Effect of nanostructured lime-based and silica-based products on the consolidation of historical renders

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Abstract

An important operation for the conservation of historical renders is the cohesion restitution of the binder-aggregate system, based on the use of materials with consolidating properties. Inorganic consolidants are usually preferred to organic ones due to better compatibility and durability.

The aim of this work is the experimental characterization of two nanostructured consolidant products; a commercial nanolime, optimized with the addition of a reduced concentration of ethyl silicate, and a commercial nanosilica product underwent experiments to verify their consolidation efficiency.

Nanostructured lime-based and silica-based products present interesting properties such as homogeneous distribution and high stability. Nanolimes were applied in combined applications with ethyl silicate, a well-known compatible product for consolidation intervention. The combined application guarantees some benefits and improves the mechanical and microstructural performance of these products. A nanosilica product was tested to better understand some known disadvantages (e.g. reduced penetration depth) and so its performances. Consolidant products were applied on weak lime mortar samples (prismatic samples and single mortar layer applied on bricks); these mortars were optimized by studying different binder-aggregate ratios, to simulate old lime mortar with cohesion loss.

Consolidation effects were periodically evaluated to understand the treatments efficacy. Physical-mechanical characterization was performed on treated mortar samples, analysing superficial hardness and compressive and flexural strength. Microstructural observations and X-ray microanalyses of the consolidation products and of the consolidated mortar samples are also reported.

Keywords: Consolidation products, Nanolime, Nano-silica, Historical renders

1. Introduction

Mortars are materials widely used as building materials for construction and/or decorative purposes; their plasticity, adhesion, easy application, protective and aesthetic functions make it a very versatile building material. However they present, mostly as external renders, a protective function concerning aggressive actions and are particularly exposed to degradation agents.

The most common degradation phenomena are visual and chromatic alterations, formation and deposition of by-products, material loss and mechanical resistance decrease, which result in powdering, cohesion loss and detachments (Tavares 2008). Extremely decayed surfaces are present in several Portuguese buildings as well in European monument and façades, and consolidation action has to be considered during conservation interventions (Costa 2012).

The cohesion recovery between mortar particles, released by binder loss, is reached through the application of organic or mineral consolidants. Synthetic compounds, such as acrylics and epoxy resins, are easier to apply, more flexible and present better adhesiveness, but often do not obey to the fundamental rules of physical-chemical compatibility with the substrate. Inorganic consolidants (e.g. silicates, barite, limewater) are therefore becoming preferred due to better compatibility and durability.

Limewater is considered the most traditional consolidant product, presenting well-known efficiency, such as economic advantages and full compatibility. Limewater however usually contains no more than 2 g/L of calcium hydroxide, contributing to low consolidation effect (Hansen 2003). The use of some additions could help to increase the solubility of calcium hydroxide and its fixing and penetration degree, increasing its efficiency; moreover the resource to calcium hydroxide nanoparticles should improve the concentration and depth penetration, as shown in various studies (Chelazzi 2013).

The development of inorganic nano-consolidant materials offers the possibility of having compatible new and promising products for stone and plaster consolidation (Zonorza-Indart 2012, Persia 2012).

Nanolime dispersions of calcium hydroxide are white to opal fluids containing stable calcium hydroxide nanoparticles, dispersed in an alcoholic medium. Nanoparticles have hexagonal shaped form and size range between 50 and 600 nm, synthesized under controlled conditions (Dei 2006).

The small size of the $Ca(OH)_2$ nano-sols allows a highly active surface, high reactivity, high carbonation rate and deep penetration. Their Stability is caused by electrostatic repulsion forces between the positively charged calcium hydroxide nanoparticles, and by extremely small particle size (Ziegenbalg 2012).

Several scientific researches surrounding these nanotechnologies have evidenced contrasting results, and the potentiality of these nano-materials is still under debate (Hull 2012).

Silica-based consolidant products, especially products based on tetra-ethyl-ortho-silicate (TEOS), have been widely used in stone consolidation, ensuring a reduction of the material porosity. Silicic acid esters (SAE) are the most common consolidants for stone consolidation; after hydrolysis these products cause the formation of amorphous silica, consisting in disordered lattices of tetra-coordinated silica, which acts as a consolidant in the presence of humidity and forms ethyl silicate (Zendri 2007).

Another interesting nanostructured consolidant product is nanosilica. It is commercialized as aqueous dispersion of nanostructured colloidal silica (particles size 10-20 nm); after water evaporation, nanosilica particles aggregate each other inducing the formation of a silicate gel matrix (De Ferri 2011). One of the main advantages compared to classical SAE products is that nanosilica could be applied in wet conditions, presenting a drying time of 3-4 days.

In this work, the characterization of two different compatible consolidant products, namely a commercial dispersion in alcohol of lime nanoparticles additivated with silicic acid esters (SAE) and a commercial aqueous dispersion of nanosilica, is reported. The characterization of these products was carried out and their effect on damaged mortars was evaluated through tests on mortar specimens before and after treatment. Consolidant products were applied on weak mortar specimens and the evolution of their effect was accompanied and periodically evaluated.

2. Materials

2.1 Specimens - Mortar samples preparation

Consolidation products were applied on mortar with a simulated cohesion loss. Mortar specimens were prepared varying the binder/aggregate ratio (Tavares 2008) in order to formulate a mortar with low binder content and consequent low cohesion. The binder used was a commercial Portuguese calcitic hydrated lime (CL 90). The aggregate used was a mixture of 3 different calibrated sands with mean particle sizes < 2mm. The aim was to get a well graduated sand, similar to an average sand used for render mortars.

After previous experimentations, the binder/aggregate ratio of 1:4 (in volume) was selected since it guarantees the desired effect of a low cohesion mortar without significant loss of material. The water:binder ratio selected was 2:1 (mass), as it proved adequate workability (Borsoi 2012).

After the optimization of the mortar composition, different samples were prepared (Fig. 2) namely prismatic specimens (40x40x160 mm) and ceramic bricks (28x19 cm) with a single mortar layer of 1.5 cm thickness.

2.2 Consolidant materials

The aim was to use consolidant products which present physico-chemical compatibility with the treated surface and improve moderately the mechanical properties of the treated surface, achieving a mass consolidation (a suitable penetration depth). Moreover these products should recover the cohesion loss, respecting the water absorption properties of the treated material and avoiding aesthetic alterations.

Two inorganic consolidant products were selected: a commercial dispersion in alcohol of nanostructured particles of lime (Nanorestore®, CTS), combined with a low concentration (5% in mass) of silicic acid ester (SAE) (Estel 1000®, CTS), and a commercial available nanosilica (Nano-Estel®, CTS). Different concentrations of SAE were tested (5, 10, 20 and 50, in mass %) with nanolime. Based on those previous experimentations, the lowest concentration of ethyl silicate (5%) was chosen, in order to moderately increase the mechanical strength, avoiding superficial micro-tensions.

The nanostructured silica-based product (Nano-Estel®, CTS) was tested to verify its performances and verify possible drawbacks, such as reduced penetration depth and possible superficial films. Firstly a dilution of the nanosilica product with demineralized water was carried out, since the commercial product is an aqueous dispersion; dilutions with water: nanosilica ratios (in volume) of 1:1 to 1:10 were tested. A proper dilution is important for a suitable consolidation treatment, since this product presents high nanosilica concentration. Previous experimentation indicate the 1:8 ratio as the most suitable, since it guarantees an adequate dry residue and a moderate mechanical increase, avoiding chromatic alterations.

Table 1 reports some important consolidant characteristics as pH, setting time and dry residue.

Tab. 1 - Consolidation products characteristics

Consolidation products	Consolidant identifications	pH at T=19.6ºC	Dry residue (g/L)
Nanolime + 5% Silicic acid esters (SAE)	NLSE	9,95	24
Nanosilica (1 part) diluted in water (8 parts)	NS	9,45	57

2.3 Consolidants Application on lime mortar specimens

The selected nanostructured products were primarily homogenized by ultrasonic treatment; furthermore SAE was added to nanolime and mixed through magnetic stirring (500 rpm/minute) for 5 minutes, to obtain a homogeneous consolidation product.

The consolidants applications were made in a conditioned room, at 22±2º C and 50 % RH, using the manual spraying technique at a distance of 20-30 cm from the surface (Tavares 2008).

The two consolidant products were nebulised in ten applications on the specimen's surface; applications were performed consecutively, nebulizing the first application on the mortar surface, waiting for its complete absorption on the surface and, after few minutes, going forward with the second application, and so the other applications. Consolidant products amounts were surveyed by weight measurements, being 90-100 ml (with NLSE) and 80-90 ml (with NS) for each mortar applied on bricks; that equates to a quantity of 0.17-0.19 ml/cm^2 for NLSE treatment, and 0.15-0.17 ml/cm^2 for NS treatment.

During the application, it was evident the easier application of the NLSE, probably due to the alcoholic solvent and its high wettability, which could increase the penetration depth of the product.

Otherwise, the dispersion and absorption on the treated surface of NS was different and appeared slower compared to NLSE, probably due to its aqueous dispersion.

3. Methods

Microstructural, microchemical and physico-mechanical experimental procedures were performed on the treated mortar specimens in order to evaluate the efficacy of the consolidation treatments. This paper presents the results obtained at 90 days from consolidant product application.

The improvement of the strength was verified by durometer hardness Shore A (ASTM-D2240, 2004; ISO 7619, 1997) on the surface of the mortar applied on bricks. This equipment measures the penetration resistance of a metallic pin on the analysed material.

A force machine ETI HM-S was used for flexural and compressive strength (EN 1015:11). The flexural tests were performed by producing the tensile stress on the treated surface of three prismatic specimens for product. The compressive strength analysis was performed on each 'half-specimen' obtained from the flexural strength tests, being the value reported an average of 6 specimens/treatment.

An Olympus SZH microscope was used for stereoscopical observations analysing freshly mortar fractured surfaces. Images were recorded digitally with an Olympus DP-20 digital microscopy camera. Chromatic variations on the treated specimens were evaluated with the NCS (Natural colour System) Scale.

SEM/EDS analyses were performed on freshly mortar fractured surfaces. Specimens were previously coated with gold film and observed in a SEM JEOL JSM-6400 coupled with an Oxford energy dispersive

X-ray Spectrometer (EDS).

Water absorption under low pressure was checked with Karsten tubes. The procedure performed is based on a methodology adopted by RILEM (RILEM 1980) and was carried out on the mortars applied on bricks. This test simulates the pressure of above 140 km/h wind on the vertical surface of the specimens where pipes are applied. Two Karsten pipes were glued with mastic adhesive to each specimen, testing 3 specimens/treatment.

4. Results and discussion

4.1 Compressive and flexural strength

Flexural and compressive strength of untreated and treated prismatic specimens (90 days after consolidation treatment) were performed and are reported in table 2.

Tab. 2 – Mechanical strength results (average and standard deviation values)

Specimens		Flexural Strength (N/mm^2)	Compressive Strength (N/mm^2)
Untreated		0,28±0,03	0,43±0,02
Treated	NLSE	0,38±0,04	0,66±0,04
	NS	0,43±0,05	0,73± 0,04

A significant increase in the compressive and tensile bending strength of the treated materials is achieved with both consolidants. The highest values were obtained with the application of NS, with improvement of about 42% in the flexural strength and almost 70% in the compressive strength, compared to the untreated specimens. The results obtained with NLSE are lower compared to the specimens treated with NS, but they nevertheless show an increase (about 36% in the flexural strength and 53% in the compressive strength). A moderate improvement of the mechanical resistance is suitable, and this condition is satisfied in the case of both consolidant products used. Toniolo (Toniolo 2010) considered that a consolidation treatment should improve the flexural strength without exceeding 1.5 times the value of untreated samples. However in a case study the value of the treated mortar depends on the initial conservation state of the mortar, which must be characterized. The flexural/compressive strength ratio is uncommonly high for the untreated specimens, showing the fragility, due to small cracks, of the low binder mortar; after treatments this ratio became close to 0.5-0.6, which is the normal ratio for air lime mortars, revealing the high deformability and ductility of those mortars (Veiga 2010).

4.2 Durometer hardness (Shore A)

The superficial hardness (material's resistance to permanent indentation) of the specimens was verified 90 days after the application of the product through a durometer (Shore A). Hardness values (fig. 1) illustrate an improvement of the treated specimens compared to mortar reference, coherent with the trend of the flexural and compressive values.

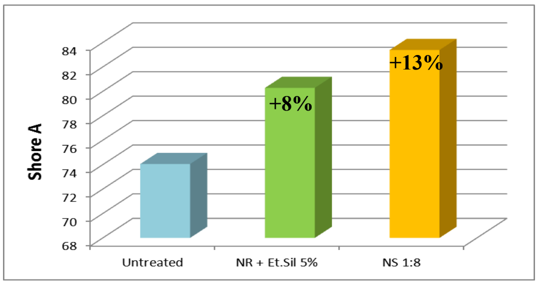

Fig. 1 - Superficial hardness values of treated and untreated mortars (durometer Shore A).

The NLSE and NS treatments, however, present a moderate increase of the superficial hardness (respectively, 8% and 13%) compared to the untreated specimens. A relatively low improvement of the superficial hardness is preferred, since a reduced quantity of consolidant product is applied on the mortar specimens and a high superficial hardness could represent an accumulation of consolidant on the surface, that is, a reduced penetration depth. The values of the treated specimens reflected the trend of precedent studies made on ancient lime-based mortars (Tavares 2008, Veiga, 2010).

4.3 Karsten Tubes

Karsten tubes were used to verify the possible variation of the water absorption properties of the treated mortars; values were registered in seconds needed for the absorption of 4 ml of water and are presented in table 3.

Tab. 3 – Karsten tubes test values (average values and standard deviation)

Consolidant products	Time needed for water absorption: average and standard deviation (sec)
Untreated	36,50 ± 4,92
NLSE	40,16 ± 7,43
NS	62,33 ± 13,04

Results illustrate that water permeability shows just a slight reduction with NLSE treatment compared to untreated specimens. NS treatment confers higher variation of water absorption properties and, although the water permeability is still very high, it presents almost doubled time values compared to NLSE treatment. NLSE treatment could result in hydrophobic surface since the ethyl silicate reacts forming an impermeable layer on the surface; however the SAE percentage is reduced and with time it undergoes syneresis (extraction or expulsion of a liquid from the gel) which results in an open structure allowing water vapour diffusion and absorption. Treated surfaces convert into hydrophilic in few weeks (Ziegenbalg 2012), as shown by the present results.

Results evidence high variability and standard deviations due to the high heterogeneity and porosity of the treated mortars. However absorption time values are still low (high permeability), and consolidation treatments are therefore moderate and do not change excessively the consolidated specimens water absorption and its hygrothermal equilibrium.

4.4 Microscopic observations - Stereozoom microscopy

Stereozoom observations were performed in order to evaluate the microstructural and morphological variations due to consolidation treatments. Untreated specimens (Fig. 2a) evidence heterogeneous binder distribution, with diffuse lacunas, wide pores and micro-cracks. Specimens treated with NLSE (Fig. 2b) show a more compact surface, with a slight macroporosity decrease; the consolidant product is homogenously distributed in the treated surface, partially filling pores and lacunas.

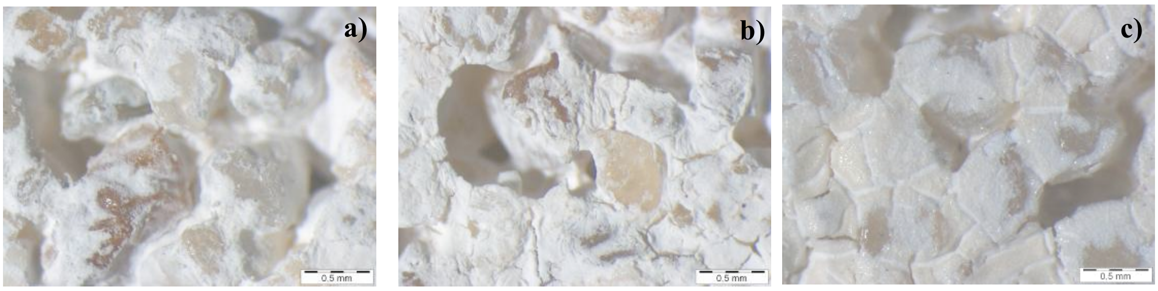

Fig. 2 – Stereozoom microphotographs (20x and 40x): a) Untreated specimen (arrows); b) Specimen treated with NLSE; c) Specimen treated with NS.

Nanolime is dispersed in an alcoholic solvent, which could help the penetration of the consolidant product as seen in previous studies (Borsoi 2012). The ethyl silicate gels, formed from the SAE hydrolysis, do not present any shrinkage effects (typical for silica-based products) on the treated surface.

In the case of building materials with large fissures and pores, e.g. mortars with cohesion loss, alcohol generally flows and wets better than water (being non-polar). The rate of diffusion of the nanolime is however 2-3 times slower than its alcohol dispersant, and these factors could interfere in a real mass consolidation, that is, consolidant penetration in depth (D'Armata 2012).

Conversely, an even more uniform distribution of the consolidation product is evident in the specimens treated with NS (Fig. 2c); NS seems to form a superficial layer and plate-like agglomerates (mostly of 0.5-1mm) with diffuse micro-cracks, which probably are linked to the shrinkage effect of NS. Nanosilica agglomerate morphology induces a micro and nano-scale roughness at the surface, but it results in a visible layer on the surface. Penetration depths will be further studied in detail in future works.

Macroscopically both products show minimal chromatic differences in comparison to the untreated mortar. NCS index were considered to evaluate the chromatic alteration of the treated mortars; compared to untreated specimens (NCS index: S0502-R50B and S0500N), NLSE treatment illustrates a slight whitening on the treated surface (NCS index: S0502-G and S0502-B) while nanosilica shows a slight yellowish patina on the treated specimen (NCS index: S0502-Y and S0501-R50B); however they maintain almost the same colour values of the reference, with changes nearly undetectable for human eyes.

4.5 Microstructural observations by SEM-EDS

The observations of the specimens treated with NLSE (Figs. 3a, 3b) show micro-sized clusters, compacted and polydispersed, of calcitic formations; consolidation film is well-distributed, embedded in the microcrystalline matrix of the original binder, guaranteeing a re-aggregating effect and an improvement of the mortar cohesion.

Nevertheless deposits of consolidant material are evident is some treated areas (arrows, Fig. 3a), with filament-like agglomerates (Fig. 3b). These agglomerates do not appear in previous studies with nanolime treatments (Borsoi 2012) and are probably colloidal silica xerogel, formed after SAE synthesis; the SAE transforms itself in a xerogel due to the evaporation of the solvent and then reacts with atmospheric humidity forming colloidal silica gel. This process takes place in hours to days (Margret 2009).

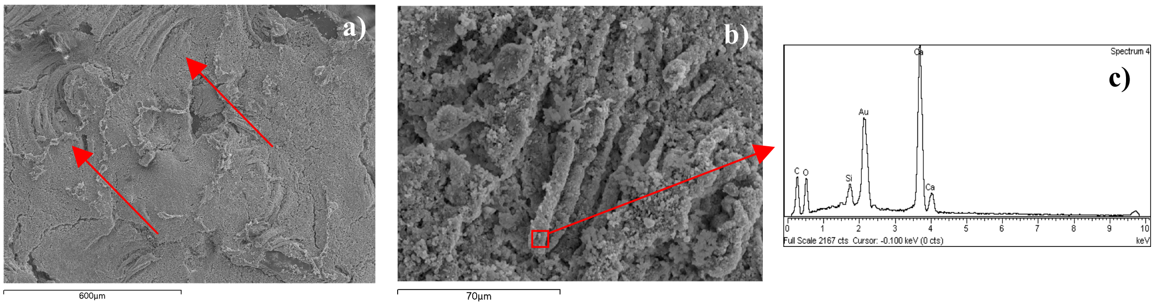

Fig. 3 - SEM microphotographs of the specimen treated with NLSE: a) homogeneous distribution on the mortar surface, with however an accumulation of material in some spots; b) formation of filament-like agglomerate, c) EDS spectrum of the agglomerates.

It is interesting to note that typical plate-like formations of ethyl silicate and typical shrinkage effect are avoided, with the formation of filament-like formations; the presence of Ca^{2+} could modify the xerogel vesicular microstructure, aiding to the development of shorter linear chains of tetrahedral silica and linear silicate (Zendri, 2007). The alcoholic dispersant (isopropanol) probably influences the formation of colloidal silica gel, preventing the formation of plate-like agglomerates and inducing the formation of filament-like structures. EDS analysis (Fig. 3c) of filament-like agglomerates confirms the presence of Ca and Si, indicating the possible presence of hydraulic compounds. These structures consist of silicon and calcium, but it is not obvious if these are chemical or physical connections (Piaszczynski 2010), that is, if neoformation hydraulic compounds are formed. Indeed any hint is given by SEM-EDS analysis concerning the formation of calcium silicate hydrate or hydraulic compounds (Ziegenbalg 2012).

NS treatment indeed illustrates the formation of a homogeneous, thick and compact consolidation film, with large plate-like agglomerates of colloidal silica (Fig. 4a). Nanosilica is a wet gel that presents a three-dimensional network of nanometer-scale oxide particles, surrounding an interconnected network of pores that are filled with fluid, typically the solvent (Margret 2012). The evaporation of the solvent (water) under ambient pressure leads to pores collapse and a highly densified *xerogel*.

Nanosilica tends to shrink and to detach from the surface, forming wide cracks (Fig. 4a), as observed in section 4.4; nanosilica treatment guarantees a superficial consolidation but appears just as adhesive agent: it fills pores and lacunas of the mortars, without effectively replacing the original lime binder.

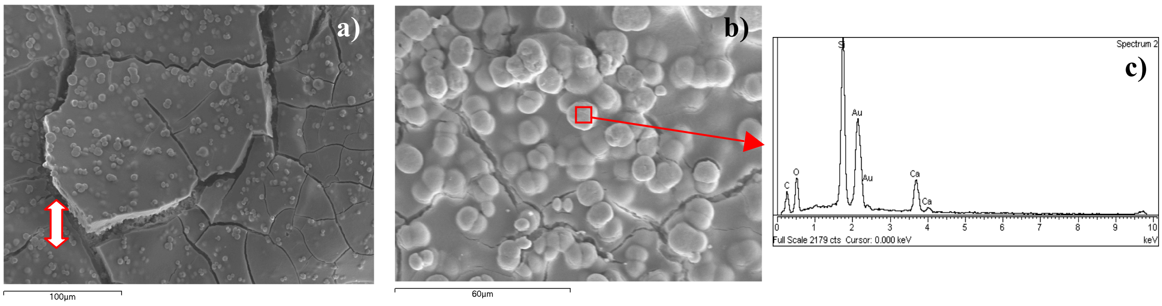

Fig. 3 - SEM microphotographs of the specimen treated with NS, (a) evidencing a compact consolidant film with cracks and plate-like aggregate detachment; b) rounded aggregates neoformation on the treated surface, c) which reveal to contain calcium and silicon (EDS spectra).

A significant concentration of spherical formations (5 to 10µm) appears on the treated surface (Fig. 4b), mostly where the nanosilica film appears as thinner; EDS microanalysis (Fig. 4c) confirms that these formations incorporate calcium, which was probably extracted from the original lime matrix in the wet silica gel. Nanosilica treatment increases consolidation and mechanical strength but it seems to present just a surficial cohesion recover, without achieving mass consolidation; it seems to allow just a minimal penetration depth, ended up mostly in the surface.

5. Conclusions

The two consolidant products tested, namely an alcoholic dispersion of nanolime combined with a low concentration of silicic acid esters (NLSE) and an aqueous dispersion of nanosilica (NS), proved to be effective in improving the mechanical properties of weak lime mortars, but they present different behavior as consolidant products. Higher mechanical increases were obtained with the NS treatment; nevertheless it presents formation of a compact colloidal silica layer on the treated surface, with typical shrinkage effects that could reduce the durability of the consolidation treatment and affect its penetration depth. NS works just as an adhesive agent, filling lacunas and pores of the original mortar, without replacing the original lime binder. NS treatment slightly decreases water permeability and bestows a slight yellowish to the treated mortars. NLSE treatment guarantees mechanical results slightly lower compared to NS treatment; a lower mechanical resistance improvement was however predictable due to the reduced consolidant amount (dry residue) inserted in the treated specimens. NLSE treatment allows a suitable consolidation intervention that does not modify the water absorption properties of the treated mortar; it could induce a slight whitening in the treated surface, but is almost imperceptible to the naked eye. Its distribution is more homogeneous, although an accumulation of nanolime appears in some areas. Some advice should be considered, after consolidant application, to prevent nano-lime deposition on the surface, such as the prevention of alcoholic dispersant evaporation or the removal of nanolime excess from the surface (D'Armata 2012).

Microstructural analysis of the treated surface by optical microscopy and by SEM-EDS illustrate a wide concentration of rounded agglomerates on the specimens treated with NS; these agglomerates incorporate silicon and calcium and appear as a physical 'encapsulation' of calcium of the original matrix (mostly $CaCO_3$), which modifies the polymerization of the nanosilica. Filament-like neoformations are visible on NLSE treated surface, and their formation is influenced both by the alcoholic dispersant and by calcium presence; typical shrinkage effect, which leads to superficial cracks, is avoided and the consolidant product appears well-connected to the treated mortar specimen. EDS analysis confirms the incorporation of calcium in these silicate-based filaments, indicating the possible presence of hydraulic compounds. Nanolime acts as a catalyst for the hydrolysis of the silicic acid ester (SAE) and as coupling agent, enhancing mortar consolidation (D'Armata 2012). Any hint is given by XRD or SEM-EDS analysis concerning the formation of calcium silicate hydrate or hydraulic compounds (Ziegenbalg 2012). This interesting topic should be studied more in detail with further analysis as XRD, TGA-DTA and NMR, which might clarify this issue.

This study concludes that there is an opportunity for nanolimes to offer a feasible conservation method for porous materials such as ancient mortars, avoiding the introduction of undesirable amount of water**;** future studies will consider long-term efficacy and durability of the nano-consolidant treatments.

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