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Obtaining of repair lime mortars by mixing aerial lime and nanosilica

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Abstract

This work deals with the effect of the nanosilica addition on the performance of aerial lime mortars. Several lime mortars were prepared and modified upon the addition of 3, 6, 10 and 20 wt.% of nanosilica. The presence of nanosilica increased the water demand of the fresh mixtures and reduced the appearance of superficial cracks after the spreading of the mortars onto a porous stone. Setting time underwent a delay when the amount of nanosilica ranged from 3 to 10 wt.%. However, samples with 20 wt.% of nanosilica showed a shortened setting time compared to plain lime mortars. Nanosilica reacted with $\text{Ca}(\text{OH})_2$ particles, yielding C-S-H compounds and, acting as a nanofiller, nanosilica also caused a pore blockage in the mesoporous range. These facts resulted in an increase in both compressive strength and durability after undergoing freezing-thawing processes. Overall, the addition of nanosilica clearly improves several characteristics of the aerial lime mortars in order to prepare enhanced mixtures to be used for restoration works.

Keywords: water demand, compressive strength, durability, nanofiller, C-S-H.

1. Introduction

The interest in using lime-based mortars has lately undergone an increase, especially for different applications, such as for rendering mortars or restoring historical monuments (Rodríguez-Navarro et al. 1998, Lanás et al. 2006, Faria et al. 2008, Sepulcre-Aguilar and Hernández-Olivares 2010, Margalha et al. 2011). The use of cement mortars for Cultural Heritage restoration work raises several drawbacks and incompatibilities that have been highlighted: high mechanical strength, efflorescence phenomena owing to formation of large amounts of soluble salts by migration of alkaline ions, low water vapour permeability and higher thermal expansion coefficient than most masonry (Mosquera et al. 2006, Seabra et al. 2009, Veiga et al. 2009). In view of these shortcomings, lime-based mortars show greater compatibility with ancient building materials and fulfil the recommendations of ICCROM (Malinowski 1981) about the use of materials similar to the original ones in repair works.

However, some problems related to the use of aerial lime-based mortars still remain such as: i) long setting and hardening time; ii) relatively low mechanical strength; iii) a high water absorption capacity through capillarity; iv) major volumetric change as a result of shrinkage (Mosquera et al. 2006). In order to reduce or even solve these problems, the use of admixtures might be considered.

The incorporation of pozzolanic admixtures such as metakaolin has been widely investigated. However, little research has been addressed to establish the performance of aerial lime mortars modified upon the addition of nanostructured silica (also called nanosilica, NS) (Álvarez et al. 2013, Fernández et al. 2013). According to the reported action of NS in cement-based mortars, two diverse effects take place: the pozzolanic reaction between NS and calcium hydroxide (CH) yielding calcium silicate hydrates (C-S-H) and the occurrence of the filling effect, which improves the particle size distribution, thus reducing porosity. These effects result in enhanced mechanical strength (Shih et al. 2006, Quercia et al. 2012).

Therefore, the main goal of this work is to prepare aerial lime mortars in which NS has been incorporated in increasing amounts. The behaviour of these mortars has been assessed in both fresh and hardened state. The evaluation of the durability of the mortars allowed us to draw conclusions about their potential employment as repair materials.

2. Experimental

Mortars were prepared mixing as binder slaked aerial lime (Class CL 90-S, according to the European norm EN 459-1:2011, supplied by CALINSA) and a calcitic sand - pure limestone - as aggregate. The selected binder/aggregate ratio was 1:1 by volume (1:3 by weight). The nanosilica used was a colloidal suspension of silica with pH = 9.68 and a solid / liquid ratio of 0.28, as supplied by the manufacturer (Ulmen Europa SL). The diameter of the spherical particles of NS ranged from 20 to 150 nm, as proved by TEM examinations (Figure 1).

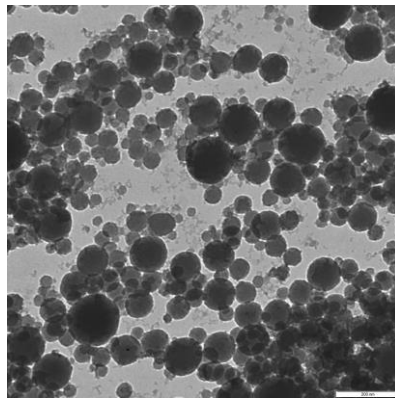


Figure 1: TEM micrograph of NS particles.

Five different batches of samples were prepared varying the amount of NS added: a control group (0% NS), and mortars with 3, 6, 10 and 20 wt.% NS (with respect to the weight of lime).

The amount of water was optimized for the fresh mixtures of the control group in order to obtain a suitable mortar consistency. The workability of the control group mortars was considered optimal when the spread in the flow table test was maintained in the range of 175 ± 5 mm, which was reached with a water/binder ratio of 1.12.

For mortar preparation, lime and aggregate were firstly blended for 5 min using a solid admixtures mixer. Water (and, if required, nanosilica suspension) was then added and mixed for 90 s at low speed in a mixer. For the fresh state, consistency of the samples was measured through the mini-spread flow test, by measuring the slump after the standardized procedure (EN 2000). Furthermore, water-retention capacity, setting time and evolution when applied on support were also studied. This last test consisted of spreading a ca.15 mm layer of mortar on an absorbent support (brick or porous stone) and checking the evolution. The aim of this test was to study the possible macroscopic cracks formation owing to the shrinkage of the mortars.

For measurement of the properties at hardened state, mortars were moulded in prismatic 40x40x160 mm casts and de-moulded 5 days later. Curing regime was ambient laboratory conditions until the test day (RH $60 \pm 10\%$ and $20 \pm 5^\circ\text{C}$). Different curing times were set: 7, 28, 91 and 182 days; at least 3 specimens of each mortar were tested at each curing time in order to make results representative. The

reported results are an average of all of them. Characterization of the mortars included the measurement of the compressive strengths, mineralogical characterization (by powder X-ray diffraction and by FTIR-ATR) and microstructural examination. For the latter, hardened specimens were subjected to a freeze-drying water removal procedure (immersion of the specimen in liquid N₂ for 5 min, and subsequent sublimation at -40 °C under 1 Pa vacuum for 24 h). Then, pore size distribution and specific surface area (by means of mercury intrusion porosimetry and N₂ adsorption isotherms at 77 K – BET method -) were obtained. SEM-EDS examination allowed us to study the morphology and microstructure of the samples.

Finally, some durability tests by means of freezing-thawing cycles were also executed in mortars after 28 curing days.

3. Results and discussion

The addition of NS systematically demands a larger amount of mixing water, as proved by the progressive decrease in flowability (reduction in the slump diameter) that can be seen in Table 1.

Table 1: Fresh state properties of the mortars.

| Sample | Control group | 3% NS | 6% NS | 10% NS | 20% NS |
|---------------------|---------------|-------|-------|--------|--------|
| Slump (mm) | 173 | 168 | 167 | 146 | 126 |
| Water retention (%) | 96.0 | 97.7 | 96.0 | 96.0 | 97.0 |
| Setting time (min) | 215 | 402 | 980 | 494 | 208 |

As in the case of cement mortars, the larger the specific surface area supplied by the NS, the higher the water demand was (Quercia et al. 2012). Despite the fact that when there is improved packing, the larger amount of free water could lubricate solid particles, thus allowing the fresh paste to flow easily, in the current work the increase in NS amount involved a slump decrease. This fact can be explained taking into account, on one hand, that the foreseeable formation of C-S-H-gel increases the water consumption and, as a consequence, the water demand (in this case observed by the flowability drop). On the other hand, the trend of NS to build agglomerates (a reported problem when using nanosized particles) could explain this bad packing (Quercia et al. 2012).

By means of laser diffraction, measurements of the particle size distribution showed that a plain NS suspension has a unimodal distribution, with a sharp peak at 0.30 µm particle diameter (Figure 2a). Taking into account the TEM observations, the agglomeration phenomenon was evident. Besides, the analysis of the particle size distribution of a pure lime suspension resulted in a distribution with peaks at 0.30, 10 (the main particle diameter in volume percentage) and 50 µm. A shoulder at ca. 200 µm was also observed (Figure 2b). However, when NS and lime were mixed, PSD graph depicted a quattrimodal distribution but with inverted intensity of the central peaks. The most relevant findings were a pronounced increase of the third peak (shifted towards larger diameters between 50 and 60 µm) and the displacement of the shoulder at larger particle diameter towards larger diameters (ca. 300 µm) (Figure 2b). The consumption of the lime particles with 0.30 and 10 µm of diameter and the appearance of larger particles (60 and 300 µm) evidenced the interaction between NS and lime particles. NS particles acted as condensation centres, reacting with some lime particles and leading to C-S-H formation (Shih et al. 2006).

Water retention showed negligible variations upon the addition of NS. Setting time of the mortars underwent a delay as the percentage of NS increased up to 10% NS, with a maximum at a loading of 6% NS. However, the presence of 20% of NS shortened the setting time with respect to the control group. The water demand of the samples, the drying of the mortars over the curing process, the formation and ulterior hydration of the C-S-H compounds and the beginning of the carbonation came together to explain this variability. The most remarkable feature is that the addition of 20% NS yielded mortars with reduced setting time, thus improving their usage for practical applications.

Another advantage resulting from the progressive additions of NS is that it prevented the appearance of cracks in the extended layers of mortars when applied onto a porous stone, as depicted in Figure 3. As it can be seen, in both the control specimen and the specimen with 6% NS, superficial cracks are visible. As the NS percentage increased, the abundance of the cracks tends to diminish (see picture for sample with 10% NS) and in the presence of 20% NS cracks were not observed.

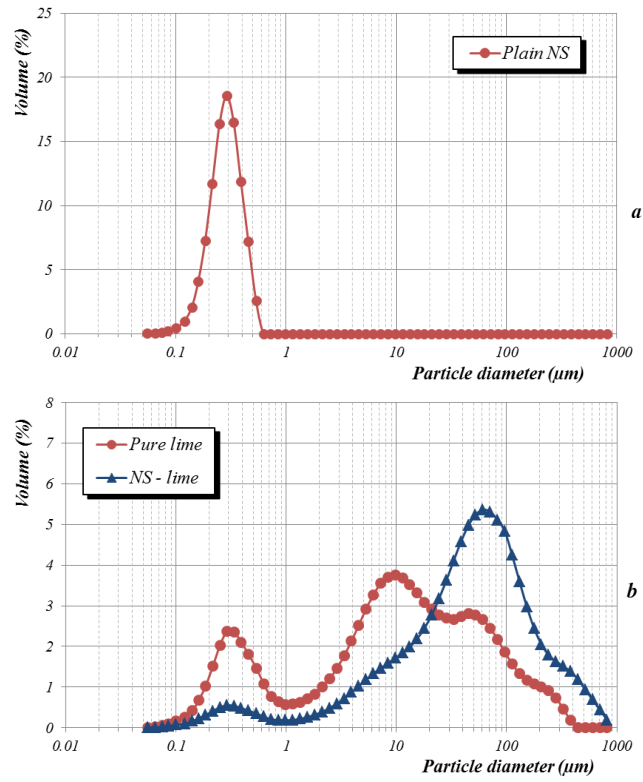


Figure 2: Particle size distribution of a) Plain NS suspension; b) Pure lime and lime+NS suspensions.

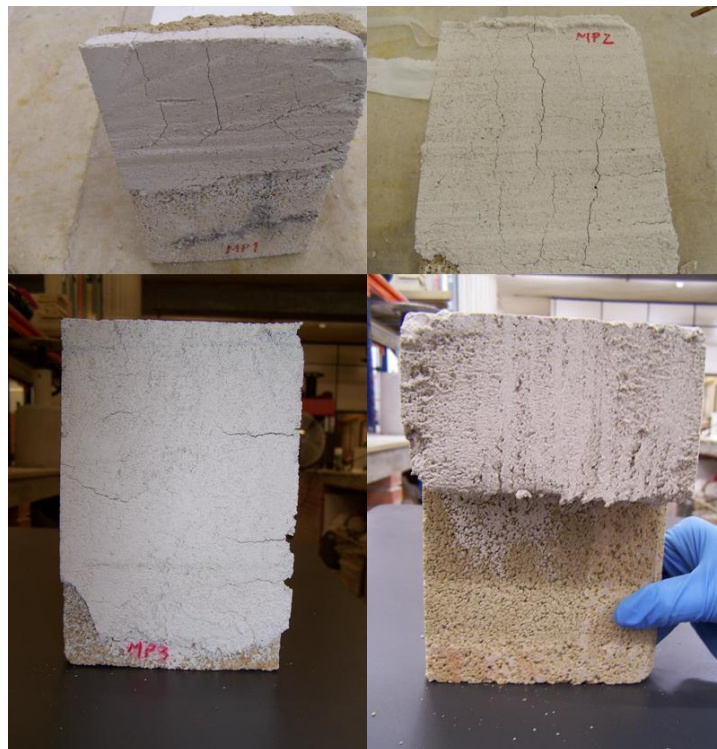


Figure 3: Evolution of the spreading of the mortars on a porous block (samples with 0, 6, 10 and 20%NS).

Regarding the hardened state properties, a noticeable increase in the strengths could be observed in the NS-bearing mortars (Figure 4). As a logical explanation, the strength rises was due to the C-S-H formation. Through the reaction between CH particles and reactive SiO₂ of the NS, calcium silicate hydrates (C-S-H) were formed. This reaction involved a polymerization of the silica of the nanoparticles, which underwent an increase of the average chain length in their internal structure. A broad IR band at around 1100 cm⁻¹ is associated with Si-O-Si asymmetric stretching vibrations. A shift of the former band to higher wavenumber (cm⁻¹) was observed in our samples when NS percentage increases, which means a higher degree of polymerization due to the formation of C-S-H phase (Björnström et al. 2004).

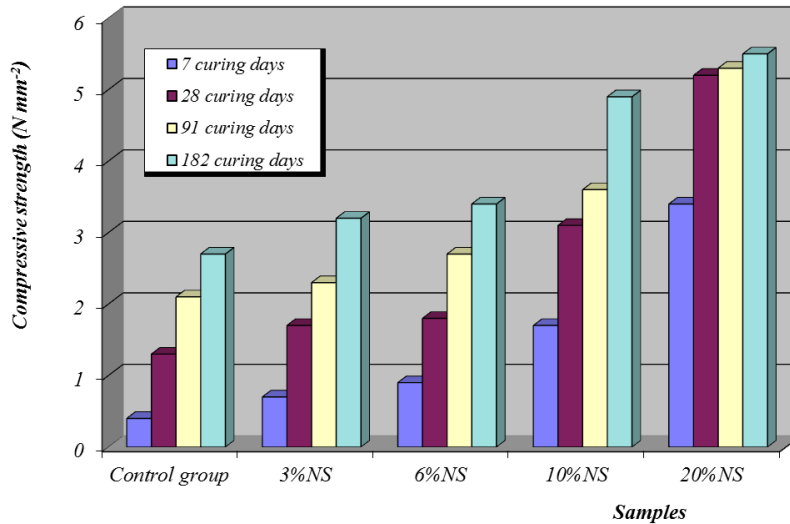


Figure 4: Compressive strengths of the mortars vs. curing time.

In addition, a noticeable filling effect is yet another factor exerting influence on the strengths increase for NS-bearing mortars. Owing to the small particle sizes, NS blocked the pores, thus resulting in a reduction in the mean pore size. This fact can be observed in the pore size distribution measured for the control group, 3%NS and 6%NS containing samples after 91 curing days (Figure 5). The progressive increase in NS shifted the mean pore size towards lower diameters (0.80 μm for control group, 0.55 μm for 3%NS and 0.43 μm for 6%NS). At the same time, the filling effect for the small pores can also be tested when a significant amount of NS is present (6%NS).

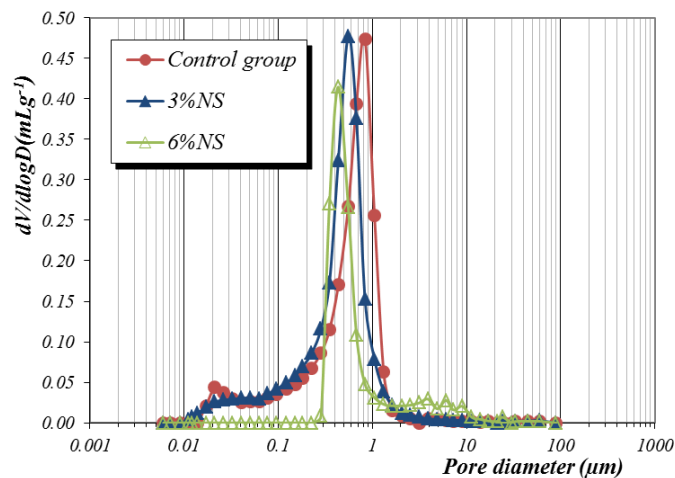


Figure 5: Pore size distributions (MIP) of control group, 3%NS and 6%NS samples.

A more detailed study of this small pore range was performed by means of N₂ adsorption isotherms. By applying the BJH method, the pore size distribution in the lower range has been revealed. Figure 6 shows the PSD graphs for both control and 3%NS samples, after 7 curing days. It must be emphasized that just a 3 wt.% NS produced such a notable change in the PSD of micro- and mesopores. These changes can be well understood assuming the aforementioned role as nanofiller of the nanosilica incorporated. The presence of NS reduced the number of large and medium capillary pores in the approximate range of 20 to 100 nm (the average pore volume of that range expressed in mm³ per gram of sample decreased from 18.64 to 11.17), as a result of the fact that silica nanoparticles were interspersed between the lime particles. These results are in good agreement with the MIP data, in which – as above discussed – in spite of the fact of NS addition, a negligible amount of pores lower than 100 nm was detected. The presence of intercalated NS particles resulted in a wider PSD but with smaller pores, with maximum population at 10 nm.

The nanofiller effect, which provokes the changes in the pore size distributions, contributed to the enhancement of the compressive strengths.

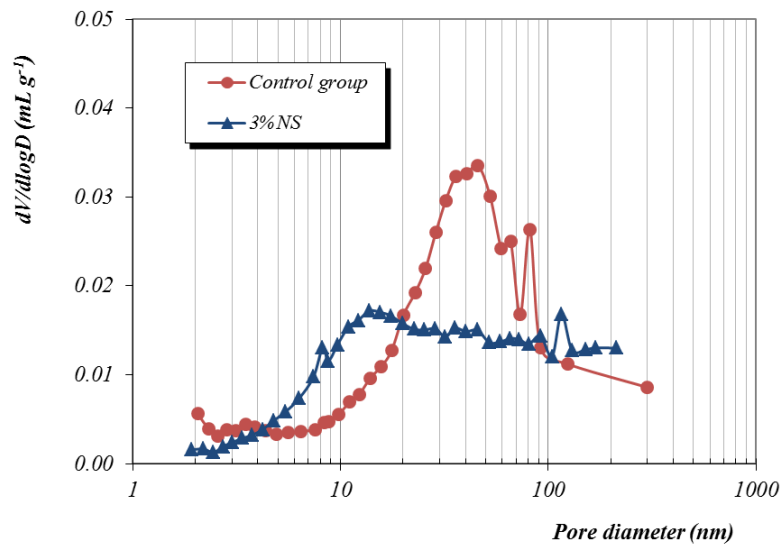


Figure 6: Pore size distribution in the mesoporous range (N₂ adsorption isotherms, BJH method): control group and 3%NS samples.

The SEM examination (Figure 7) of the samples showed large porosity and agglomerations of scaleno-rhombohedral calcite crystals together with some hexagonal plate-like crystals of uncarbonated portlandite (Ca(OH)₂) for the control sample.

The NS addition clearly resulted in a pore size reduction together with the appearance of some thin foil and honeycomb-shaped C-S-H structures. The increase in the polymerization degree and the parallel porosity reduction also was observed as the percentage of NS raised.

As for durability purposes, freezing-thawing cycles were carried out and the results showed that the presence of NS clearly improved the durability of the specimens. Figure 8 depicts the endurance of NS-treated samples when compared with the poor performance of a plain lime mortar (completely ruined after just 4 cycles, Fig. 8a). Conversely, the compactness and physical integrity of samples with NS remained almost unaltered over a larger number of cycles. Fig. 8b shows the 3% NS specimens with only a visible fissure in the middle after 6 F-T cycles, whereas Fig.8c and d show the 10% and 20%NS specimens with a non-swollen and intact structure after 6 F-T cycles.

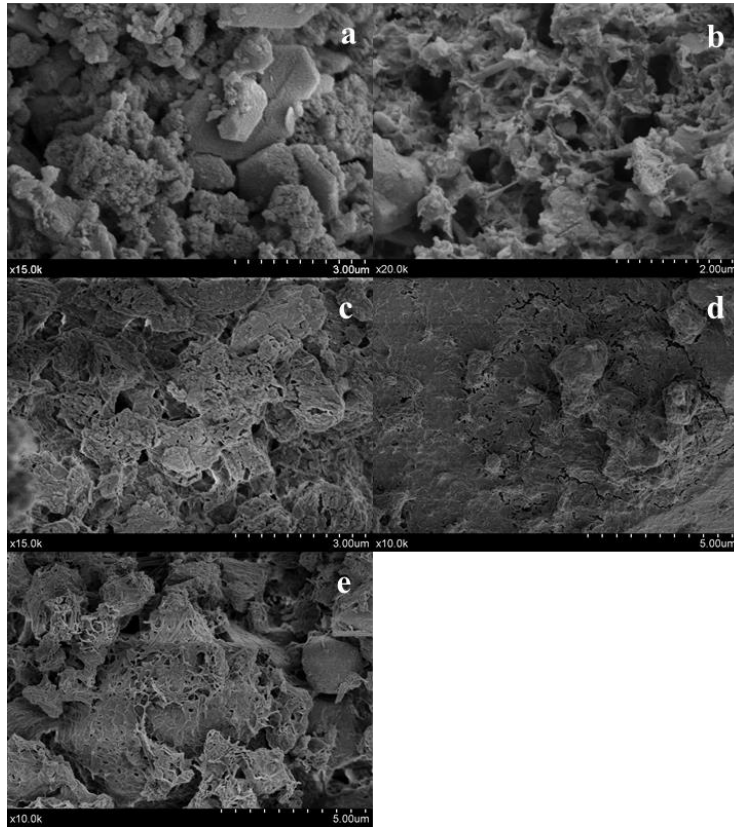


Figure 7: SEM micrographs of the mortars: a) plain mortar; b) 6%NS; c) 10%; d) and e) 20%NS.



Figure 8: Mortars after being subjected to freezing-thawing cycles: a) control mortars after just 4 F-T cycles, b) 3% NS specimens after 6 F-T cycles; c) 10% NS samples after 6 F-T cycles, d) 20% NS mortars after 6 F-T cycles.

4. Conclusions

The addition of nanosilica, especially in relatively large amounts, clearly improves several characteristics of the aerial lime mortars. Compressive strengths and durability when subjected to freezing-thawing cycles were increased proportionally to the percentage of nanosilica added. Nanosilica has been found to easily react with the $\text{Ca}(\text{OH})_2$ particles, giving rise to different C-S-H structures, among which the honeycomb shape is predominant. In addition, NS also behaves as a nanofiller, filling pores mainly in the mesoporous range. The incorporation of NS causes an increase in the water demand of the fresh mixtures. Although in this work the combined use of NS and a plasticizing agent has not been tested, it could be a reasonable alternative for obtaining repair mortars.

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