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Synthesis and characterization of nanosilica products for the consolidation of stones.

N. M. E. Stucchi[1], E. Tesser[2*], F. Antonelli[2], A. Benedetti[1]

[1] *Department of Molecular Science and Nanosystem, Università Ca' Foscari di Venezia, via Torino 155/b, 30172 Mestre-Venice. Italy, benedett@unive.it*
[2] *LAMA – Laboratory for Analysing Materials of Ancient origin – Iuav University of Venice, San Polo 2468/B, 30125 Venice. Italy, lama@iuav.it – *etesser@iuav.it*

Abstract **– Nanosilica-based consolidants are promising nanostructured strengthening agents mainly used for consolidation of mortar and cements. Their use shows some positive aspects that encourage their application in stone consolidation field. Several preliminary studies underline that the nanosilica particles increase the reactivity and the penetration depth than other products having a great effect on silicate stone [1]. In this context, the aim of the present work is to formulate a specific nanosilica product suitable for the consolidation of Bianco Sardo, Pietra di Firenzuola and Pietra di Muggia. In this study, two phases have been underlined: (i) the synthesis of the nano-compound, (ii) the application of the product synthetized for the consolidation purpose.**

I. INTRODUCTION

Silicone based products in organic solvents have been widely applied as protective and strengthening agents during conservative treatments on monumental stones and architectural surfaces [2]. Comprehensive examinations revealed good chemical stability of silane and siloxane products, which guarantee a good penetration depth, polymerizing within the stone porous structure through sol-gel reaction mechanism and increasing the cohesion of the material [3]. However, in some cases, their use revealed undesired drawbacks on treated surfaces during weathering processes, such as chromatic alterations, formation of very brittle gel, powdering and biodegradation. [4]

For these reasons, during the last decades, a strong impulse has been arise for developing innovative conservative products based on nanosilica particles scattered in aqueous, polymeric or inorganic matrix, in order to ensure better performances in the treated inorganic substrates. The development of this nano-consolidant offers the possibility of having compatible new and promising strengthening agents for stone and plaster conservation.

Several chemical methods have been developed for the synthesis of silica nanoparticles: (i) sol-gel process, (ii) micro emulsion and (iii) flame synthesis [5, 6]. The commonest is the Stöber method devised since 1968 by Fink and Bohn [7]. The Stöber method showed some positive aspect that made scientist to opt for it over other methods: it required a less quantity of surfactants [8], it produces well mono-dispersed silica nanoparticles [9,10]. The sol-gel process of Stöber method permit to obtain pure material, studies on this kind of reaction involved two steps: the hydrolysis of TEOS monomers (nucleation), catalyzed by ammonia solution and with a low concentration of water, and the condensation process that lead to the formation of silica nanoparticles having dimensions between 5-2000 nm [11]. According to the literature [6], it is possible to develop nanosilica particles with a specific dimensional range studying the mole ratio of the reagents.

Due to their specific physical-chemical characteristics and nanometrical dimensions, theoretically, nanosilica improve the penetration depth of the treatment, promote hydro-repellence of the treated surfaces, avoid the biological colonization and, consequently, guarantee the conservation of the substrates over time. However, its use in the restoration field is still really controversial.

Nowadays, the nanosilica-based consolidants more diffused are Nano Estel®, an aqueous colloidal dispersion of silicon dioxide with dimension of 10-20 nm, and the water suspension Syton X30. Their use on Tokali in Göreme and the Church of the Forty Martyrs at Sahinefendi (Turkey) [12] of Nano Estel® and on a yellow Tuff for an experimental work [13] and of Syton X30 on the Precolombine archaeological site of Tajin (Mexico) [14] revealed the conservation of the porous structure of the stone materials and the increasing of the resistance of salts. From the other hand several studies demonstrated low penetration and low superficial cohesion in nanosilica treated substrates [15]. Moreover, Zornoza et al. [16] showed that nanosilica exposed to high RH environments forms agglomerated amorphous silica, which loose silanol groups on the surface and keep a high amount of adsorbed water.

Against this background, the present work aims to develop a promising nanosilica compound useful for the consolidation of silicate stones (e.g. granites and

sandstones). For this purpose, two types of silica nanoparticles with a different dimensional range 50-100 nm and 100-150 nm have been synthesized. A water-ethanol solution has been used as carrier for the nanoparticles.
Three different lithotypes Pietra di Firenzuola, Pietra di Muggia and Bianco Sardo, sound and after deterioration by salts crystallization, frost and thaw and thermal shock, have been treated using the nanosilica solutions by capillary absorption.
Porosimetric measurements, capillary absorptions, microscopic observations, colorimetrical analysis, ultrasounds measurements, sponge-tests have been used for the characterization of the lithotypes before and after the application of the consolidant products.

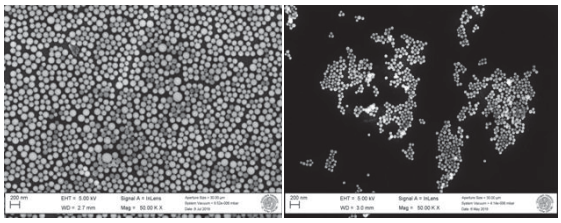

Fig. 1: S1 and S2 SEM-BSE images

Fig. 2: Application of nanosilica treatment by capillary absorption for granite sample

II. EXERIMENTAL

A. Stone substrates

Two sandstones, Pietra di Firenzuola (pietra serena di Firenzuola) and Pietra di Muggia, and a granite, Bianco Sardo, have been chosen for the purpose of the research, due to the chemical compatibility between stone compositions and SNP.
Pietra di Firenzuola is a mainly feldspathic sandstone with a matrix rich in clay minerals and poor in calcite. It outcrops in many areas of the Tuscan-Emilian and Umbrian Apennines, but it is essentially quarried at Firenzuola, near Florence. The stone is characterized by a grey-bluish colour (Figure 2a), which tends to yellow-grey by natural weathering. Pietra di Firenzuola suffers degradation by air-pollution and salts crystallization. For this reason, it has been widely used for internal covering both in Italy and abroad [17].
Pietra di Muggia is a sandstone characterized by clasts of quartz, feldspars and volcanic-rock fragments embedded into a fine clay matrix and poor carbonate cement [18] (see Figure 2b). It is a grey-bluish stone with red-orange areas due to the iron oxidation products. It comes from the Muggia Peninsula and it is widely adopted in external covering thanks to its well-known high hardness.
Bianco Sardo is a coarse-grained granite from Buddusò (Olbia-Tempio Pausania Province) in the Italian Sardinia island. It is mainly composed by quartz, K-feldspars, plagioclase and few biotite crystals, which gave to the material the typical white/grey matrix spotted by small black grains, as shown in Figure 2c. The large availability of this material and its suitability to all kind of finishing, allowed a wide use of this stone and a great diffusion, thanks also to its good physical-mechanical characteristics [17].
For each material, 6 specimens of 5 cm x 5 cm x 5 cm have been prepared.
The sound samples have been characterized by physical and morphological analysis through microscopic observations, capillary absorption measurements, mercury intrusion porosimetry (MPI), evaluation of ultrasound velocity, colorimetric and sponge tests.
The evaluation of the porosity and pore size distribution allowed to choose the best SNP dimensions to apply to each lithotype. Three samples were submitted to degradation processes: salts crystallization [19], (ii) frost and thaw [20] and thermal shock [15].

B. Synthesis of nanosilica

Nanoparticles with two different dimensional range (S1 100-150 nm and S2 50-100 nm) have been synthesized with Stöber method, using Ethanol as solvent (ETA 70 for the synthesis of S1 - absolute ethanol for the synthesis of S2). As reagents was used Milli-Q water, a 30% Ammonia solution (Sigma) and TEOS (tryethilorthosilicate) purchased by Aldrich.
The growth of the nanoparticles during the time of reaction (24 h) has been verified by SEM observation has been used in order to control the dimension of the synthesized particles.
To be applied as consolidant to the stone materials, nanoparticles have been disperse using Ethanol supply. The literature reports [13] deeper penetration depth of consolidants in stone substrates using alcohol as carrier. Right before the application the solution has been diluted in water (EtOH: H_2O 75:25 w/w).

C. Application method

The adopted application method, capillary absorption,

was choosen in light of the results obtained in restoration site and represent the most suitable method for the present case study. The time of application was 5 hours during which environmental parameters (temperature and relative humidity - %RH) were kept under control. Ten ml of substances were used for the initial absorption process. More solution was added when requests. Deteriorated and sound materials were treated using both S1 and S2 solutions. In particular, two sound samples of each stone were treated respectively with both the silica SNP solutions (S1 and S2). On the other hand, degraded samples were treated only by S1 solution.

D. Analytical methods

A SEM-FEG ZEISS SUPRA VP was used to investigate the nanoparticles synthesized, obtaining images useful for the control of the dispersion of the particles, these photographs have been analyzed by Image-J software in order to check the dimensional range.
All the specimens were first examined under a Leica F12I stereomicroscope with increasing magnification (from 0.75 x, to 6x) in order to describe the macro/meso-physical and morphological characteristics of the surfaces.
The total open porosity, the average pore radius of the porous medium and the possible relationships between mineralogy and porous network were investigated with porosimetric analyses by means of mercury intrusion (MIP) (Thermo Scientific Pascal 140-240 series) following the Italian NorMaL 4/80 recommendation [21].
Hydric parameters of the lithotypes were determined by capillary absorption method (UNIEN1925,2000).
The monitoring of the weight of the samples before and after the application of the formulated product permits to evaluate the quantitative of SNP absorbed, the actual evaporation of Ethanol and the condensation reaction.
The physical and morphological analyses used for the characterization of the lithotypes were repeated after the product applications in order to control the effectiveness of the consolidation treatment.
Moreover, before and after the treatments, the ultrasound propagation velocity of compressional (Vp) pulses was measured by a portable Matest instrument in the three perpendicular directions on cubic samples. Once the compressional wave velocities had been determined, the total (ΔM) and relative (Δm) anisotropies were calculated (UNI EN 771).
In the same way, Sponge test was used on untreated and treated surfaces according to the UNI 11432 recommendation [22]. The contact time was 3 minutes due to the low porosity of the stones and the test was repeated 3 times for each sample.
Colour changes induced by the application of nanosilica solutions were evaluated by colorimetric measurements on treated specimens using a Konica Minolta CM-2600d colorimeter. The analyses were carried out according to the ENI 15886:2010 standard [23]. A mask with 5 holes was built, using a polyethylene slide, to enable accurate repositioning of the instrument always in the same area of the sample. The results were reported in the CIELab1976 system. Each set of data shown hereinafter is the mean value of the 5 areas for each sample.
The cross-sections of the samples were studied using a Leitz LABORLUX 12 POL S optical microscope at 40x and 100x magnifications and photographed with a Leica CLS150E camera. A note was made of the permanence of the consolidant and its distribution in the microstructure of the samples. They were then embedded in a cold setting epoxy resin. The cross-sections were studied under a Philips XL 30 SERIES SEM and the distribution (plus the maximum penetration depth) of the conservative treatment were studied and measured. Semi-quantitative assessments of element composition were made by EDS using a EDAX X-ray dispersive spectrometer equipped with a thin beryllium window. The accelerating voltage was 25 KeV.

III. RESULTS

A. Characterization of stone materials

In order to select the nanosilica dimensions which best fit the porous structure of the stones, porosimetric analysis and capillary absorption measurement have been performed on sound untreated materials. Bianco Sardo is the least porous stone and revealed accessible porosity between 0,45% and 0,56%, with pores distribution in the range 15 nm - 300 nm and a peak of the graph at 15 nm. Pietra di Firenzuola is the most porous considered lithotype having accessible porosity equal to 6,02%. The highest frequency of pores distribution is in the range 15 nm - 200 nm, with two peaks in the graph at 20 nm and 150 nm. Finally, Pietra di Muggia showed heterogeneity in its pores structure. Indeed, macroscopically zones with different colours (orange and grey) are observable, that can be assumed by different chemical and mineralogical structure. The percentage of the accessible porosity varies between 1,98% and 3,58% and the dimensional range is almost between 8 nm and 70 nm, revealing the smallest medium size of the porous, with a peak at 10/12 nm in some samples and at 30 nm in some others. The results obtained from the porosimetric analysis are strictly linked to those obtained from capillary absorption measurements. These confirmed for the Pietra di Firenzuola the highest values of accessible porosity (MI value 1411.91 g/m^2) and the lowest for Bianco Sardo (MI mean value 171.77 g/m^2). High heterogeneity has been observed in the results of Pietra di Muggia (MI values between 314.85 – 628.51 g/m^2). The slopes of the

absorption curves show a great capacity of Bianco Sardo to absorb a large amount of water in the first 15 minutes decreasing then the absorption velocity, whereas Pietra di Firenzuola and Pietra di Muggia show a gradient flatter and more time required for reaching saturation.
The ageing processes underlined a low resistance to salts crystallization of Pietra di Firenzuola, whereas Bianco Sardo and Pietra di Muggia suffered thermal shock, as demonstrated by morphological observations and ultrasound velocity measurements.

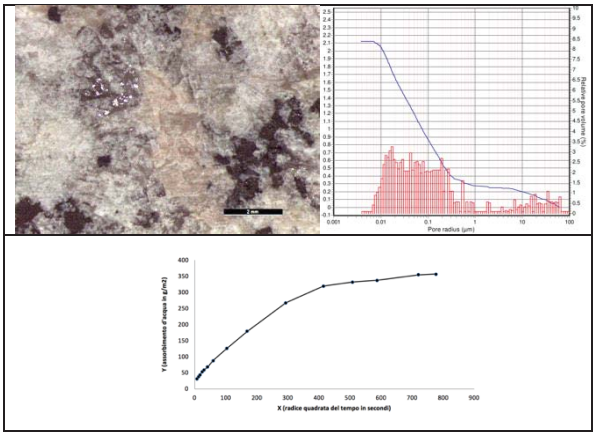

Fig. 1: micrograph of Granite; Graph of pores dispersion; Graph of water absorption.

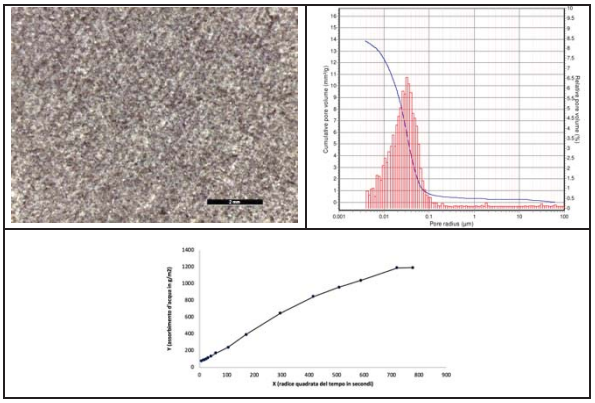

Fig. 2: micrograph of Pietra di Muggia; Graph of pores dispersion; Graph of water absorption.

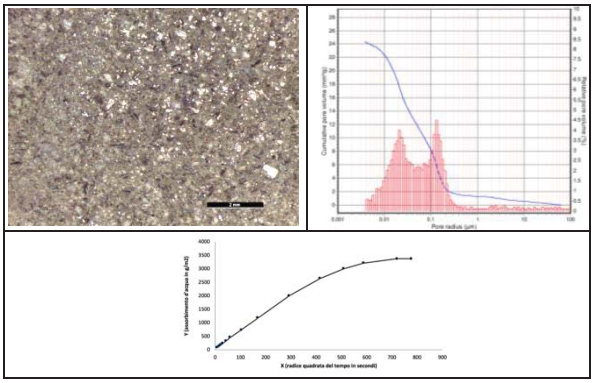

Fig. 3: micrograph of Pietra di Firenzuola; Graph of pores dispersion; Graph of water absorption.

B. Synthesis of nanosilica.

Thanks to the results obtained from the characterization of stone materials, nanosilica with two dimensional ranges have been synthetized: S1 100-150 nm and S2 50-100 nm.
Some difficulties came up on the synthesis phases. From the literature [9], the kinetic balance has not been yet fully unraveled and some external agents can affect the size, the size distribution, interior structure and chemical characteristics of Silica Particles, especially in the size range below 200 nm.
In this work, some dimensional issues of the nanoparticles have been observed during the synthesis process. Since the phases of the synthesis reaction have been unchanged, it can be supposed that environmental humidity and temperature affect the synthesis reaction.
Despite the small dimension of silica nanoparticles, which should allow the penetration of the consolidant in the stone accessible porosity, it has been observed that humidity cause aggregation and agglomeration of silica nanoparticles, preventing the penetration of the product. In fact, silica tends to hold high amount of water, forming silanol groups that tend immediately to condensation reactions. In this way, nanosilica particles increase their size and tend to polymerize forming amorphous structure that tend to begin crystalline, as it can be observed to the optical microscope. For this reason, nanosilica particles should be stocked in a dried environment and it is recommended to use ethanol as carrier adding water right before the application of the product preventing silica agglomeration.

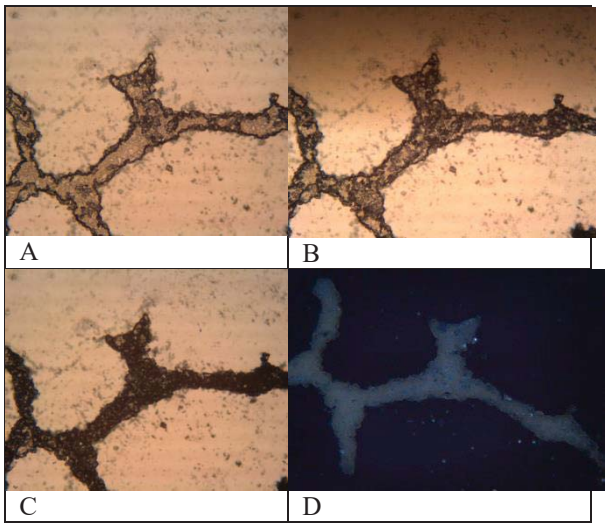

Fig. 4: Nanosilica particles micro images at A. t.0. B. t. 1 (30 s.) C. t.2 (60 s.) D. with cross polar, which shows Crystalline luminescent structure. Long size images 2.5 mm.

C. Nanosilica consolidation.

Periodic monitoring of weight and morphology of treated samples permit to understand the consolidation effect.
The weights increase progressively for all the samples after the application, the weight of Pietra di Firenzuola increases more than the other lithotypes, whereas Granito shows only a little variation of weight parameter. It can be assumed that the variation of weight of each stones is comparable with the different quantity of product adsorbed. Moreover, the continuous increasing of weight can be related to the absorption of environmental humidity and the consequent reaction of condensation of silica in the pores structure. From the microscope observation at different enlargements (0,75/1/2/4 x) it has been possible to verify the unchanged aspect of the surface after the application of the consolidant, then confirmed by colorimetric analysis.

IV. CONCLUSIONS

In this study, a nanosilica compound with two different dimensional range of particles have been synthesized and evaluated in terms of consolidation effectiveness on two sandstones and a granite. The characterization of stone materials and, in particular, of porous structure allowed the author to select the best fitting dimensional range for the consolidation purpose. Some issues on environmental humidity and temperature have been discussed during the synthesis and the application processes. The effectiveness of the consolidant applied on sound and deteriorated materials have been verified and the results obtained showed promising aspects.

REFERENCES

[1] F. Iucolano, A. Colella, B. Liguori, D. Calacaterra "Suitability of silica nanoparticles for tuff consolidation". Construction and Builiding Materials 202, 2019, pp. 73-81

[2] E. Tesser, F. Antonelli "Evaluation of silicone based products used in the past as today for the consolidation of Venetian monumental stone surfaces". Mediterranean Archaeology and Archaeometry 18 (5), 2018, pp. 159-170.

[3] L. Lazzarini, M. Laurenzi Tabasso "Il restauro della pietra", CEDAM, Padova, 1994, pp.

[4] E. Tesser, L. Lazzarini, R. Ganzerla, A. Antonelli A. "The decay of the polysiloxane resin Sogesil XR893 applied in the past century for consolidating monumental marble surfaces". Journal of Cultural Heritage 27, 2017, pp. 107-115

[5] I.A. Rahman, V. Padavettan, "Synthesis of silica nanoparticles by sol-gel: size-de- pendent properties, surface modification, and applications in silica-polymer nano- composites—a review", J. Nanomater, 2012, pp. 1–15.

[6] X.D. Wang, Z.X. Shen, T. Sang, X.B. Cheng, M.F. Li, L.Y. Chen, Z.S. Wang, "Preparation of spherical silica particles by Stober process with high concentration of tetra-ethyl-orthosilicate", J. Colloid Interface Sci. 34, 2010, pp. 23–29.

[7] Yandong Han, Ziyang Lu, Zhaogang Teng, Jinglun Liang, Zilong Guo, Dayang Wang, Ming-Yong Han, and Wensheng Yang "Unravelling the Growth Mechanism of Silica Particles in Stober Method: In-situ Seeded Growth Model", Langmuir, 2017, pp. 1-60

[8] X. Jiang, X. Tang, L. Tang, B. Zhang, H. Mao. "Synthesis and formation mechanism of amorphous silica particles via sol-gel process with tetraethylorthosilicate", Ceramics International 45, 2019, pp. 7673-7680

[9] R.F.S. Lenza, E.H.M. Nunes, D.C.L. Vasconcelos, W.L. Vasconcelos, "Preparation of sol–gel silica samples modified with drying control chemical additives", J. Non- Cryst. Solids 423–424, 2015, pp. 35–40.

[10] A. Najafi, S. Ghasemi, "A study of APC surfactant role on the surface characteristics, size and morphology improvements of synthesized mesoporous silica nanopowder through a sol-gel process", J. Alloy. Compd. 720, 2017, pp. 423–431.

[11] D.L. Green, J.S. Lin, Yui-Fam Lam, M.Z.C. Hu, Dale W. Schaefer, M.T. Harris, "Size, volume fraction, and nucleation of Stober silica

nanoparticles." Journal of Colloid and Interface Science 266, 2003, pp. 346-358.

[12] M.F. La Russa, S.A. Ruffolo, N. Rovella, C.M. Belfiore, P. Pogliani, C. Pelosi, M.Andaloro, G.M. Crisci "Cappadocian ignimbrite cave churches: stone degradation and conservation strategies" Period. Mineral. 8, 2014, pp. 187-206

[13] M.F. La Russa, S.A. Ruffolo, M.A. Buergo, M. Ricca, C.M. Belfiore, A. Pezzino, G.M. Crisci, "The behaviour of consolidated Neapolitan yellow Tuff against salt weathering" Bull. Eng. Geol. Environ., 2017, pp. 115-124

[14] D. M. Grimaldi, A. P. Nora, J.H. Porter "The preservation of sandstonereliefs at the archeological site of Tajin, Mexico, using colloidal silica" in: C University (Ed.), in: 12th International Congress on the Deterioration and Conservation of Stone, 2012, pp. 12-22

[15] J.S. Pozo-Antonio, J.Otero, P.Alonso,X.Mas i Barberà. "Nanolime- and nanosilica-based consolidants applied on heated granite and limestone: Effectiveness and durability", Construction and Building Materials, 2019, pp. 852-870

[16] A. Zornoza-Indart, P. Lopez-Arce, "Silica nanoparticles (SiO2): Influence of relative humidity in stone consolidation", Journal of Coultural Heritage 18, 2016, pp. 258-270

[17] G.Blanco "Manuale di progettazione marmi e pietre". Gruppo Mancosu Editore. 2008.

[18] S. Furlani, F. Cucchi, "Short-term surface changes on sanstone rocks", Annales, Ser. hist. nat. 17, 2007, pp. 241-248

[19] UNI EN 12370 "Determinazione della resistenza alla cristallizzazione dei sali", 1999, pp. 1-8

[20] UNI EN 12371 "Determinazione della resistenza al gelo", 2003, pp. 1-8

[21] NorMaL 4/80, Distribuzione del volume dei pori in funzione del loro diametro (CNR-ICR, Roma, 1980)

[22] UNI 11432. Beni Culturali. Materiali lapidei naturali ed artificiali. Misura della capacità di assorbimento di acqua mediante spugna di contatto. Novembre 2011.

[23] EN 15886:2010 Conservation of cultural property. Test methods - Colour measurement of surfaces