EVALUATION OF COMMERCIAL CONSOLIDATING AGENTS ON VERY POROUS BIOCALCARENITE

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Abstract

Nowadays, the conservation of heritage buildings is an essential and important event. Different kinds of materials are available for restoring both natural and artificial stone substrates, and new commercial products have been proposed in recent years. In the present research work we investigated the effectiveness of an alkylalkoxysilane-based commercial consolidant (named VP5035) with respect to the well known tetraethoxysilane (TEOS, commercially labeled as DN). The two products were evaluated when applied on laboratory specimens of a very porous bio-calcarenite, i.e. Lecce stone (PL). Different experimental techniques were used to investigate the performances of both commercial products. At first, chromatic variation, static contact angle, water capillary absorption, permeability to water vapor were measured in order to evaluate the effects induced by treatments on the stone surface. The properties of treated stone were also investigated by Fourier-Transform InfraRed (FTIR-ATR) and scanning electron microscopy combined with energy-dispersive X-ray spectroscopy (SEM-EDS). Measurements concerning surface cohesion and resistance to weathering effect induced by salt crystallization were performed in order to evaluate the consolidation performances of the two consolidants. These results suggest that the commercial product VP5035, when applied on Lecce stone displays a promising dual consolidating-protective behaviour.

Keywords: Stone consolidation; Conservation process; TEOS; biocalcarenite; SEM-EDS; Salt crystallization

Introduction

Several conservation products have been introduced in the last decades to consolidate cultural heritage items and to protect them from different deterioration factors (physical, chemical, biological and air pollution). They are based on inorganic or organic compounds, including many synthetic polymers [1-4]. However, all those products still have some limitations.

For instance, poor durability, drastic changes of the stone matrix, and poor physico-chemical compatibility with the substrate are commonly associated with treatments performed by organic materials. Although inorganic-based consolidants have some advantages such as good durability and a physical-chemical high compatibility with the stone materials [1, 5], they

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often exhibit low penetration depth and, as a consequence, they provide the poor strengthening effect to the stone substrate. The application of polymeric materials (e.g. polyacrylates, polyesters, polyurethanes) as consolidating agents aim to reinforce the substrate by introducing a macromolecular lattice into the stone matrix, which can bind the grains together and induce at least a partial recovery of the mechanical properties of the stone. Unfortunately, the polymeric compounds also very often undergo yellowing due to UV radiation, and/or biodegradation due to microbial and fungal growth [2-3, 6].

Currently, alkoxysilanes (e.g. tetraethoxysilane, TEOS) represent a class of widely used stone consolidants [7-9], whose effectiveness derives from hydrolysis-condensation reactions, that lead to the formation of amorphous silica inside stone pores [9]. Moreover, these types of consolidants are particularly suitable for sand stones. Nevertheless, they are used and tested with controversial results even on substrates consisting mainly of carbonates [1].

TEOS efficacy is also related to the solvent (it is generally dissolved in white spirit or alcohols) which is used for its application. In fact, solvent not only favour a deeper penetration into the stone substrate pores, but also affects the alkoxysilane condensation reaction and hence, the resulting mechanical and physical properties of treated stones. TEOS undergoes hydrolysis by reacting with water (formation of Si-OH groups) and subsequent condensation (formation of Si-O-Si bonds) providing a silica gel. In silicate stones, condensation reaction can directly involve silanol groups on the surface of different stone grains, which are therefore covalently bound to the neo-formed silica (silica gel with silicate substrate can form strong Si-O-Si bonds). TEOS-based consolidation treatments are commonly characterized by very good stability toward thermal weathering, solar light irradiation and oxidation processes, and hence ensuring a high durability [10]. Nevertheless, the effectiveness of TEOS suffers some limits due to different reasons such as a fast condensation process which can induce crackings inside the stone matrix, loss of elasticity of neo-formed silica phase, which induces shrinking processes inside the stone pores, and consequent weakening of the overall consolidation effect [11]. Therefore, different formulations have been proposed in order to overcome these drawbacks. As an example, TEOS can be applied in combination with alkyl-alkoxysilanes or polyalkylsiloxane [11]. After drying, the neo-formed silica gel generated by these mixtures is expected to be more elastic due to the presence of organic chains or linear siloxane segments, which are connected to silicate network of the gel lattice. Moreover, the presence of organic moieties provides water repellent behaviour and a consequent protecting effect to the treated stones [12].

In this study, the preservation effectiveness of the commercial product named as VP5035 based on the compounds resulting from a combination of alkoxysilanes and alkyl-alkoxysilanes was evaluated and compared to that of plain tetraethoxysilane (commercial product named as DN) on very porous bio-calcarenite stone, i.e. Lecce stone (PL). It is a fossiliferous bio-calcarenite with a very high open porosity (generally more than 30% [6, 13-14]). The main component of PL is calcite (93–97%) with amounts of quartz, feldspars, and muscovite [6]. Lecce stone has been widely used to erect buildings, churches and monuments in southern Italy, particularly during the Baroque period, and it is still used in contemporary buildings as well as in the restoration of old ones [6]. Due to its very high porosity, PL is normally subject to several weathering mechanisms by physical and chemical agents [15-17]. Therefore, finding a proper consolidating product for this type of stone materials is highly desired by conservation scientists and restorers.

Hence, in order to investigate the performances of the commercial product VP5035 with respect to TEOS (DN) as a consolidating agent, they were applied on PL specimens by a standard brushing procedure [18]. After that, morphological and micro-structural features of treated PL as well as distribution of applied products in the stone matrix were investigated by SEM-EDS experiments. Effectiveness of consolidating agents was evaluated by measuring some physico-chemical properties such as chromatic variation, static contact angle, water capillary absorption, permeability to water vapor, surface cohesion, and resistance to

weathering effect induced by salt crystallization. FTIR (ATR mode) spectra were also collected to better characterize the stone surface after treatments. Furthermore, the same consolidants (VP5035 and DN) have been also applied to specimens of three different stone substrates (Serena Stone, Carrara Marble, and Brick) in order to preliminary evaluate their performance on these materials.

Experimental

Materials

Isopropanol solutions of TEOS (70%, 0.97 g/cm^3, commercial name: DN) and of VP5035 (75% of active materials, 0.95 g/cm^3) were provided by Chem Spec Srl (Peschiera Borromeo, Milan, Italy) and used without any purification.

Lecce stone (PL) specimens were provided by Tarantino and Lotriglia (Nardò, Lecce, Italy). Before treatment, squared $5 \times 5 \times 1$ and $5 \times 5 \times 2$ cm specimens were smoothed with abrasive, carbide paper (No: 180 mesh), washed with deionized water, dried in an oven at 60 °C and stored in a desiccator to reach room temperature according to the standard method (UNI 10921 Protocol) [19].

Methods

Application of products. DN and VP5035 were used as received according to the provider recommendations and applied by brushing until the stone surface get saturation (about 1 minute). Treated specimens were labeled as PLDN and PLVP, respectively, while untreated PL specimens was labeled as PL$_{nt}$. After that, they were kept in the laboratory condition (T= 20 °C) for 3 weeks before starting measurements, in order to allow all the possible reactions to take place. Therefore, all analyses were performed after fully drying of the products on the stone surfaces, as confirmed by periodically measuring the weight of the specimens after treatment.

Testing Methods and instrumental techniques. Chromatic variations of treated samples with respect to the untreated samples were measured by Konica Minolta CM-2600d spectrophotometer, determining the L*, a* and b* coordinates of the CIELAB space, and the global chromatic variations ΔE*, according to the UNI EN 15886 protocol [20]. Water contact angle measurements on the treated stone specimens were carried out by a CAM 200 apparatus (KSV Instruments). The amount of absorbed water as a function of time was determined on the $5 \times 5 \times 2$ cm specimens in accordance to the UNI EN 15801 protocol [21] and water vapor permeability was determined according to UNI EN 15803:2010 protocol on the $5 \times 5 \times 1$ cm specimens [22]. The 'Scotch Tape test' (STT) was performed as reported in the literature [6], while the chemical weathering test was performed by evaluating the effect of salt crystallization according to the Spanish standard UNE-EN (12370) [1, 23]. Infrared spectra were collected by a PerkinElmer Spectrum 100 FT-IR spectrometer in the ATR mode. Scanning electron microscopy (SEM) images (backscattered electron, BSE) and energy-dispersive X-ray spectra (EDS) were collected by a Tescan FE-SEM, MIRA XMU series, equipped with a Schottky field emission source, operating in both low and high vacuum and which is located at the laboratory of Arvedi, CISRiC, University of Pavia, Italy. Before SEM-EDS experiments, samples were gold sputtered (about 10 nm) using a Cressington sputter coater 208HR.

Results and Discussion

Preliminary analyses of treated stone specimens

After 3 weeks from the application, the weight increase experienced by PL specimens after treatment with VP is slightly higher than DN-treated specimens (1.28±0.28 and 0.96 ±0.15 Kg m^2, respectively, see Table 1). It may be due to the higher absorption of VP than the DN in PL and to the presence of alkyl-alkoxysilanes component in VP.

Both color and contact angle were measured on untreated and treated specimens in order

to assess the differences of chromatic and hydric properties of the stone substrate after treatments. Overall chromatic variations (ΔE^*) observed in comparison with the plain Lecce stone are reported in Table 2.

Table 1. Weight differences of Lecce stone after treatments

Consolidants	Weight differences (Kg/m^2)	
	5×5×2 cm	5×5×1 cm
PLDN	0.96 (±0.15)	0.69 (±0.12)
PLVP	1.28 (±0.28)	1.04 (±0.08)

Table 2. Chromatic variations and contact angle values measured on the stone specimens

Consolidants	ΔE^*	α (°)
PLDN	3.85 (±0.27)	115 (±4)
PLVP	8.28 (±0.83)	137 (±1)

ΔE^* values clearly indicate that the application of VP affects the original color of the Lecce stone ($\Delta E^* = 8.28 \pm 0.83$) much more than DN ($\Delta E^* = 3.85 \pm 0.27$). Taking into account changes observed for the chromatic coordinates (L^*, a^*, b^*), both treatments mainly affects L^* parameter that is related to the brightness. In particular L^* value undergoes a distinctly larger decrease after VP than DN treatment ($\Delta L^* = -7.20 \pm 0.73$ and -3.14 ± 0.25, respectively).

It should be noted that an overall chromatic variation (ΔE^*) larger than the standard value 5 is commonly related to changes that can be detected by the naked eye [24].

Table 3. Results of water capillary absorption and water vapor permeability tests

Treatments	Q_f/ mg cm^{-2}	CA/ mg cm^{-2} $s^{-1/2}$	Perm/ g m^{-2} 24h
PLnt	525 (±12)	9.4 (±0.5)	185 (±29)
PLDN	68 (±5)	0.5 (±0.2)	144 (±7)
PLVP	27 (±1)	0.1 (±0)	82 (±15)

Static contact angles (Table 2) measured on the surface of treated specimens are distinctly higher than 90°, indicating that both treatments induce a hydrophobic character. In particular, an angle larger than 130° has been observed for samples treated with VP, suggesting that alkyl moieties coming from the alkyl-alkoxysilane component of the consolidant provide a considerable water-repellent behaviour.

Values of water amounts absorbed in 96 hours (Q_f) and coefficient of average absorption in 30 minutes (CA), determined for untreated and treated PL by water capillary absorption test are listed in Table 3. The kinetic of capillary suction is strongly affected by both treatments. In particular, application of VP extremely decreases the capillary absorption both during the first 30 minutes of the experiment, as suggested by the very low CA value (0.1 mg cm^{-2} $s^{-1/2}$), and at longer times, as shown by Q_f value that is about 20-fold lower than the corresponding value determined for untreated PL.

Water vapor permeability values determined after the application of the considered consolidants are also reported in Table 3. PL specimens treated with DN undergo a reduction of their permeability of about 22 %, while the application of VP induces a more considerable permeability reduction (about 56%).

Capillary and permeability results indicated that both the tested products strongly affect the hydric properties of the considered biocalcarenite. It can be related to a significant modification of the stone porous structure and, in the case of VP, to the hydrophobic features of

the applied material.

FTIR analyses

FT-IR analyses were carried out to monitor the process of gel formation of the consolidating products. The products were applied on an inert substrate (i.e. grass slides) and they were kept in the laboratory at ambient temperature (20 °C). Spectra were collected at different time intervals (in total 21 days) in order to monitor the gel formation process (Figure 1). Both products showed quite similar behaviours.

As regards to the polymerization of the DN, we observed some changes around 3400 cm^{-1}: the broad band that appears at 3400 cm^{-1} after 3 days from the application can be ascribed to the stretching of the silanol O-H bonds formed from the hydrolysis of Si-OEt groups. Its intensity progressively decreases as the condensation of Si-OH bonds to give Si-O-Si species. The sharp bands observed at the beginning in the 3000-2800 cm^{-1} range and related to symmetric and asymmetric stretching of the C-H bond in O-Et groups decrease with time and almost disappear after 21 days owing to hydrolysis and consequent loss of EtOH. Similarly the bands due to bending of the C-H bonds (about 1500-1200 cm^{-1}) become less intense with time up to almost complete disappearing (Figure 1a). The broad and intense band in the 1000-1200 cm^{-1} region, which is ascribed to the stretching of the Si-O bond, undergoes less drastic variations, as all the species involved in the gel formation process absorb in this wave number range.

The product of VP also shows an intesity variation of the band centered at about 3400 cm^{-1}, which is related to the stretching of the silanol OH bond formed by the hydrolysis of the alkoxy silane groups. As the hydrolisis-condensation process proceeds, the intensity of the absorptions related to stretching and bending of C-H bonds 3000-2800 and 1200-1500 cm^{-1}, respectively) decreases due to the loss of O-Et groups (Figure 1b). Differently from TEOS, these signals do not completely disappear because of the alkyl chains that are directly bound to silicon, which are not involved in the hydrolisis reaction. With regard to the characteristic bands of the Si-O stretching vibrations, the intense band at about 1100 cm^{-1} is shifted towards lower wavenumbers (1040 cm^{-1}) when the formation of Si-O-Si framework propagate into stone matrix.

According to the FTIR analyses, it is possible to assume that the polymerization process (gel formation) of both DN and VP was almost completed with 21 days in the laboratory conditions. This result is important to predict the behaviour of those two products inside the stone specimens.
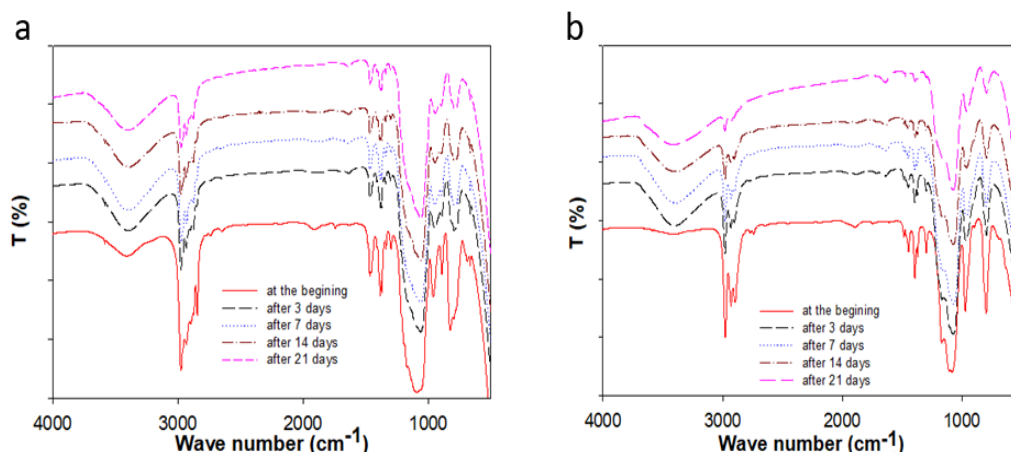

Fig. 1. FTIR (ATR mode) spectums of consolidating products after keeping in the laboratory conditions in different time intervals: (a) DN, and (b) VP

SEM-EDS analyses

SEM-EDS experiments were performed to investigate the modifications of morphology and micro-structure induced by treatments on the stone material. SEM-EDS micrographs taken on the cross-section of untreated and treated stone specimens are reported in Figure 2. It can be cleary seen the morphology of Lecce stone: the porous structure and also the presence of bio-fossils (Figure 2a). Images showed that stone matrix is not drastically changed after treatment: typical particular of PL are still visible. EDS analyses were also performed on the same samples in order to investigate chemical composition of stone matrix. EDS spectrums of stone treated with both DN and VP show a distinctly more intense peak corresponding to Si, if compared with untreated PL (see Figure 2b, d, and f). It should confirm that the silicon-containing consolidant materials have been deeply adsorbed by the stone substrate. Nevertheless, it shold be noted that Lecce stone is a quite heterogeneous material, mainly made by carbonate, but containing non-negligible amount of silicate components, which could affect the results of EDS analyses. Moreover, SEM observations of PLDN and PLVP samples show that neo-formed materials containing large amount of silicon are present in correspondance of large pores, confirming the penetration of consolidating agents inside the stone matrix (see Figure 2c and e).
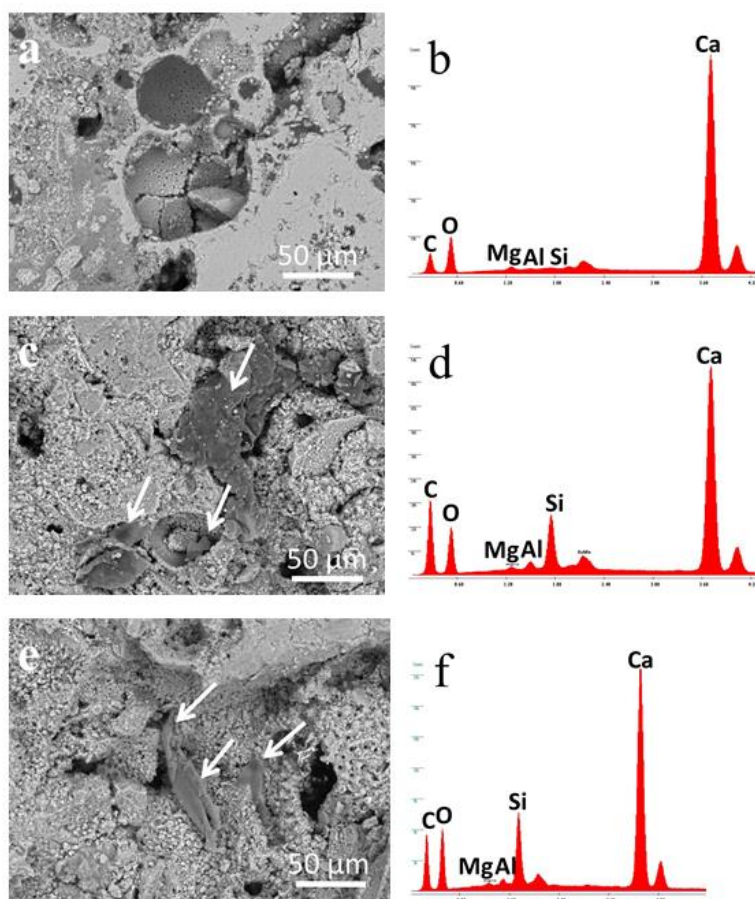

Fig. 2. SEM-EDS images of untreated and treated stone:
(a) and (b) PLnt, (c) and (d) PLDN, and (e) and (f) PLVP

Scotch tape test

The adhesive tape test (Scotch Tape Test) is one of the main experiments that have been used for over 40 years to assess consolidation efficiency of conservation treatments for degraded stone [25]. It allow to investigate the surface strength of the stone specimens after a consolidation treatment. The test was performed on PLDN, PLVP, and untreated PL specimens. The corresponding results are summarized in Table 4. The overall amount of solid removed (per area unit) after 10 peeling cycles on untreated stone is much larger (about ten-fold) if compared to the stone treated with DN or VP. The resistance to peeling effect is slightly higher in the case of PLVP (0.12 ±0.03 mg cm^{-2} of overall removed material) than PLDN (0.16±0.02 mg cm^{-2}).

The experiment also showed that amount of material peeled off from PL$_{nt}$ surface is still considerable after the first 6-7 peeling cycles, proving the surface fragility of the substrate and the poor cohesion of the more external grains, which are highly exposed to degradation factors (Figure 3). On the other hand, surfaces of the treated specimens underwent a very small material loss even after the first adhesive tape application and the amount of removed material remains very low after every peeling cycle (Figure 3). These results suggest that both consolidating products provide a considerable strengthening effect to the surfaces of Lecce stone.

Table 4. Results of scotch tape and salt crystallization tests

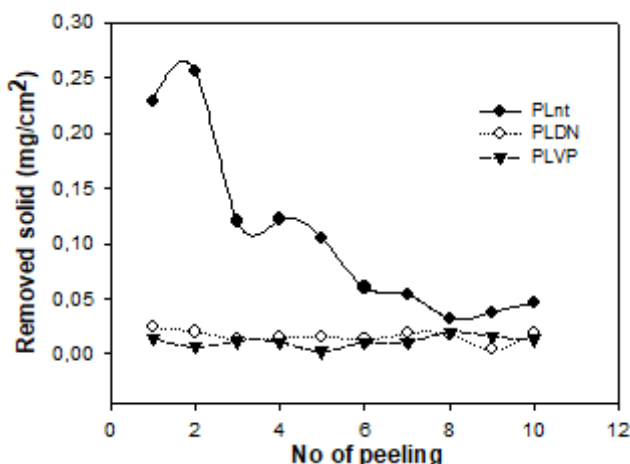| Treatments	Removed materials (mg/ cm^2)	DWL (%)
PLnt	1.06 (±0.15)	77.95 (±1.83)
PLDN	0.16 (±0.02)	58.74 (±5.32)
PLVP	0.12 (±0.03)	9.08 (±1.01)

Fig. 3. The amount of removed materials from the stone surface during the scotch tape test

Evaluation of the strengthening effect

The main goal of consolidation is to reinforce the stone. Effectiveness of the consolidation treatment in terms of internal cohesion enhancement was evaluated by determining the resistance of treated stone specimens to the salt crystallization. Salt crystallization is considered one of the most powerful weathering processes for stone materials. In fact, during crystallization, stone pores suffer a pressure increase, which may induce

disaggregation and consequent weight loss [1, 6, 23]. Therefore, the salt crystallization test may provide important information about the damage experienced by stone during the weathering as well as about the strengthening effect of consolidants. During the test, treated and untreated specimens were immersed in aqueous sodium sulfate (14 % (w/w)) until saturation, then they were dried to induce salt crystallization. This procedure was repeated for 15 times and specimens weight was registered after each cycle. Performance of applied consolidating agents was evaluated by calculating the final dry weight loss (DWL%, Table 4). Results collected during the test are graphically summarized in Figure 4, while Figure 5 reports the pictures of the different stone specimens during the test (after different cycles). Untreated PL underwent a progressive material loss after the fourth crystallization cycle and a weight loss of about 78% was observed at the end of the test. The very strong damage experienced by PL_{nt} specimens along the test is clearly visible in the pictures reported in Figure 5.
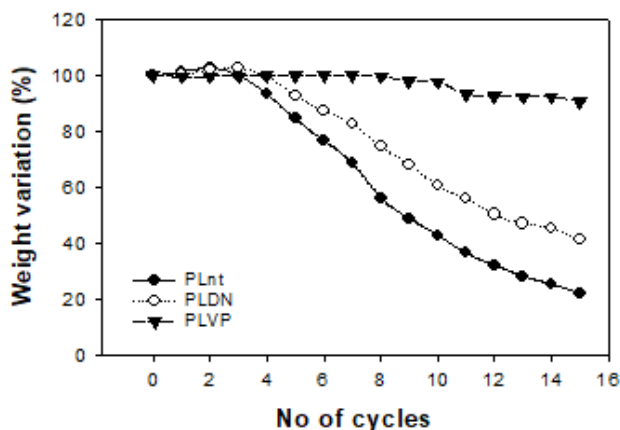

Fig. 4. Percentage values of weight change during the salt crystallization test
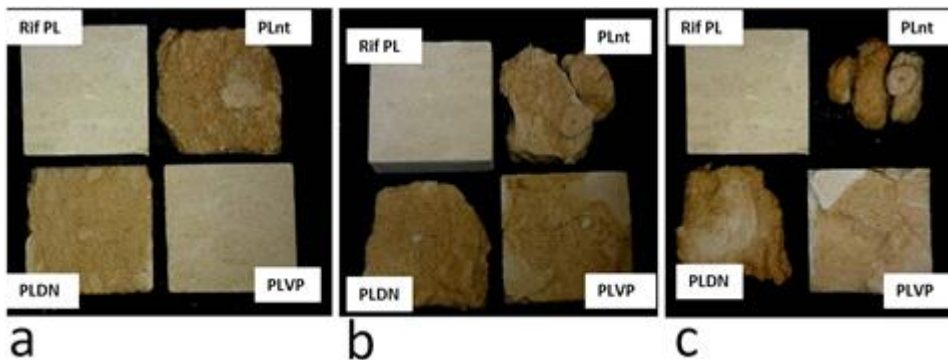

Fig. 5. Image of stone specimens during the salt crystallization test:
(a)after 6 cycles, (b) after 10 cycles, and (c) after 15 cycles

Specimens treated with VP showed a high resistance to salt crystallization. In fact, their weigh was almost unaltered after the first 10 cycles and the overal amount of material lost at the end of the test corresponds to about 9%. On the contrary, TEOS (DN commercial product) did not display satisfactory consolidating behaviour, differently from what observed in previous study [1]. PLDN specimens started to decrease their weigh after the fifth cycle and the final DLW% (about 59%), although distinctly lower than untreated PL, is much higher than PLVP. These results suggest that alkyl-alcoxysilane components that are contained in the VP5035

commercial formulation play an important role in providing an increased resistance towards damage induced by salt-crystallization when compared not only with the plain porous stone substrate but also with the TEOS-based consolidating treatment.

Conclusions

In the present study, the consolidation efficiency of the commercial product (VP5035) with respect to the well-known TEOS (commercial DN) when applied to a very porous biocalcarenite (Lecce stone, PL) was assessed by using different experimental techniques.

The investigations carried out on PL specimens showed that VP5035 can be considered an effective consolidating product, which display also interesting water-repellent properties. In particular, these results indicate for VP5035 better performance than well known TEOS (DN) especially, when the resistance to salt crystallization is concerned. Nevertheless, the treatment investigated in this work disclosed also some drawbacks: (i) a considerable variation of stone color after application; (ii) an excessive reduction of permeability to water vapour.

We considered that the undesirable alteration of chromatic and hydric properties could be related to the high level of the applied material, since VP5035 was used as received without any dilution. Preliminary experiments on PL specimens treated with VP5035 after reducing its concentration by 50% (with 2-propanol) showed that chromatic variation is almost acceptable ($\Delta E^* = 4.69 \pm 0.85$). More experiments will be performed in order to assess the optimal concentration range that can provide the best performance in terms of consolidating effectiveness and compatibility with the stone substrate.

Moreover, a study on the effectiveness of VP5035 (and DN) after application on different stone substrates (Serena stone, Brick and Marble) is in progress in the laboratory.

Acknowledgements

References

[1] M. Licchelli, M. Malagodi, M.L. Weththimuni, C. Zanchi, *Nanoparticles for conservation of bio-calcarenite stone*, **Applied Physics A, 114**, 2014, pp. 673–683.

[2] M. Favaro, R. Mendichi, F. Ossola, U. Russo, S. Simon, P. Tomasin, P.A. Vigato, *Evaluation of polymers for conservation treatments of outdoor exposed stone monuments, Part I: photo oxidative weathering*, **Polymer Degradation Stability, 91**, 2006, pp.3083-3096.

[3] C.E. Corcione, R.Striani, M. Frigione, *Novel hydrophobic free-solvent UV-cured hybrid organic–inorganic methacrylic-based coatings for porous stones*, **Progress in Organic Coatings, 77**, 2014, pp.803–812.

[4] C. Grissom, A.E. Charola, A. Boulton, F. Mecklenburg, *Evaluation over time of an ethyl silicate consolidant applied to ancient lime plaster*, **Studies in Conservation, 44**, 1999, pp.113-120.

[5] L. Dei, B. Salvadori, *Nanotechnology in cultural heritage conservation: Nanometric slaked lime saves architectonic and artistic surfaces from decay,* **Journal of Cultural Heritage, 7**, 2006, pp. 110–115.

[6] M.L. Weththimuni, M. Licchelli, M. Malagodi, N. Rovella, M.F.La Russa, *Consolidation of bio-calcarenite stone by treatment based on diammonium hydrogenphosphate and calcium hydroxide nanoparticles*, **Measurements, 127**, 2018, pp.396-405.

[7] G.W. Scherer, G.S. Wheeler, *Silicate consolidants for stone*, **Key Engineering Materials, 391**, 2009, pp.1–25.

[8] P. Maravelaki-Kalaitzaki, N. Kallithrakas-Kontos, D. Korakaki, Z. Agioutantis, S. Maurigiannakis, *Evaluation of silicon-based strengthening agents on porous limestones*, **Progress in Organic Coatings, 57**, 2006, pp. 140–148.

[9] G. Graziani, E. Sassoni, E. Franzoni, *Consolidation of porous carbonate stones by an innovative phosphate treatment: mechanical strengthening and physical-microstructural compatibility in comparison with TEOS-based treatments*, **Heritage Science**, **3**, 2015, pp. 1-6.

[10] G. Wheeler, Alkoxysilanes and the Consolidation of Stone (Research in conservation), The Getty Conservation Institute, Los Angeles, 2005.

[11] P. Maravelaki-Kalaitzaki, N. Kallithrakas-Kontos, Z. Agioutantis, S. Maurigiannakis, D. Korakaki, *A comparative study of porous limestones treated with silicon-based strenghthening agents*, **Progress in Organic Coatings, 62**, 2008, pp.49-60.

[12] E. Zendri, G. Biscontin, I. Nardini, S. Riato, *Characterization and reactivity of silicatic consolidant*, **Construction and Building Matherials, 21**, 2007, pp.1098-1106.

[13] P. Croveri, M. Chiavarini, *Evaluations of the effectiveness of innovative perfluoropolyurethane polymers as consolidants for porous materials*, Elsevier, Amsterdam, 2000, pp. 263–271.

[14] A. Calia, A.M. Mecchi, G. Quarta, *A research into intrinsic parameters material to the durability of highly porous building stones*, Elsevier, Amsterdam, 2000, pp. 49–58.

[15] M. Licchelli, S.J. Marzolla, A. Poggi, C. Zanchi, *Crosslinked fluorinated polyurethanes for the protection of stone surfaces from graffiti*, **Journal of Cultural Heritage, 12**, 2011, 34-43.

[16] M. Licchelli, M. Malagodi, M.L. Weththimuni, C. Zanchi, *Water-repellent properties of fluoroelastomers on a very porous stone: Effect of the application procedure*, **Progress in Organic Coatings, 76**, 2013, 495–503.

[17] M. Licchelli, M. Malagodi, M.L. Weththimuni, C. Zanchi, *Anti-graffiti nanocomposite materials for surface protection of a very porous stone*, **Applied Physics A, 116**, 2014, 1525–1539.

[18] A.P.F. Pinto, J.D. Rodrigues, *Consolidation of carbonate stones: influence of treating procedures on the strengthening action of consolidants*, **Journal of Cultural Heritage, 13**, 2012, pp.154–166.

[19] UNI 10921:2001, Beni culturali, Materiali lapidei naturali ed artificiali, Prodotti idrorepellenti, Applicazione su provini e determinazione in laboratorio delle loro caratteristiche, 2001.

[20] UNI EN 15886:2010, Conservazione dei Beni Culturali, Metodi di prova, Misura del colore delle superfici, UNI Ente Italiano di Normazione, 2010.

[21] UNI EN 15801:2010, Conservazione dei beni culturali, Metodi di prova, Determinazione dell'assorbimento dell'acqua per capillarità, 2010.

[22] UNI EN 15803:2010, Conservazione dei beni culturali, Metodi di prova, Determinazione della permeabilità al vapore d'acqua, 2010.

[23] V. Zedef, K. Kocak, A. Doyen, H. Ozsen, B. Kekec, *Effect of salt crystallization on stones of historical buildings and monuments, Konya, Central Turkey*, **Building and Environment, 42**, 2007, pp.1453–1457.

[24] R. Liu, X. Han, X. Huang, W. Li, H. Luo, *Preparation of three component TEOS-based composites for stone conservation by sol-gel process*, **Journal of Sol-Gel Science and Technology, 68**, 2013, 19-30.

[25] M. Drdacky, J. Lesak, S. Rescic, Z. Slizkova, P. Tiano, J. Valach, *Standardization of peeling tests for assessing the cohesion and consolidation characteristics of historic stone surfaces*, **Materials and Structures, 45**, 2002, pp. 505-520.

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