% NS	450	50	1:2.75	0.55	13	2.6	110.4