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THE EVALUATION OF NANOSILICA PERFORMANCE FOR CONSOLIDATION TREATMENT OF AN HIGHLY POROUS CALCARENITE

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Abstract

The innovative properties of the nano - materials can have advantageous application in the restoration and conservation of the cultural heritage with relation to the tailoring of new products for protection and consolidation of stone. Their potential use in this field needs to be assessed taking into account specific requirements such as effectiveness, harmfulness and durability. This paper reports on the experimental activity concerning the application of a nanosilica based product for the consolidation of stones having high porosity. The study deals with the assessment of the suitable methods and amounts of product to be applied and the determination of several basic requirements in order to evaluate the properties of the treated stone, such as the surface distribution and the penetration depth within the porosimetric network, the stone surface colorimetric parameters, the superficial strengthening effects, as well as the behaviour with respect to the capillary water penetration and vapour permeability.

Keywords: stone consolidation, silica nanoparticles, porous stone

1. Introduction

New products are, increasingly on, available for stone conservation. Thanks to the advanced material technologies many new materials with innovative properties and new potential applications, such undoubtedly are the nanostructured materials, have been realized for applications in the field of the cultural heritage, i.e. protection and consolidation. The properties of these new advanced materials have been explored as nanoparticles based single systems (Salvadori and Dei, 2001; Zendri et al., 2007; Ciliberto et al., 2008; Licciulli et al., 2011) or in addiction to other components. This is the case of the chemical engineering of PMC (Miliani et al., 2007, Kim et al , 2008) and polymers-nanoparticles composites, where various kinds of inorganic oxides nanoparticles are combined with pre-existing products, thus introducing a large spectrum of new advanced performances (de Ferri et al., 2011; Manoudis et al., 2007). Other than from their chemical properties, the issues of the products for stone conservation depends on the support characteristics, thus meaning that treatments might to be tuned on the different substrates taking into account specific requirements such as effectiveness, harmfulness and durability with respect to the stones to whom they are applied.

This paper reports on the experimental activity concerning the application of nanosilica for stone consolidation. The study moves from a collaboration activity with the Cericol Research Center, Colorobbia Italia, that is the supplier of the product, within a research project aimed to study conservation treatments for highly porous stone materials. A commercial water based product, already experienced for capitals marbles of the Pisa Tower (Baldi, 2008; Baldi, 2012), was tested on a soft and porous calcarenite used in the Apulian region (Souther Italy), in order to assess its performances on porous stones. Generally speaking, soft and porous stones were widely used in the past as building materials, due to a relative facility of extraction and cutting in spite of their low durability. The poor resistance to the chemical–physical decay processes make them particularly affected by decohesion problems, thus demanding consolidation treatments for restoring physical–mechanical characteristics on their surface and adhesion to the non-deteriorated support.

The suitable methodology of the treatment and the optimal amounts of the products to apply to the stone were evaluated by the assessment of the superficial distribution and penetration depth of nanosilica, as well as by the evaluation of the colour surface properties of the treated stones. The best treatment that was identified by this preliminary screening was then evaluated with reference to the strengthening effect on the stone surface, as well as with respect to the water vapor permeability and capillary water absorption, by comparing mechanical and hydric parameters before and after the product's application.

2. Materials and methods

2.1 The nanosilica product

A nanosilica based product in aqueous medium was used, PARNASOS® ZG00009. It was formulated by Ce.Ri.Col and is produced by Colorobbia Italia.

The synthesis procedure is based on the hydrolysis in water of tetraethyl orthosilicate $Si(OC_2H_5)_4$, following the reaction:

$Si(OR)_4 + H_2O \rightarrow HO\text{-}Si(OR)_3 + R\text{-}OH$

The amount of water and catalyst present are chosen to obtain a complete replacement of OR groups by OH groups. In addition, a condensation reaction takes part to form a siloxane [Si-O-Si] bond from partially hydrolyzed molecules.

The sol is then de-stabilized arranging the pH value < 4.0.

The residue is washed, dried at 80°C and re-dispersed in water to a pH value > 9.0.

The stable nanodispersion of rounded silica particles has a mean size of about 30 nm (PdI 0.40) with a Z-potential of 35 mV.

PARNASOS® ZG00009, has a concentration in nanosilica of 30 % w/w. Density of this product is 1.20 g/mL and viscosity at 20°C is 12 (mPas/sec).

2.2. The stone

A calcarenite, locally named "pietra gentile" (GS stone), was used for the application of the nanosilica treatments. This stone is representative of soft and porous stones, widely used within historical-architectural heritage, as well as in many sites and archaeological artifacts in the Apulia region (Southern Italy) (Tucci et al, 2008; Sileo, 2012).

It is a very fine calcarenite, white coloured and with a massive structure, made of fine fossil remains having the average size of 200 microns ca., and lythoclasts within a micritic groundmass finely mixed with poor microsparitic cement. From a petrographic point of view it ranges from medium-fine *wackestone* to *packstone* (Dunham R.J., 1962), (Figure 1), due to the irregular and very variable structural characteristics. The open integral porosity of the stone choose for this work is about 30%, with pore radius distribution mainly between 4 and 0.5 µm.

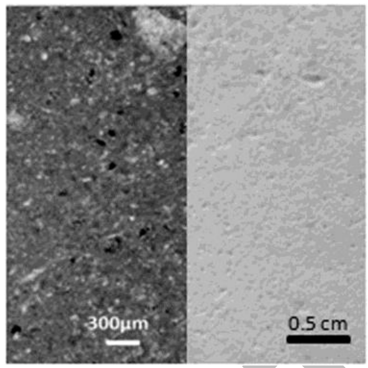


Figure 1. GS medium-fine calcarenite [wackestone, thin section photomicrograph, polarised light, crossed nicols (left); macrophotograph (right)]

2.3 The stone treatments

As it is well known, the treatments have to be tuned with relation to the characteristics of the stones to be treated. Previous experiences of application of this product were performed on the weathered marbles of the Pisa tower (Italy), where the capitals were treated by capillarity. This method is suitable for " mobile" objects of limited extension, whilst it would not be proposed as a work site method for large scale surface interventions. Moreover, in the case of the highly porous stones, the great absorption of the product involved in the treatment is an aspect that needs to be evaluated with reference to the sustainability in both economic terms and compatibility with the original characteristics of the preexisting stones. By consequence, the first problem of the treatment of the stone under study with the nanosilica was the choice of the product amount and the application method. Different treatments (A,B,C,D) were realised, following the application methodology by capillarity and by brush.

After the cutting and cleaning with a soft brush, the samples were washed with deionized water in order to remove the stone dust and then they were dried in oven at 60°C. The dry weight was assumed when the difference between two consecutive weight measurements was less than 0.1% of the initial weight of the sample. Before the treatments, the stones were stabilized at the laboratory controlled conditions (22 ± 2°C, 45 ± 5% R.H.) for 24 hours. After the treatments, the samples were dried until the constant weight at T = 22 °C, R.U. = 40%.

The following treatments were applied to the stone.

Treatment A. Application by capillarity; moving from the results of the capillary absorption test, the absorption time of one hour was adopted in order to ensure almost the material saturation by the solution. The GS stone has high water uptake (400 mg/cm2 at 8 days) and quick over time (85% of the total absorbed water at 1 hour).

Treatment B. Application by brush; several consecutive applications were realised until the product was refused by the stone specimens.

Treatment C. Application by brush; the product was applied in four steps, with a time lapse of 10 minutes from each other, until the stone refuse.
Treatment D. Application by brush; half a maximum solution's amount experienced in B was applied (100 mg/cm^2) by several consecutive applications.

The application details are summarised in Table 1. With reference to the amounts of the applied solution, it was found that the application of the treatment step by step, with a time lapse from each other, inhibited the absorption of the solution. In this case it was noticeably lower than the maximum allowed by consecutive applications by brush.

Table 1. Application details of the treatments

Treatment	Application method	Amount of applied solution	Amount of nanosilica
		(mg/cm^2)	
A	Capillarity	280	84
B	Brush, continuous applications up to the stone refuse	200	60
C	Brush, four time lapsed steps of appl. up to the stone refuse	36	11
D	Brush, consecutive applications without stone refuse	100	30

2.4 Measurements, analyses and tests

Before and after the treatments the following measurements, analyses and tests were carried out on the stone specimens.

ESEM observations and EDS analyses

Morphological observations by Environmental Scanning Electron Microscopy (ESEM, Mod. XL30, FEI Company) were performed in order to study the distribution of the treatments on the stone surface.
Qualitative/quantitative elemental analyses by Energy-Dispersive X-ray spectroscopy (EDS), allowing traceability of suitable atoms, were carried out on cross sections of the treated specimens to detect the penetration depth of the nanosilica within the stones. The following test conditions were adopted: low vacuum mode, pressure of 0.7 Torr, beam accelerating voltage of 25kV, 100 Lsec acquisition time,100 x 100μm area of each analysis.
The EDS spectra were normalized to the Ca peak., and Si was chosen as the indicator of the presence of the treatments. Indeed, it is an effective marker for the evaluation of the penetration depth of Si-based preservative products within pure calcareous stones.
In particular, ESEM observations and EDS analyses were applied to a preliminary screening for the evaluation of the optimal amounts and methods of the product application. Moving from these preliminary assessments, the suitable treatment was characterised by further investigations, as in the following items.

pH test

Phenolphthalein was used as pH indicator, in order to detect the presence and distribution of the nanosilica product within the stone. A solution of phenolphthalein at 1% concentration in ethanol was applied to the cross sections of the treated samples. pH conditions lower than 8.2 make the solution uncoloured, while pH conditions higher than 9.8, as it is in the case of the nanosilica product PARNASOS® ZG00009, lead to a red colour change.

Color measurements

They were performed in the CIELab space, using a reflectance colorimeter (Minolta Chroma Meter CR 300, illuminant C). The colour parameters L*a*b* (CIE 1976) were measured on each stone sample (NORMAL Rec. 43/93); ten measurements were taken on each sample area measuring 5x5 cm.

Porosimetric analyses

They were performed by Mercury Intrusion Porosimetry (Thermo Quest- Pascal 140 and 240)

Abrasion test

The abrasion resistance (UNI EN 14157-2004) was determined on the treated and untreated face of the same stone samples.

Static contact angle measurements

The determination of the static contact angle on laboratory specimens (UNI 11207:2007) was carried out by means of a Lorenzen and Wettre apparatus (Costech instrument); 15 measurements were performed on each sample area of 5x5 cm.

Permeability test

The permeability test was carried out on 5 specimens measuring 5x5x1 cm (NORMAL Rec. 21/85); the results were expressed as the mean value.

Capillary test

The capillary test was performed on 5 specimens measuring 5x5x2 (UNI 10589:2000); the results were expressed as the mean value.

3. Results and discussion

3.1 The suitable application's method and product amount

Stone treatments might to ensure the homogenous distribution of the products on the surface of the stones, avoiding accumulation on the surface that hide the original colour characteristics. Further requirement of the consolidation treatments is a good penetration within the stone, in order to realize the adhesion of the inconsistent superficial layers with the unweathered stone beneath.

The morphological observation of the samples involved in the different treatments revealed that the best result in terms of surface distribution of the nanosilica product was obtained for the D treatment. By comparing the sample surface of the untreated and treated samples, it was evident that the treatment D didn't alter the original grain shaped morphology of the stone surface (Figures 2, 5). On the contrary, the treatments A, B, C led to wide product accumulation areas, hiding the original morphology of the stone, as it can be observed in Figure 3, 4, where micro-cracks are also evident in the nanosilica coating on the stone surface.

Macroscopically, the accumulation of the product led to a translucent appearance of the stone surface and/or to the presence of nanosilica white powder. Figure 6 shows the surface samples of the untreated and treated stone, with reference to each treatment, observed by the stereomicroscope, using oblique illumination.

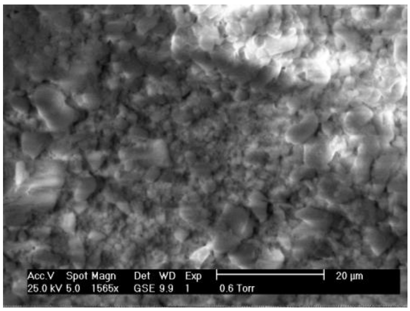


Figure 2. Untreated stone surface

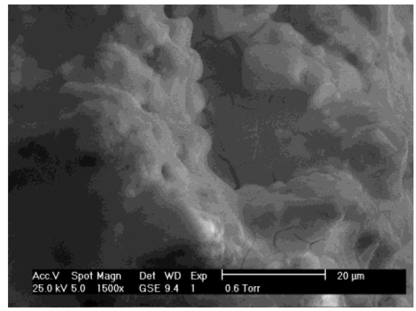


Figure 3. Treatment A. Morphology of the sample surface

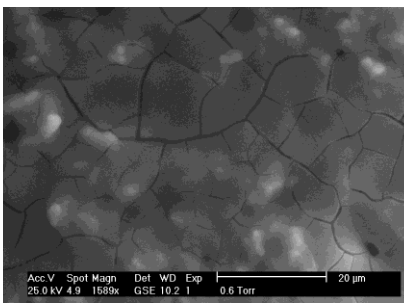


Figure 4. Treatment B. Morphology of the sample surface

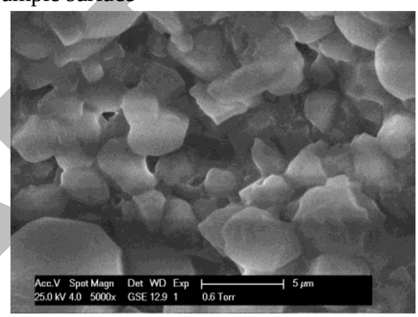
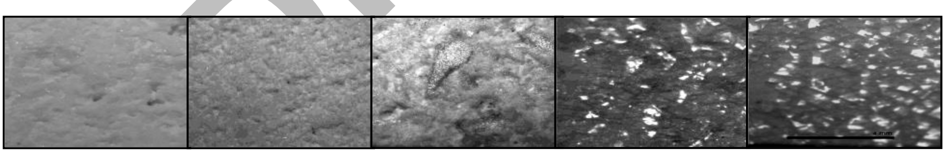


Figure 5. Treatment D. Morphology of the sample surface



Untreated Stone | Treatment | Treatment A | Treatment C | Treatment B

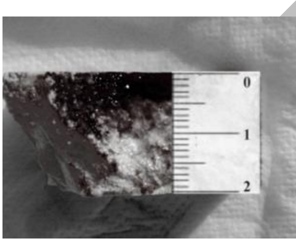
Figure 6. Surfaces of the stone after the treatments

Nevertheless, the observed alteration of the chromatic surface properties was not recorded by the colorimetry. In Table 2 the L^*, a^*, b^* color parameters before and after the treatments are listed, with the colour variation (ΔE). The lowest ΔE resulting from the application of the treatments A and B contrast with the aspect of the surface that was clearly observed by naked eye. In this case, the colorimetry seems not to be a suitable method to record the color properties of the treated surfaces. The explanation would be found in the presence of the nanosilica on the surface that realize a glossy layer. The reflection phenomena induced by the highly reflective glossy surfaces may cause measurement errors in colorimetric measurements in direct light, since most of the incident light is reflected out of the field of detection of the optical-fiber cable for measuring specimen.

Table 2. Color parameters

	before treatment			after treatment			
	L*	a*	b*	L*	a*	a*	ΔE*
A	92,67	0,39	6,41	91,00	0,48	8,16	2,42
B	92,75	0,31	5,82	91,71	0,36	6,13	1,09
C	91,49	0,39	8,16	90,41	0,49	8,24	1,09
D	93,07	0,41	5,70	90,07	0,47	7,13	3,33

A large representation of the nanosilica distribution within the stone was given by the phenolphthalein Ph test (Figure 7). The inhomogeneous penetration of the product under the surface was also evidenced, following the heterogeneity of the stone structure. The penetration depth was found to range from 5 to 10 mm under the surface, most frequently it was up to 7-8 mm.



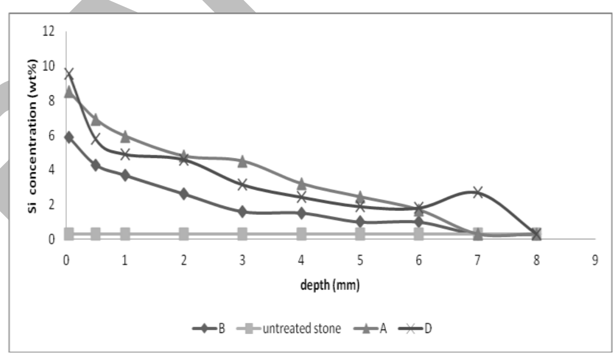


Figure 7. Depth of penetration by the phenolphthalein color test (Treatment A)

Figure 8. Distribution profile of Si within the stone by EDS analyses with reference to the each treatment.

The EDX profile of the Si content (Figure 8), starting just under the surface (50 microns) up to the constant line content of the untreated stone, is shown in Figure 9 for the A, B, D treatments. The recorded penetration depth was up to 8 mm. In spite of the different amounts of the solution that were applied by each treatment, the Si content within the stone is quite similar for A and D treatments, while lower quantity was detected in the stone that underwent to the treatment B. These results show that, irrespectively from the quantity of the solution applied by the different methods, the depth and distribution of the nanosilica particles was almost the same, thus meaning that the higher quantity of the solution applied by A and B treatments exceed the penetration capability of the nanosilica allowed by the stone. According to the ESEM observations, the treatment D was confirmed as the suitable one, giving a penetration effectiveness that is comparable with the other methods, in spite of the lower amount solution applied; it also avoid the accumulation of the nanosilica on the surface that come from the excess of the solution applied.

Moving from the results obtained by this preliminary screening, further investigations were carried out on the treatment D.

3.2 Basic properties of the treated stone

Other than good penetration within the stone material and preservation of the chromatic properties of the stone to be treated, consolidation treatment might ensure the mechanical strengthening of the consolidated material. At the same time the introduction of the consolidant has not to alter the water migration, in liquid and vapor phase, specifically the water that easily can be entrapped within the stone. Therefore the harmfulness with respect of the hydric behavior of the stone material needs to be assessed, as well as the cohesion effectiveness.

The hardening effect induced by the application of nanosilica was evidenced by the increase of 7% of the surface resistance recorded by the abrasion test. In fact, the lenght of the groove measured on the untreated and treated stone was 42 and 45 mm, respectively. The cohesion effectiveness is related to the filling of the pores due to the nanoparticles deposition within the pore network of the stone. It reflects on the variation of the open integral porosity as well as on the porosimetric distribution. The porosimetric analyses of the stone specimens in the level from 0 up to 0.5 cm under the surface recorded the variation of the porosity from 31% to 28% after the treatment. Figure 10 evidences how the porosimetric changes due to the application of the nanosilica mainly involved the smallest pores measuring less than 1 micron. The decrease of this pore fraction account for the permeability reduction of the treated stone, that was evaluated of 26%. Indeed, the decrease of the permeability after the treatment was from 200 to 147 $g/m^2 \cdot 24h$.

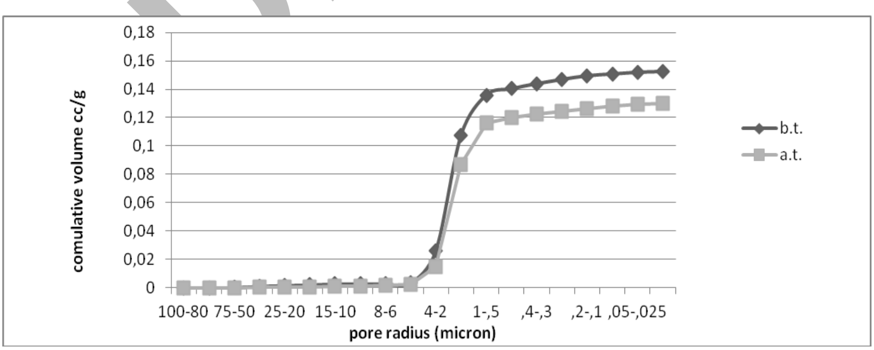


Figure 10. Cumulative volume curve at the depth's interval 0-0.5 cm (b.t.= before treatment; a.t.=after treatment)

Table 3. Evaluation parameters of the capillary absorption

	CA ($mg/cm^2\ s^{-1/2}$)	Q_{tf} (mg/cm^2)	IC_{rel}
b.t.	8.67	414	0.95

a.t.	7.99	414	

(b.t.= before treatment; a.t.=after treatment)

With respect to the stone behavior towards the liquid water, the application of the treatment doesn't change the water drop absorption on the stone surface, as it was expected; the contact angle measurements failed in the same way on the untreated and treated samples, due to the rapid water absorption.

The capillary test recorded a lower kinetics of the water uptake in the initial time (the first hour), while at the end of the test (8 days) the total absorbed water remained unchanged for the treated and untreated stone. The values of the capillarity absorption coefficient (A.C.), the total amount of the water absorbed (Q_{ft}) and the capillary relative index (C.I. rel) are summarized in Table 3.

4. Conclusions

The work carried out points out some interesting aspects entailed in the treatments of porous stones with nanosilica products. Firstly, the method of the application and the amount of the product to be applied are discriminating parameters with respect to the superficial distribution of the treatment. The application by capillarity, as well as by brushing up to the saturation of the stone lead to the deposition of nanosilica on the surface that alter the original appearance of the stone; moreover this application methods make the treatments not cost effective, due to the great product consuming related to the treatment of the porous stones. It was also evidenced that the application by brush by not consecutive steps quickly lead to stone refuse, strongly limiting the absorption of the solution by the stone. On the contrary, the different application methods do not seem influence the penetration capability of the nanosilica particles, in terms of depth and concentration within the stone, rather suggesting a role played by the concentration of the solution and/or the stone structure. The penetration depth is quite satisfactory –from 5 to 10 mm, most frequently up to 7-8 mm – depending on the heterogeneous stone structure. The consolidation effect of the nanosilica treatment lead to the increase of the mechanical resistance of the stone surface, as it was showed by the abrasion test. The cohesion power arise from the filling of the smallest pores; with relation to this mechanism of action it is suitable a previous assessment of the amount of nanosilica that is introduced within the materials, in order to avoid negative effects on the stone permeability. Finally, the study carried out evidences, once a time again, the importance of tuning the treatments on the basis of the specific stone characteristics in order to ensure the sustainability of the interventions. Sustainability is firstly in terms of compatibility with the constituent stone of the artifacts; for porous stones, that typically involve high product consuming, due to their high absorption capability, sustainability is also in terms of cost effectiveness.

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