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ORIGINAL ARTICLE

Influence of application method and number of applications of nanolime on the effectiveness of the Doulting limestone treatments

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Abstract Over the last two decades, nanolime has been recognized as a promising consolidation approach to consolidate historic calcareous substrates due to its compatibility, durability and fast carbonation. The effectiveness of nanolime products has been widely proven for superficial consolidation treatments, especially in historic wall-paintings. However, its consolidation mechanism in highly porous substrates, such as in the case of limestones or lime mortars, still needs to be fully understood. This paper aims to study the influence of application method and number of applications on the effectiveness of nanolime treatments, which has never been targeted until now. In this experimental work, the $Ca(OH)_2$ nanoparticles were freshly synthetized by anion exchange resins and applied in historic Doulting limestone samples, extracted from a capital from the Cathedral of Wells (Somerset, UK). In order to study the influence of application method on the effectiveness of treatments, samples were treated by: (1) brush; (2) spray; and (3) capillary absorption. Additionally, to study the influence of the number of applications on the consolidation effectiveness, these three application methods were applied by: (1) 1 application; (2) 5 applications; (3) 10 applications. The consolidation effectiveness of the resulting nanolime treatments was studied by assessing changes in porosity, superficial and internal stone's density, superficial cohesion, water absorption by capillarity and aesthetic properties. Results showed that repeated applications (i.e. 10 applications) of a low concentrated nanolime (i.e. 5 g/L) by spray and brush can increase the superficial cohesion, mechanical properties and density of the stone at the surface. Additionally, results suggest that the application method does not significantly affect the consolidation effectiveness of nanolime treatment, contrary to what was commonly believed. Results also show that a single application treatment of low concentrated nanolime (i.e. 5 g/L) does not significantly provide noticeable consolidation effectiveness regardless of the application method, also contrary to what was commonly believed. These results suggest that for a noticeable consolidation treatment with low

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concentrated nanolime the application must consist of several applications (> 10). This could have a high impact on the Built Heritage conservation community that commonly use nanolime in conservation activities.

Keywords Nanolime · Nanoconsolidant · Consolidant effectiveness · Limestone · $Ca(OH)_2$ nanoparticles

1 Introduction

Built Heritage structures are susceptible to several weathering processes (e.g. freeze–thaw, salt damage, dissolution, acidic attack, etc.) which lead structures to lose some of their original properties [1]. Consolidation products are commonly used to restore the strength of weakened built materials as well as decreasing the deterioration rate of the substrate. Consolidation of weakened built heritage materials is one of the most difficult tasks in the built heritage conservation practice. Indeed, this difficulty is especially challenging in the case of calcareous substrates, due to the lack of fully compatible and durable consolidants for these materials. The conservation and maintenance of the majority of European buildings, made with calcareous substrates, from ancient Greece and Rome to the mid-20th century, involved the use of the application of lime water to restore the mechanical properties. This method was used over centuries to consolidate weakened calcareous substrates such as limestones due to its high compatibility and durability with the substrate. However, this treatment presents some important limitations, such as the low solubility of $Ca(OH)_2$ in water, the reduced impregnation depth and the very slow rate of the carbonation process; which in many cases lead to unsatisfactory treatments [2, 3].

At the mid-20th century, several consolidation products were introduced into the market and slowly replaced the traditional consolidation methods due to the ease of its application, initial strength and proven effectiveness. An example of these newly developed products is the organic silica-based consolidants such as Tetraethyl orthosilicate (TEOS) or Trimethoxymethylsilane (MTMOS). Both products were specifically created to consolidate silica-based products and their effectiveness was successfully proven on several silicate stones [4–6]. However, in the case of calcareous substrates, those organic silica-based consolidants present a lack of chemical compatibility between the newly formed silica and calcareous matrix which in many cases can lead to unsatisfactory treatments [1, 7]. In recent years, other consolidants such as hydroxyapatite, calcium alkoxides or innovative materials based on nanocomposites of TEOS have also been tested with promising effectiveness [8, 9], but further research needs to be undertaken to assess their long-term effectiveness.

Nanolime, i.e. $Ca(OH)_2$ nanoparticles, was created at the beginning of the XXI century to overcome the limitations of traditional limewater technique [9–13]. The development of nanolime has slowly replaced the use of the limewater for the consolidation of calcareous substrates due to its better consolidation properties. Nanolime presents similar high compatibility and durability of traditional limewater method but reduces the application time of that traditional treatments since products present higher concentration of $Ca(OH)_2$ particles in the solvent [2]. Additionally, nanolime particles are more reactive so that the carbonation occurs faster [14] and the reduced size of nanoparticles allows better penetration into the pore structure [15]. Nanolimes have emerged as an efficient consolidant for the superficial consolidation of different historic substrates (e.g. wall-paintings, stuccos or plasters) [14] and the conservation of other cultural heritage materials such as paper [16], canvas [17], bones [18] and wood [19]. However, despite the huge number of publications in the recent decades, the complexity of the consolidation action of nanolime has not been fully understood in the consolidation of highly porosity substrates where a deeper consolidation is required.

The effectiveness of stone consolidating treatments is significantly affected by the application procedure, including both the utensils, time and the amount of product applied [20]. Many different stone consolidation products are currently being tested in the field of stone conservation. Most of those consolidation products are currently applied by brush [21, 22], total immersion [23, 24], capillary absorption [25] or spray [26]. However, there is still a lack of understanding about the influence of the application method in the effectiveness of the consolidation treatment. According to the literature, capillary absorption is easy to control in the laboratory but hardly reproducible on-site [27]. Applications by spray were reported that consumes a high amount of product (large runoff of consolidant), fast evaporation (nebulization) but small penetration depth [4]. Contrarywise, the amount of product applied by brushing is hard to control and this method can only be used for small areas [25]. It is well accepted that the penetration depth and the amount of product absorbed are key parameters in the effectiveness, but little attention has been focused on the influence of the application method on the performance of the of each product [28–32], where a slight difference in application protocol may have a big impact on the performance of the treatment [20].

The effectiveness of stone consolidating treatments is also affected by the amount of product absorbed during the consolidation [33]. Nanolime is based on the traditional limewater technique. Successful consolidation treatments by this technique were traditionally achieved by implementing uninterrupted applications of limewater solution for, in several cases, up to 80 days [2]. With the development of nanolime, the time of the application can be reduced since nanolimes have a higher concentration (e.g. 5–50 g/L vs 1.7 g/L of limewater) introducing a larger amount of particles into the substrate with each application. However, the influence of several application of nanolime, in order to deliver sufficient particles of $Ca(OH)_2$ into the substrate to obtain a successful consolidation, has not been studied yet. Previous research concluded that low concentration applications (i.e. 5 or 10 g/L) are preferable compared to highly concentrated ones (i.e. 25 or 50 g/L), since improve the penetration of nanoparticles into the substrate and reduce the whitening effect [34], as well as achieving a more homogeneous distribution of the particles within the substrate [35].

The aim of this paper is to study the influence of application method and number of applications on the effectiveness of nanolime treatments. In this experimental work, the $Ca(OH)_2$ nanoparticles where freshly synthesized and applied to historic Doulting limestone samples. For this purpose, the newly synthesized nanolime was applied on the limestone by: (1) brush, (2) spray and (3) capillary absorption to study the influence of the application procedure. Moreover, the number of applications were investigated by: (1) 1; (2) 5; and (3) 10. The consolidation effectiveness of was investigated by assessing changes porosity, surface and core stone's density, superficial cohesion, water absorption by capillarity and aesthetic properties.

2 Materials and methods

2.1 Limestone samples

The limestone (Fig. 1, CO) used in this experiment corresponds to a capital from the Wells Cathedral (Somerset, UK), which was removed from the site during a restoration intervention in the 1980s and subsequently stored at the outdoor historic stone repository at the British Research Establishment (BRE, UK). During the 1980s–1990s, Prof. Clifford Price (BRE and University College London, UK) used half of this capital for an experiment with Brethane, a consolidant patented by BRE based on MTMOS [3]. They consolidated one half and the other half of the capital remained untreated. After this experiment, the capital was stored at the same outdoor repository until we collected it in 2017. We cut the untreated part of the capital into small cubes discarding the half of the capital consolidated with Brethane. This untreated and naturally weathered half of the capital was cut into 35 × 35 × 35 mm cubes for testing, being a total of 52 cubic samples. The capital is a Doulting limestone stone composed primarily of calcite and presents a bimodal pore size distribution, formed by intermediate pores with diameters between 100 and 10 µm and finer pores with diameters between 0.2 and 1 µm. A full characterization of this limestone can be found in our previous research [36].

2.2 Nanolime

Nanolime was synthesized through a patented process based on ion exchanges processes [37] and fully described in previous publications [38–42]. During the synthesis, an anion exchange resin (Dowex Monosphere 550A OH by Dow Chemical) is added to an aqueous calcium chloride solution ($CaCl_2$ by Sigma-Aldrich) and nanoparticles are formed by chemical precipitation during the ion exchange process [37]. Following the synthesis, the nanolime was prepared at 5 g/L in 50–50% in volume W/A (water—2-propanol). These synthesized nanoparticles are characterized as plate-like hexagonal $Ca(OH)_2$ nanoparticles regularly shaped with a particle size ranging from 20

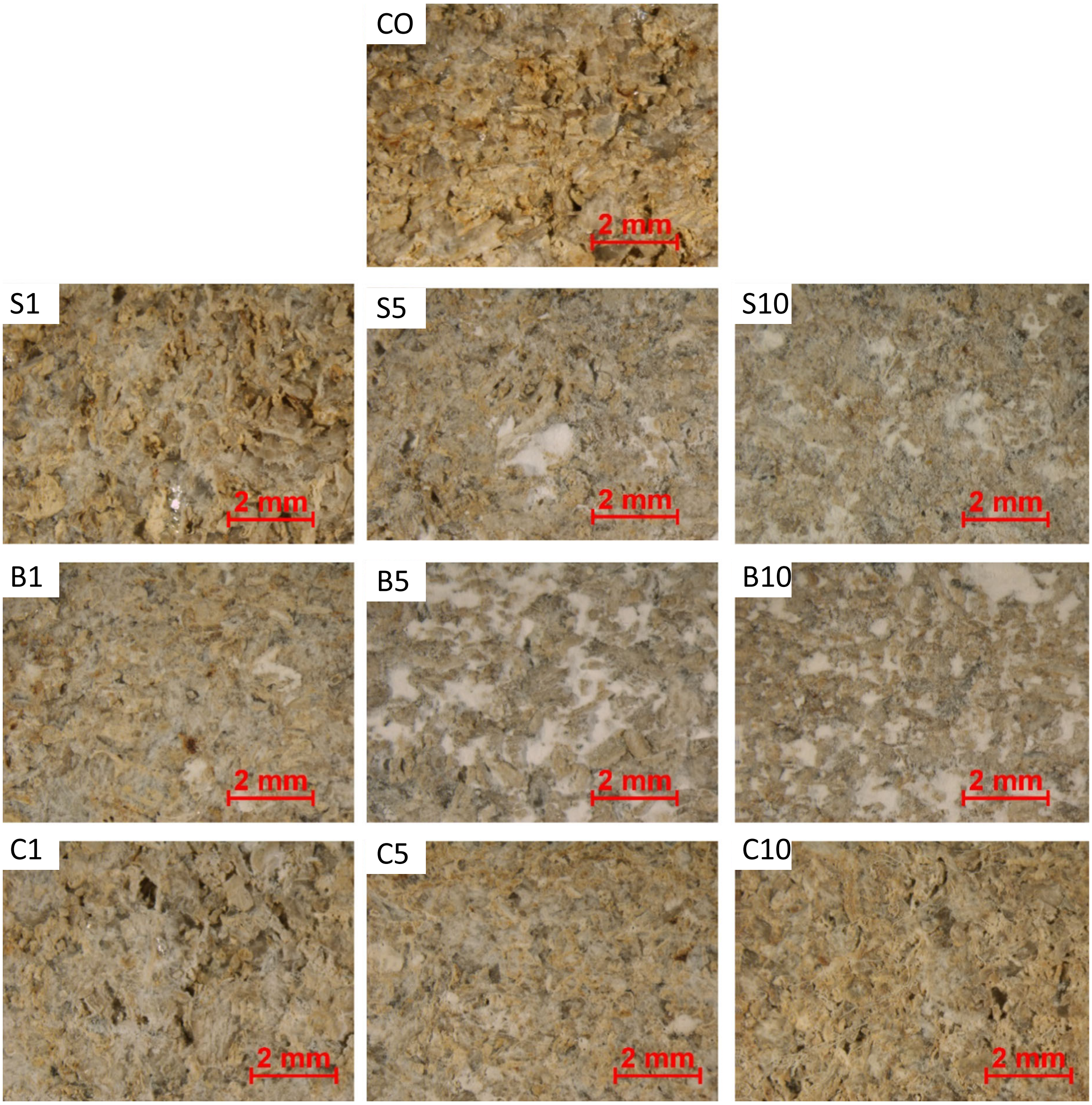


Fig. 1 Results of optical microscopy of control and treated samples after 28-day exposure at ≈ 75% RH. S: spray, B: brush and C: capillary absorption. 1: one application, 5: five applications and 10: ten applications

to 80 nm, which are highly reactive being composed of pure well-crystalline calcite after only 1 h of air exposure at 65% RH [38–40, 42, 43]. After synthesis and before the treatment, nanolime was kept in a refrigerator ($T \sim 5$ °C) to mitigate the Ca-alkoxide conversion to increase their effectiveness [44]. A full characterization of this type of nanolime can be found in our previous publication [38–40, 45].

2.3 Nanolime treatments

In order to study the influence of the application method, the newly synthesized nanolime was applied on dry specimens by: (1) spray; (2) brush; and (3) capillary absorption from the bottom. The three treatment procedures were carried out under indoor conditions ($T \sim 20$ °C and ~ 50% RH). Each nanolime dispersion was agitated before the treatment to increase the colloidal stability of the particles [39]. Treatments started 7 days after the nanolime synthesis of nanolime to increase their effectiveness [44]. Prior to the treatment, the treated cubes specimens were dried to constant mass at 60 °C in a fan assisted oven and subsequently stored in a desiccator until testing.

Before the application of the consolidant, contact capillary absorption (UNE-EN 15801:2009) was carried out on the 4 cubic specimens in order to estimate the water absorption rate of the samples and the total water absorption capacity of samples [46]. Then, 4 samples were used as control (hereinafter CO) and 12 samples were used for each procedure (spray, brush and capillary absorption). Lateral side faces of the cubic samples were closely sealed with parafilm to avoid the ingress of the product by the sides.

For spray treatment (S hereinafter), samples were placed over a plastic grid inside the fume hood and samples were sprayed vertically in parallel to the bedding layer. Treatment was carried out constantly with intervals of 10–15 s until the saturation of the stone (i.e. samples were weighted during the absorption and stopped when samples obtained asymptotical values), which corresponded to the amount of absorbed product for each application. In the case of 5 and 10 applications, application procedure was repeated 48 h later when samples were completely dry ($T \sim 20$ °C and $\sim 50\%$ RH) and total amount of absorbed product will correspond to the sum of the 5 or 10 applications.

For brush treatment (B hereinafter), samples were also positioned with the orientation of the bedding layers parallel to the ground over a metallic grid containing in a vessel and nanolime was applied by brushing in parallel to the bedding on one clean and dry surface of each limestone cube until the consolidant reached the opposite side of the sample and achieved full saturation of the product. The application was stopped when no further absorption was observed (the surface remained wet for a period of at least 1 min) and also reached asymptotical values. Samples were weighed before and after saturation. In the case of 5 and 10 applications, application procedure was repeated 48 h later when samples were completely dry ($T \sim 20$ °C and $\sim 50\%$ RH) and total amount of absorbed product will correspond to the sum of the 5 or 10 applications.

For the consolidant application through capillary absorption (C hereinafter), samples were also positioned with the orientation of the bedding layers vertical to the ground on glass rods in the base of a Petri dish-like vessel containing the newly synthesized nanolime. Cubic samples were immersed (up to 1 mm) in the nanolime and it was left to absorb by capillary action until saturation (i.e. when no more increasing values in weight were observed) and asymptotic values. During the consolidation process, the vessel was constantly refilled with consolidant and vessel was sealed by a parafilm to minimise the solvent evaporation. In the case of 5 and 10 applications, application procedure was repeated 48 h later when samples were completely dry ($T \sim 20$ °C and $\sim 50\%$ RH) and total amount of absorbed product will correspond to the sum of the 5 or 10 applications.

For the three application procedures, 4 samples were treated by only 1 application (1 was added to the acronym of each application procedure), 4 samples were treated and repeated up to 5 applications (5 was added to the acronym of each application procedure) and 4 samples were treated and repeated up to 10 applications (10 was added to the acronym of each application procedure).

All samples were weighed before and after each application (spray, brush and capillary absorption) to obtain the amount of nanolime absorbed by each cube at the moment of the saturation of each application. The difference in weight between "saturated" and "dry" values was considered the amount of nanolime absorbed in each application. In the case of samples treated by 5 or 10 applications, the same procedure was repeated and final total amount of absorbed nanolime corresponded to the sum of the 5 of 10 applications. The amount of absorbed material was expressed as the weight of product per volume (g/cm^3). Additionally, since it was known the nanolime concentration (i.e. 5 g/L), it was also estimated the total amount of $Ca(OH)_2$ particles absorbed by the specimen as a result of the treatment (g). The authors understand this is slightly more accurate rather than just indicating the number of applications without providing an empiric number. This protocol has been also applied in previous studies [39–41]. There is a vast number of articles in the literature testing the effectiveness of nanolime. However, most of papers did indicate the number of applications (most used are 1, 2, 4, 6 and 8). This could be misleading since they don't provide the total amount of particles introduced in each application into the sample, thus making it difficult to stablish a reliable comparison between different experiments. This is due to the fact that the term of "application" does not provide an empiric number to compare and the introduced particles might differ between cases involving different materials and applications. Therefore, to provide a more reliable application for comparative purposes, it has been accounted the amount of particles absorbed during the application to assure that all samples receive the same amount of particles in order to study the influence of the three application methods.

Upon application, the samples were stored for a period of 28 days at RH ~ 75% in a desiccator with a saturated solution of NaCl [47] to accelerate carbonation and promote the formation of pure calcite [38, 42, 45]. A set of untreated control samples was also stored in the same conditions. Then, samples were dried to constant mass at 60 °C in a fan assisted oven and subsequently stored in a desiccator until testing.

2.4 Consolidation effectiveness

In order to assess the degree of carbonation of the nanolime in the pores after 28 days, one of the treated cubes was split in two faces and one internal face was immediately sprayed with a 1% phenolphthalein solution (70% ethanol—30% water-) [48], which due to the alkalinity of nanolime (pH ~ 12), it turns pink in a basic solution (nanolime) and remains colourless in a non-basic medium ($CaCO_3$).

Optical microscopy was used by means of a Nikon SMZ800 in order to observe the macroscopic morphology of the surface. Additionally, in order to observe the possible presence of carbonated nanolime in the pores, one cube for each testing condition was dry cut in half (from the treated face) with a Buehler IsoMet 1000 using a Buehler diamond blade at low velocity of 150 r.p.m. This low velocity was intentionally selected in order to mitigate the possible formation of new fractures in the samples. After the fracture, all samples were thoughtfully air-sprayed and gently cleaned with ethanol (50 vol.% in distilled water) to remove the dust and to avoid any possible relocation of the consolidant in other areas of the stone. One of the resulting halves approximately 1 × 3.5 cm, was sectionally observed to estimate the distribution within the pores of the calcite crystals originated from the carbonation of nanolime, penetration of the treatments and possible surface pore-clogging resulting from the treatments.

In order to assess a reduction of porosity as a result of the treatment, the open porosity accessible to water by vacuum was measured according to UNE-EN 1936:2006 [49] and apparent porosity at atmospheric pressure was measured by ASTM C 67-00 [50]. Both tests were carried out on four samples of each testing conditions and results were compared to control samples. The average of measurements was used to calculate the difference between testing conditions and compared to control samples.

Ultrasounds Pulse Velocity (UPV) measurements were determined to study differences in the stone's density between the surface (outer 1 cm from the treated surface) and the core (centre of the specimen) of the specimens as a result of the consolidation and compared to control samples. In order to observe differences in the stone density between the surface and the core, measurements were taken by using two positions of the transducers: (1) in parallel to the treated face and very close to the surface (1–0.5 cm depth); (2) in parallel to the treated face in the centre of the sample (depth of approximately of 1.75 cm). A non-portable Geotron -CONSONIC C2-GS (Geotron-Elektronik, Pirna, Germany) was used to determine the Ultrasound P-wave velocity on the samples and data was collected by the lighthouse software. The frequency of Pulse Velocity was constant at 10 MHz. The direct transmission technique was implemented using two pointy transducers (UPE-D), pressed on the opposite ends of the specimens. Velocity is calculated by the following formula:

$$V = L/T$$

"V" is the P-wave velocity (m/s), "L" is the distance between transducers (m); and "T" is the time to travel (s).

Measurements were taken in perpendicular to the bedding of the stone. 45 measurements were taken on each of the four samples of each testing conditions (45 measurements per each test both at the surface and the centre) and results were compared to control samples.

Capillary absorption curves and the water absorption coefficient (WAC) were calculated according to EN 13755 [51]. This test was carried out on the four samples of each testing conditions and results were compared to control samples. The water absorption coefficient was calculated as the average of four samples of each testing conditions.

The increase in surface hardness was measured by means of Proceq's Equotip 550 portable hardness tester Leeb, Rockwell and UCI [52]. This test was carried out to study the hardness of the surfaces before and after the four treatments and results were compared to control samples. For this test, the probe was used the Equotip Leeb Impact Device D (Proceq) and the Equotip surface hardness vale (HLD) was calculated as an average of at least 45 points selected by shifting each other few millimetres on each sample. The average of measurements was used to calculate the difference between testing conditions and compared to control samples. The hardness measurements are made by using the dynamic rebound testing method according to Leeb, the static Portable Rockwell hardness test and the Ultrasonic Contact Impedance (UCI) method. *L*-value, also known as Leeb-number or Leeb-hardness value (HLD), is obtained by using this equation:

$$\mathrm{HLD} = v_{\mathrm{r}}/v_{\mathrm{i}} \times 1000$$

where V_{r} is the rebound velocity and V_{i} is the impact velocity.

The influence of nanolime treatment on surface cohesion was also evaluated by 'Scotch Tape Test' (STT) according to ASTM 2009 [53], and following the guidelines established by Drdácký et al. to avoid systematic errors of the ASTM standard [54]. The test was carried out on the four samples of each testing conditions and results were compared to control samples. Scotch Tape Tests consisted of 9 measurements for each sample. The average of measurements was used to calculate the difference between testing conditions and compared to control samples.

Colorimetric changes on the surfaces induced by the consolidation treatment were determined by means of a CM-700d Minolta spectrophotometer. Measurements of the treated and control surfaces samples were taken straight after observing the samples by the optical microscope and before analysing the samples by the other techniques, i.e. Porosity, UPV, WAC, Equotip and STT to mitigate the impact of those techniques in the colour of the surface. Measurements were taken in CIELAB and CIELCH colour spaces [55, 56]. The parameters in CIELAB space were the lightness (L^*) from black (0) to white (100) and the polar coordinates a^* from red ($+a^*$) to green ($-a^*$) and b^* from yellow ($+b^*$) to blue ($-b^*$). In CIELCH colour space, L^* was also included and also chroma or saturation (C^*_{ab}) and the hue (h_{ab}) were obtained. The measurements were made in specular component included (SCI) mode, for a spot diameter of 8 mm, using illuminant D65 and with an observer angle of 10°. Despite Sanmartín et al. [57] reported that for stones less heterogeneous than the granite, the fewer number of measurements are enough to determine the colour of the stone, the colour data collection was performed as for granitic stones [58] which consisted of 45 measurements on each of the four samples of each testing conditions. Then, colour differences (ΔL^*, Δa^*, Δb^*, ΔC^*_{ab}, ΔH^*) and global colour change (ΔE^*_{ab}) were computed taking the colour of the control stones as the reference value. Global colour change (ΔE^*_{ab}) was calculated by the formula (CIE 1986, 2007):

$$\Delta E^*_{ab} = \sqrt{\Delta L^{*2} + \Delta a^{*2} + \Delta b^{*2}}$$

One of the halves obtained for each sample with a Buehler IsoMet 1000 of the treated samples (B10) and a control sample were C-sputtered and observed under a Scanning Electron Microscope (SEM) to evaluate the morphology and distribution within the pores of the calcite crystals originated from the nanolime carbonation. The equipment used was an FEI Quanta 200 unit with a secondary electron (SE) and backscattered electrons (BSE) detectors. Applied optimum conditions of observation were an accelerating potential of 20 kV, a working distance of 10 mm and a specimen current of ~ 60 mA.

3 Results and discussion

3.1 Consolidation effectiveness

The phenolphthalein test carried out on one of the internal faces of the cut open treated cubes shows that there was no Portlandite present in the pores following 28-day exposure at ~ 75% RH, which confirms that the nanolime has fully carbonated in the pores regardless the application method and number of applications.

Visual observations of the treated surface showed that samples treated by brush and spray yielded a higher increase in the whitening (Fig. 1), which is clearly attributed to a significant accumulation of nanoparticles into the fissures and superficial cavities of the surface. The resulting whitening of the surface was also observed in previous results with the same type of nanolime [42]. The thickness of the superficial layer was not constant due to the roughness of the stone. The deposit of nanoparticles into the superficial voids of the stone reached depths of up to 2 mm. It was not possible to confirm that a higher number of applications would reach deeper into the stone. In on-site applications, this whitening can be partially mitigated by wiping the surface with an alcohol dampened cloth after treatments [59]. However, this approach was not considered in this study to evaluate the accumulation of the nanoparticles on the surface after the application of each method. Results confirmed that treatments by brush and spray caused a significant whitening on treated samples when 5 and 10 applications were carried out (Fig. 1-S5, S10, B5 and B10). Contrarywise, no significant chromatic alteration of the treated surfaces was observed for samples treated with one application of two treatment methods (Fig. 1-S1 and B1). Samples treated by capillary absorption yielded no significant increase in the whitening of the samples regardless of the number of applications (Fig. 1-C1, C5 and C10).

Results of the total amount of absorbed material (g/cm^3) showed that specimens treated by capillary absorption absorbed higher amount of nanolime during the treatment (Table 1), which is in the line with Ferreira-Pinto and Delgado-Rodrigues' research which also concluded this treatment method obtain a higher amount of consolidant in the samples [20]. Results also showed that samples treated by brush absorbed slightly higher amount of product compared to the samples treated by spray. The amount of the $Ca(OH)_2$ particles introduced in the samples has been estimated based on the total amount of product absorbed by the specimens which discard the amount of solvent with no consolidating effect. The estimation of introduced nanoparticles has shown that, after 10 applications, samples treated by spray, brush and capillary absorption were impregnated with a total of $Ca(OH)_2$ nanoparticles of approximately 0.53 g, 0.66 g and 0.93 g, respectively. Despite the clear absorption of nanolime, treated samples obtained no increase in the total weight of the samples after the treatments (Table 1). This could be attributed to the fact that some stone material (small disintegrated grains) was lost after removing the lateral-side´s parafilm, which can make unnoticeable any potential slight increase in weight as a result of the consolidation treatment.

Open porosity (%) was calculated by UNE-EN 1936:2006 and ASTM C 67-00 in order to study changes in the open porosity as a result of the consolidation treatment. Both tests were carried out for comparative testing. The results for both tests show that all treatments had slightly induced a change in the total open porosity regardless of the application method or the number of applications (Table 2). This result in the line with previous studies where treatments of nanolime induced a very slight reduction in the overall open porosity of large size pore substrates [36, 39, 40], and with open porosity reduction also only noticeable at the outer surface up to a depth of 1 cm [39]. Samples treated by spray where the application was repeated 5 and 10 times, showed slightly higher reduction in open porosity compared to the brush and capillary absorption samples, which might be attributed to a higher presence of carbonated crystals in the samples. However, the high standard deviation of those samples made this result statistically not conclusive. This is also noticeable in the increasing values of porosity of samples S5 and B10, which are also within the standard deviation error.

UPV measurements were taken in order to observe differences in the density of the stone induced by the treatments. Results of the UPV showed that treatments increased the density of the stone in the outer surface of samples (Table 3), similar to previous studies [60]. This increase was clearly more noticeable in the samples which were treatment was carried out by brush and spray than samples treated by capillary absorption. Additionally, the number of applications for both brush and spray treatments, also presented a relation to the number of applications. Samples treated up to 10 times obtained the higher increase in the density of the stone in the surface. This result was slightly more pronounced in the samples treated by brush, which was attributed to the fact that slightly more amount of consolidant was introduced than for those which were sprayed (Table 1). On the contrary, this increase in the stone´s density has not been observed in any of the samples where the UPV was measured in the centre of the sample, which suggests that nanolime particles did not reach the core of the samples. UPV measurements of capillary absorption

Table 1 Amount of nanolime absorbed during treatment, estimation of introduced nanoparticles and increase of weight after the treatment on samples treated by spray, brush and capillary absorption with 1, 5 and 10 applications. *n* = 4

Number of applications	Total product absorbed during treatment (g/cm^3)	Estimation of introduced nanoparticles (g)	Δ Weight after treatments (g)
Spray (S)			
1	0.27 (± 0.05)	0.05	0.01 (± 0.01)
5	1.68 (± 0.17)	0.31	0.03 (± 0.03)
10	2.87 (± 0.14)	0.53	0.04 (± 0.01)
Brush (B)			
1	0.37 (± 0.06)	0.03	0.01 (± 0.02)
5	1.91 (± 0.18)	0.26	0.04 (± 0.03)
10	3.56 (± 0.26)	0.66	0.06 (± 0.04)
Capillary absorption (C)			
1	0.49 (± 0.29)	0.09	0.01 (± 0.02)
5	2.55 (± 0.21)	0.05	0.02 (± 0.03)
10	5.08 (± 0.12)	0.93	0.01 (± 0.01)

Standard deviations between parenthesis

Table 2 Open porosity measured by UNE-EN 1936:2006 and ASTM C 67-00 and porosity reduction of the surfaces tested by spray, brush and capillary absorption with 1, 5 and 10 applications

Number of applications	Open porosity accessible to water by vacuum UNE-EN 1936:2006		Open porosity accessible to water at atmospheric conditions ASTM C 67-00	
	Open porosity (%)	Reduction (%)	Open porosity (%)	Reduction (%)
Control (CO)	34.42 (± 2.30)		32.61 (± 1.60)	
Spray (S)				
1	34.36 (± 1.70)	0.17	31.91 (± 2.16)	2.15
5	32.63 (± 2.30)	5.20	33.19 (± 3.17)	− 1.78
10	31.45 (± 4.90)	8.63	31.16 (± 2.44)	4.45
Brush (B)				
1	33.21 (± 3.80)	3.51	32.26 (± 2.19)	1.07
5	33.39 (± 3.00)	3.00	32.30 (± 3.02)	0.95
10	34.29 (± 1.30)	0.38	33.60 (± 3.3)	− 3.10
Capillary absorption (C)				
1	34.57 (± 0.70)	− 0.44	31.70 (± 2.04)	2.79
5	36.21 (± 1.50)	− 5.20	31.50 (± 2.50)	3.40
10	35.35 (± 0.70)	− 2.69	31.68 (± 2.41)	2.85

Standard deviations between parenthesis

n = 4

treated samples show that this method yielded a less pronounced consolidating effect in terms of increasing the density of the stone. This is attributed to the fact that this type of nanolime presents a poor colloidal stability (sedimentation rate ∼ 6% per hour) [38–40], which might mitigate the ingress and deposition of particles in the pores during the absorption of the product.

Table 3 Ultrasounds P-wave velocity and increase of the Ultrasounds P-wave velocity (ΔUPV—m/s and % increase) of the surfaces treated by spray, brush and capillary absorption with 1, 5 and 10 applications and compared to control samples. $n = 180$

Number of applications	Treated surface			Core of the sample		
	UPV (m/s)	ΔUPV (m/s)	ΔUPV (%)	UPV (m/s)	ΔUPV (m/s)	ΔUPV (%)
Control (CO)	2467 (± 83.7)			2660 (± 52.0)		
Spray (S)						
1	2581 (± 86.4)	114	4.6	2598 (± 78.9)	− 63	− 2.3
5	2673 (± 127.2)	206	8.4	2647 (± 81.8)	− 13	− 0.5
10	**2819 (± 160.4)**	**352**	**14.3**	2638 (± 74.2)	− 23	− 0.9
Brush (B)						
1	2541 (± 116.7)	73	3.0	2572 (± 113.3)	− 89	− 3.3
5	2654 (± 100.1)	187	7.6	2623 (± 64.4)	− 37	− 1.4
10	**2927 (± 164.2)**	**460**	**18.7**	2622 (± 56.1)	− 38	− 1.4
Capillary absorption (C)						
1	2596 (± 151.9)	129	5.2	2586 (± 27.8)	− 75	− 2.8
5	2600 (± 152.3)	132	5.4	2594 (± 123.8)	− 66	− 2.5
10	2618 (± 90.7)	150	6.1	2591 (± 63.0)	− 69	− 2.6

Standard deviations between parenthesis

Bold numbers are the samples statistically different from control

The capillary water absorption curves and coefficient (WAC) of control and treated samples are reported in Fig. 2 and Table 4. Treated samples present similar water absorption rates compared to control samples. The capillary rise in porous materials was closely related to pore size distribution. Pores between 1 mm and 1 µm diameter induce higher capillary absorption coefficient [61]. Previous results showed this limestone presents a bimodal pore structure with most of the pores in the range of 10 and 100 µm (corresponding to the capillary rise) and between the range of 0.2 and 1 µm [36]. Optical microscopy observations also showed that this stone presents highly population of pores with large pore size diameter > 100 µm. The main decrease in Water Absorption Coefficient (WAC) was observed for the samples treated by spray and brush where the treatment was repeated 5 and 10 times (Table 4). This can be attributed to the higher reduction of the capillary pores (the pores in the range of 10 and 100 µm) by the treatments which could slow down the capillary rise [61]. WAC is in line with UPV results which suggest that both S10 and B10 samples present higher stone´s density at the surface, which it could reduce pore size and absorption rate. However, the differences found were not statistically significant. Contrarily, treated samples by spray and brush where the treatment was only carried out by one time, i.e. S1 and B1, both presented a slight increase of the water absorption coefficient (Table 4). This could be attributed to lesser reduction of the population of pores with a diameter between 1 mm to 1 µm, or resulting from a partial filling of the large pores with diameter sizes larger than 100 µm. Additionally, samples treated by spray and brush where the treatment was repeated 10 times yielded a slightly higher reduction of the total water absorbed by capillary (Fig. 2a, b), which could be also related to the higher reduction of open porosity accessible to water due to the higher presence of calcite crystals in the samples. Samples treated by capillary absorption presented similar curves to each other and to control, which was in the line with previous results which suggest that nanolime treatments caused low impact on the Water Absorption rate [36, 39, 40].

The superficial hardness of treated samples was measured by Equotip and compared to control samples (Table 5). Results clearly showed that samples treated by spray and brush slightly increased the overall surface hardness. This effect was noticeable especially

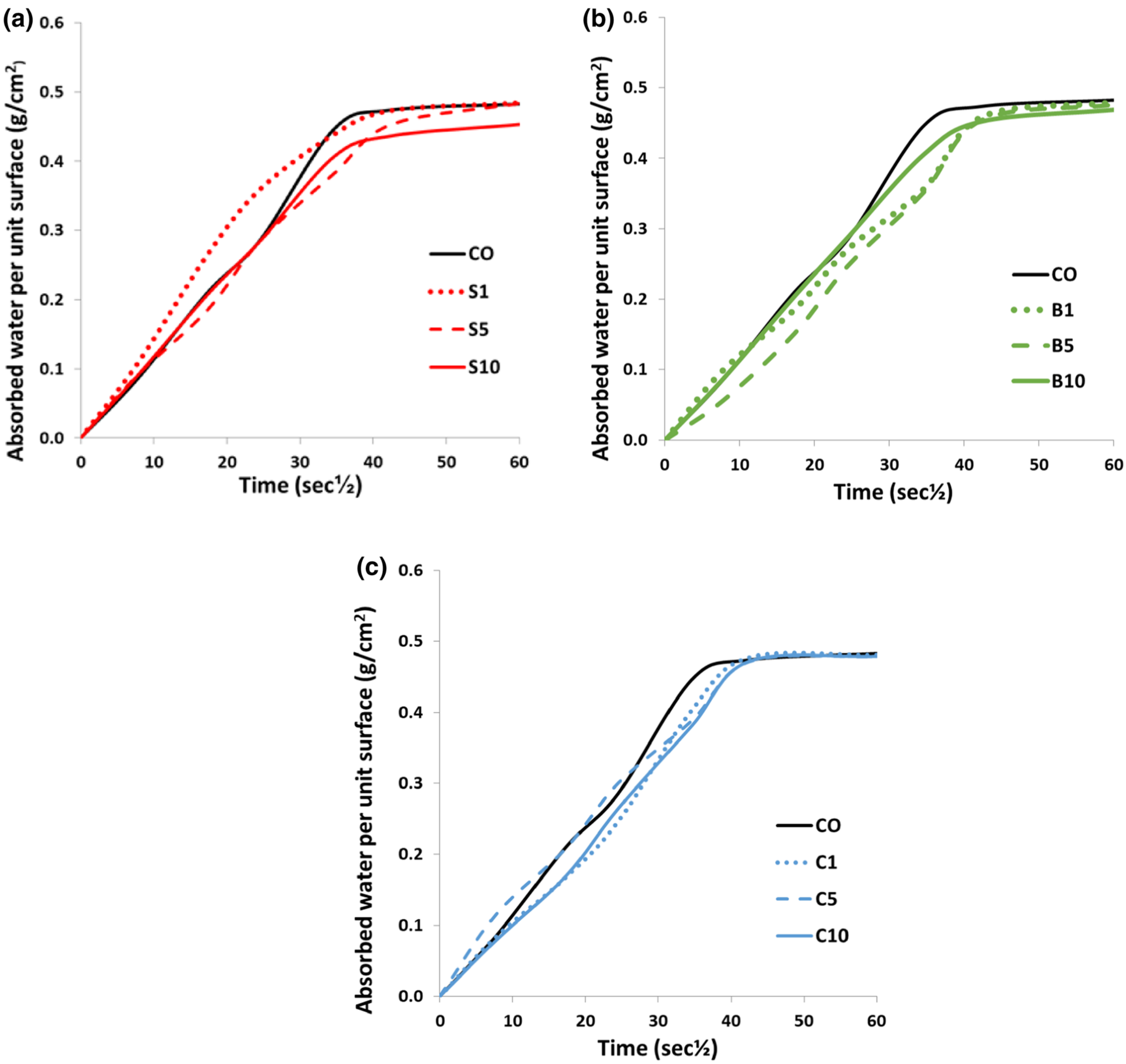


Fig. 2 Water Absorption by Capillary (WAC) curves of control (CO) and treated samples: **a** samples treated by spray (S1, S5 and S10); **b** samples treated by brush (B1, B5 and B10); and **c** samples treated by capillary absorption (C1, C5 and C10)

on the samples where the treatment was carried out by 10 applications (Table 5). On contrary, samples treated by capillary absorption induced a significantly lower increase in the surface hardness, which can be also attributed to the fact that nanolime particles synthesized by anion exchange resins tend to sediment over time due to the low colloidal stability of this type of nanolime, especially when compared to the commercial products [39, 42, 45]. This might have prevented the penetration of $Ca(OH)_2$ particles in the specimens compared to the other application methods. However, this could be also attributed to the fact that most nanoparticles of $Ca(OH)_2$ could have deposited but at a few mm depth, therefore not influencing the surface hardness as spray and brush techniques, where accumulation of $Ca(OH)_2$ mostly occurs on the surface, as noticed in previous studies [59, 62]. Further research needs to be carried out to elucidate this hypothesis. Samples treated by brush also presented a slightly higher increase in surface hardness compared to the samples treated by spray, which could be attributed to the higher amount of particles introduced

Table 4 Water Absorption by Capillary Coefficient (WAC) of the control and surfaces treated by spray, brush and capillary absorption with 1, 5 and 10 applications. *n* = 4

Number of applications	Water absorption coefficient WAC (Kg/m^2 × h$^{0.5}$)	Decrease of WAC (%)
Control (CO)	6.71 (± 0.34)	
Spray (S)		
1	7.28 (± 0.05)	− 8.49
5	**6.23 (± 0.14)**	**7.15**
10	**6.31 (± 0.19)**	**5.96**
Brush (B)		
1	7.08 (± 0.19)	− 5.51
5	**6.32 (± 0.24)**	**5.81**
10	**6.31 (± 0.13)**	**5.81**
Capillary absorption (C)		
1	6.86 (± 0.22)	− 2.23
5	6.53 (± 0.28)	2.68
10	6.87 (± 0.36)	− 2.38

Standard deviations between parenthesis

Bold numbers are the samples statistically different from control

Table 5 Surface hardness (HLD) and increase of surface hardness (ΔHLD) of control and treated surfaces by spray, brush and capillary absorption with 1, 5 and 10 applications. *n* = 180

	HLD	ΔHLD	ΔHLD (%)
Control (CO)	263.9 (± 54.2)		
Spray (S)			
1	286.9 (± 44.2)	23.1 (± 70.0)	8.7
5	300.4 (± 67.1)	36.5 (± 95.1)	13.8
10	354.3 (± 56.9)	90.4 (± 78.6)	34.3
Brush (B)			
1	293.9 (± 23.8)	29.9 (± 59.2)	11.4
5	305.9 (± 41.7)	41.9 (± 68.4)	15.9
10	**380.4 (± 32.7)**	116.4 (± 63.3)	44.1
Capillary absorption (C)			
1	267.8 (± 52.5)	3.9 (± 75.5)	1.5
5	269.5 (± 35.0)	5.6 (± 64.5)	2.1
10	275.7 (± 61.3)	11.8 (± 81.9)	4.5

Standard deviations between parenthesis

Bold numbers are the samples statistically different from control

in the samples (Table 1) and the higher presence of the product in the surface observed by optical microscope (Fig. 1).

The superficial cohesion of treated samples was measured by the Scotch Tape Test and compared to control samples (Table 6). Results clearly showed that samples treated by spray and brush significantly increased the surface cohesion whereas samples treated by capillary absorption induced a significantly lower increase in the superficial cohesion, which was in the line with the Equotip results. In both spray and brush treatments, treated samples obtained a > 80% increase in the superficial cohesion on samples treated by 5 and 10 applications. This was in the line with previous researches that concluded that similar treatments by brush or spray with this type of nanolime yielded a similar increase in the superficial cohesion (> 80% Δ of released material) [36, 38–42].

Colorimetric data showed that in all cases, besides of C5 and C10, b* decreased, suggesting a shifting of

Table 6 Released material and increase of the superficial cohesion (ΔReleased Material) by Scotch Tape Test (STT) applied on the control and treated surfaces by spray, brush and capillary absorption with 1, 5 and 10 applications. n = 180

Number of applications	Released material (mg/cm^2)	Δ Released material (%)	SD
Control (CO)	26.85		9.14
Spray (S)			
1	12.30	54.20	12.60
5	3.60	86.60	14.20
10	1.70	93.60	9.98
Brush (B)			
1	10.40	61.20	9.70
5	3.00	88.80	11.30
10	1.60	94.00	12.20
Capillary absorption (C)			
1	21.00	21.80	13.90
5	16.80	37.30	11.40
10	14.40	46.30	10.50

Scotch area: 3 × 1.5 cm; (SD) standard deviation is calculated based on the difference between the released material before and after treatment

the typical yellow coloration towards a paler coloration (whitening) due to the nanoparticle deposits on the surfaces as it was also found by the stereomicroscope and was also noticeable in the increase of L* in all cases except for C5 (Table 7). Additionally, results might suggest that a* slightly decreased (red coloration loss), although this parameter was the least affected by the consolidation with nanolime. Samples treated by brush induced the highest global colour changes (ΔE^*_{ab} for B5 = 10.83 ± 4.99 CIELAB units and for B10 = 8.94 ± 6.75 CIELAB units). These global color changes due to whitening were significantly high since treated surfaces were not gently wiped with a solvent dampened cloth immediately after the application to avoid the formation of superficial deposits of nanolime, as suggested in previous studies [39, 58]. As also observed by the stereomicroscope, the samples treated by the highest number of applications (10) did not induce the greatest aesthetical modification and subsequently highest ΔE^*_{ab}, i.e. both S5 and S10 showed similar ΔE^*_{ab} and B10 showed a slightly lower ΔE^*_{ab} compared to B5 Colorimetric results finally concluded that samples treated by spray with 5 and 10 applications and by

Table 7 Chromatic changes (ΔL^*, Δa^*, Δb^*, ΔE^*_{ab}), of the surfaces before and after treatments by spray, brush and capillary absorption with 1, 5 and 10 applications. n: 180 measurements

Number of applications	ΔL^*	Δa^*	Δb^*	ΔE^*_{ab}
Spray (S)				
1	0.48 (± 0.69)	− 0.18 (± 0.15)	− 0.86 (± 0.59)	1.21 (± 0.47)
5	1.58 (± 3.25)	− 0.33 (± 0.72)	− 1.73 (± 3.61)	4.25 (± 2.73)
10	2.85 (± 1.84)	− 0.74 (± 0.57)	− 3.72 (± 3.04)	4.78 (± 3.54)
Brush (B)				
1	2.78 (± 1.24)	− 0.73 (± 0.35)	− 3 (± 1.38)	4.17 (± 1.85)
5	7.14 (± 3.31)	− 1.93 (± 0.92)	− 7.9 (± 3.63)	10.83 (± 4.99)
10	5.95 (± 5.59)	− 1.72 (± 1.43)	− 5.9 (± 4.60)	8.94 (± 6.75)
Capillary absorption (C)				
1	0.75 (± 0.71)	− 0.22 (± 0.30)	− 0.83 (± 1.29)	1.45 (± 1.11)
5	− 0.06 (± 0.41)	0.01 (± 0.06)	1.09 (± 0.86)	1.19 (± 0.79)
10	0.3 (± 1.59)	− 0.04 (± 0.59)	0.74 (± 2.83)	2.73 (± 1.35)

Standard deviations between parenthesis

brush regardless of the application number induced ΔE^*_{ab} higher than 3.5 units which are stated as the threshold for a visible color change identified by an unexperienced human eye [63]. According to Rodrigues and Grossi [64], from the conservation point of view, the aesthetic alterations can be classified as: low risk ($\Delta E^*_{ab} < 3$ CIELAB units), medium risk ($3 < \Delta E^*_{ab} < 5$ CIELAB units) and high risk ($\Delta E^*_{ab} > 5$ CIELAB units). Considering that, samples treated by spray with one application and all the samples treated by absorption capillarity ($\Delta E^*_{ab} < 3$ CIELAB units) were low risky conservation methodologies, and the rest of the conditions, considering the standard deviations obtained, can be considered as high risky interventions, from the aesthetical point of view. However, previous research showed that the surface whitening (high risk, $\Delta E^*_{ab} > 5$ CIELAB units) yielded after application of this type of nanolime significantly decreases to low risk ($\Delta E^*_{ab} < 3$ CIELAB units) after exposing samples cycles of RH/T without reducing the mechanical properties [39].

Cross-sections of treated samples were observed by optical microscopy to observe the macroscopic morphology of the samples after treatments. Figure 3b–d showed micrographs of the cross-sections from treated limestone with the three different procedures with the highest number of applications (S10, B10 and C10) comparatively to the control surface (Fig. 3a). Figure 3 shows the cut carried out with a Buehler IsoMet 1000 using a Buehler diamond blade at low velocity of 150 r.p.m did not originate new fractures in the stone. Additionally, it can be observed the presence of carbonated nanolime in the samples (whitening), both in the surface and in some inner pores up to a depth of 2 mm. On the S10 surface, it was observed the accumulation of carbonated nanolime on the surface, while on B10 and C10, this identification was less evident. Additionally, it can be also observed that treatments did not cause any block of the pores, as this is also evident by the WAC test.

According to previous results, the size of calcite resulting from the carbonation of this type of nanolime is approximately 1–10 µm [39], which is too small to be observed by a standard optical microscope. However, this differs from other researches where carbonated nanolime inside a porous calcareous substrate (visualized using cross-sections) associated with the

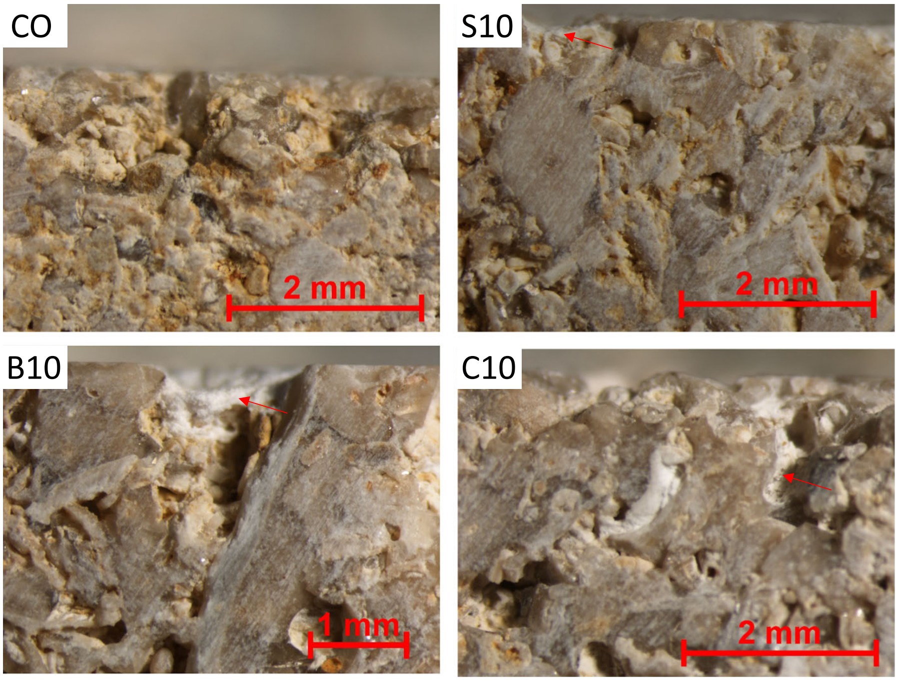


Fig. 3 Cross-sections micrographs of the treated and control samples by optical microscopy: **a** control sample; **b** samples treated by spray and repeated up to 10 applications; **c** samples treated by brush and repeated up to 10 applications; **d** samples treated by capillary and repeated up to 10 applications

nanolime penetration was clearly observed by optical microscope [64]. This could be attributed due to:

1. the different pore network structure and grain size of Maastricht limestone compared to the Doulting limestone used in this experiment. Maastricht limestone presents significant-high open porosity (50%) and a unimodal pore size diameter (35–40 µm) while Doulting limestone presents a lower open porosity (34%) and a bimodal pores with diameters between 100 and 10 µm and finer pores with diameters between 0.2 and 1 µm.
2. the different nanolime products utilized in both studies which present different properties such as colloidal stability, particle size, carbonation rate and crystallinity [39].

In order to estimate the presence of carbonated nanolime in the pores at microscopical level, the cross-sections of the control sample (Fig. 4a, b) and B10 (Fig. 4c–g) were observed by SEM. The control sample showed a matrix composed mainly of polyhedral-and-rhombohedral calcite crystals with approximately a size of 10 µm (Fig. 4b). Conversely, B10 seems to show the presence of precipitated nanolime which was significantly accumulated in the fissures and voids of the surface (Fig. 4c), as observed by optical microscopy. The observed calcite resulting from nanolime (Fig. 4c, g) presented morphologically similarities to calcite crystals observed in other studies carried out with the same type nanolime, which are characterized as similar prismatic-rhombohedral but with reduced size (approximately 1 µm) [38, 39]. The presence of this type of calcite resulting from nanolime was also observed in some of the voids up to a depth of 5–6 mm from the treated surface (Fig. 4f, g). This is in the line with previous researches that estimate that the penetration of nanolime is approximately 6 mm, which penetration highly differ regarding the pore structure [36].

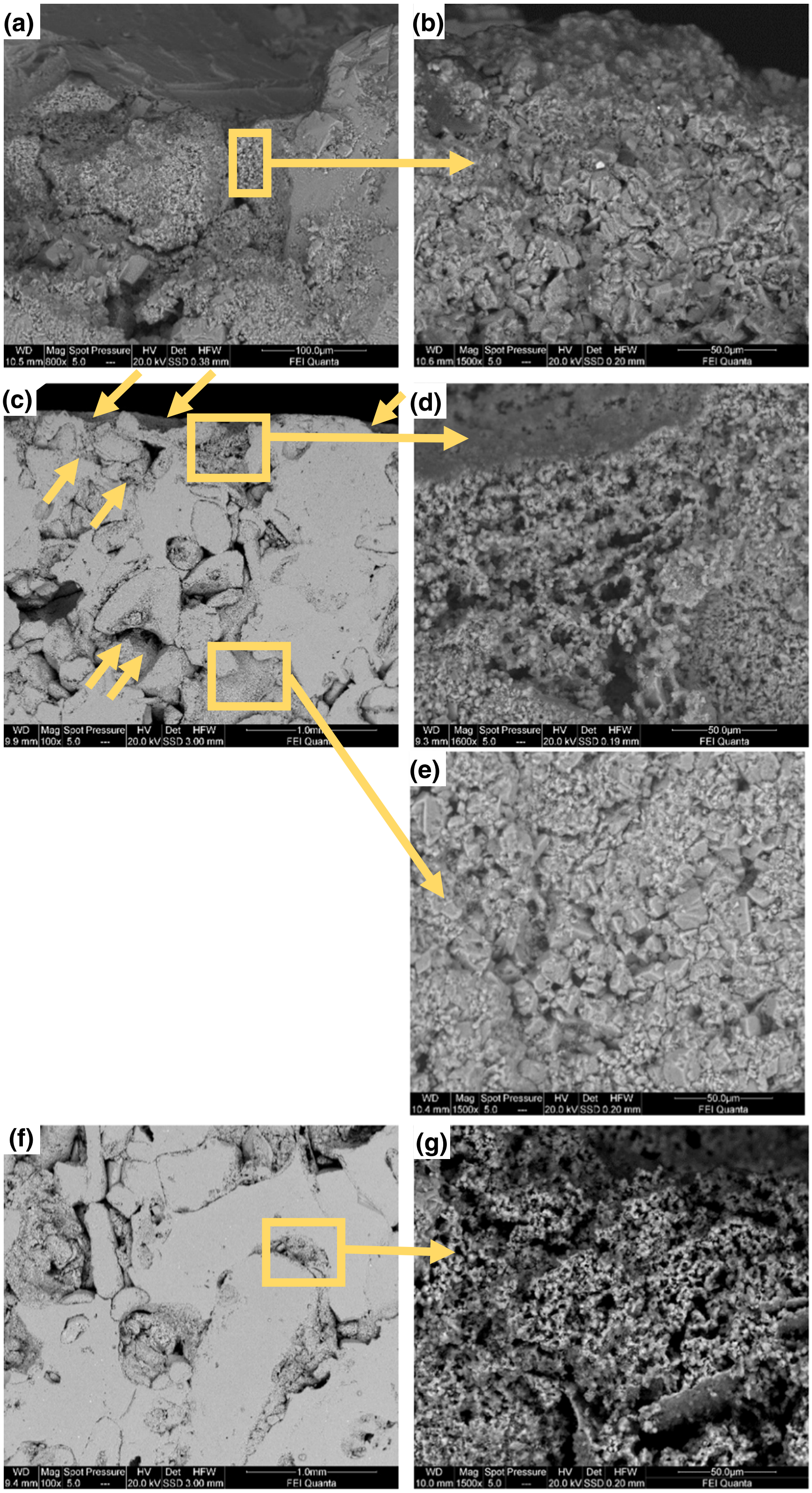
4 Conclusions

All samples treated by capillary absorption yielded the lowest increase in the surface stone density, surface cohesion and whitening on the surface regardless of the number of applications. This was attributed to the sedimentation rate of the particles of this type of nanolime due to their low colloidal stability, which might mitigate the ingress and deposition of particles in the pores during the absorption of the product. This result suggested that nanolime synthesized by anion exchange resins may not be applied by capillary absorption to enhance nanolime effectiveness.

Conversely, samples treated by spray and brush yielded similar results in terms of increasing values of stone density in the outer 1 cm, superficial cohesion, water absorption coefficient and superficial whitening regardless the number of applications. Samples treated by those methods where treatment was repeated 10 times, yielded slightly higher consolidation effectiveness in terms of: i) higher increase in surface stone´s density and surface cohesion; ii) decreasing values of water absorption coefficient while also obtaining high chromatic alterations (whitening). Whitening value could be significantly reduced if treated surfaces are gently wiped with a solvent dampened cloth immediately after the application to avoid the formation of superficial deposits of nanolime, as observed in other studies [59, 62]. Moreover, as also noticed in previous studies [39], surface whitening decreases after several cycles of RH/T without reducing the mechanical properties. Thus, the concerns regarding the aesthetic alteration are moderate. Results suggested that an application of low concentrated nanolime dispersion (i.e. 5 g/L) where the treatment is repeated up to 10 applications can certainly provide an effectiveness consolidation in terms of superficial cohesion and a slight increase of the stone density in the surface, which is noticeable up to a depth of 5–6 mm from the surface, which is in the line with previous studies. On the other hand, results also suggest that treatments by spray and brush where the application was one single saturation, yielded a lower increase of the stone density and surface cohesion, which it can be attributed to the lower amount of nanolime particles in the pores which provided lower consolidating effect.

Thus, results of this study show that a single application treatment of low concentrated nanolime (i.e. 5 g/L) does not significantly provide noticeable consolidation effectiveness regardless of the application method, contrary to what was commonly believed. These results suggest that for a noticeable consolidation treatment with low concentrated nanolime (i.e. 5 g/L) the application must consist of several applications (> 10).

Fig. 4 SEM micrographs of cross-sections of the control and the B10: **a** Control sample at 800×; **b** detail of control sample at 1500×; **c** B10 treated face (up) and penetration up to 2 mm at 100×; **d** detail of carbonated nanolime on B10 at 1600×; **e** detail of calcite originally from the stone on B10 at 1500×; **f** B10 at depth of 5–6 mm at 100×; **g** detail of B10 of carbonated nanolime at depth of 5–6 mm. Arrows indicate the presence of carbonated nanolime



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Compliance with ethical standards

Conflict of interest The authors declare that there is no conflict of interest and take a neutral position to offer an objective evaluation of the consolidation process.

References

1. Doehne E, Price CA (2009) Stone conservation: an overview of current research, Research in conservation series. Getty Conservation Institute, Los Angeles
2. Brajer I, Kalsbeek N (1999) Limewater absorption and calcite crystal formation on a limewater-impregnated secco wall-painting. Stud Conserv 44(3):145–156
3. Price C, Ross K, White G (1988) A further appraisal of the'Lime Technique' for limestone consolidation, using a radioactive tracer. IIC J Stud Conserv 33(4):178–186
4. Wheeler G (2005) Alkoxysilanes and consolidation of stone, Research in conservation Series. Getty Conservation Institute, Los Angeles
5. Salazar-Hernandez C, Zarraga R, Alonso S, Sugita S, Calixto S, Cervantes J (2009) Effect of solvent type on polycondensation of TEOS catalysed by DBTL as used for stone consolidation. J Sol-Gel Sci Technol 49:301–310
6. Mosquera MJ, Pozo J, Esquivias L (2003) Stress during drying of two stone consolidants applied in monumental conservation. J Sol-Gel Sci Technol 26:1227–1231
7. Pozo-Antonio, J.S., Otero J., Alonso P., Mas i Barberà X., (2019), Nanolime- and nanosilica-based consolidants applied on heated granite and limestone: effectiveness and durability Construction and Building Materials. 201, 20, 852-870
8. Sassoni E, Naidu S, Scherer GW (2011) The use of hydroxyapatite as a new inorganic consolidant for damaged carbonate stones. J Cult Herit 12(4):346–355
9. Sierra-Fernandez A, Gomez-Villalba LS, Rabanal ME, Fort R (2017) New nanomaterials for applications in conservation and restoration of stony materials: a review. Materiales de Construcción 67(325):e107
10. Dei L, Salvadori B (2006) Nanotechnology in cultural heritage conservation: nanometric slaked lime saves architectonic and artistic surfaces from decay. J Cult Herit 7(2):110–115
11. Daniele V, Taglieri G, Quaresima R (2008) The nanolimes in cultural heritage conservation: characterisation and analysis of the carbonatation process. J Cult Herit 9(3):294–301
12. Otero J, Charola AE, Grissom CA, Starinieri V (2017) An overview of nanolime as a consolidation method for calcareous substrates. GE Conserv 1(11):71–78
13. Rodriguez-Navarro C, Ruiz-Agudo E (2017) Nanolimes: from synthesis to application. Pure Appl Chem 90(3):523–550. https://doi.org/10.1515/pac-2017-0506
14. Baglioni P, Chelazzi D, Giorgi R et al (2014) Commercial $Ca(OH)_2$ nanoparticles for the consolidation of immovable works of art. Appl Phys A Mater Sci Process 114(3):723–732
15. Baglioni P, Chelazzi D, Giorgi R (2015) Nanotechnologies in the conservation of cultural heritage: a compendium of materials and techniques. Springer, New York
16. Sequeira S, Casanova C, Cabrita EJ (2006) Deacidification of paper using dispersions of $Ca(OH)_2$ nanoparticles in isopropanol. J Cult Herit 7:264–272
17. Giorgi R, Dei L, Ceccato M et al (2002) Nanotechnologies for conservation of cultural heritage: paper and canvas deacidification. Langmuir 18(21):8198–8203. https://doi.org/10.1021/la025964d
18. Natali I, Tempesti P, Carretti E et al (2014) Aragonite crystals grown on bones by reaction of CO_2 with nanostructured $Ca(OH)_2$ in the presence of collagen. Implications in archaeology and paleontology. Langmuir 30(2):660–668
19. Poggi G, Toccafondi N, Chelazzi D et al (2016) Calcium hydroxide nanoparticles from solvothermal reaction for the deacidification of degraded waterlogged wood. J Colloid Interface Sci 473:1–8
20. Ferreira Pinto AP, Delgado Rodrigues J (2012) Consolidation of carbonate stones: influence of treatment procedures on the strengthening action of consolidants. J Cult Herit 13:154–166
21. Sassoni E, Franzoni E, Scherer B, Pigino GW, Naidu S (2013) Consolidation of calcareous and siliceous sandstones by hydroxyapatite: comparison with a TEOS-based consolidant. J Cult Herit 14:103–108
22. Franzoni E, Graziani G, Sassoni E (2015) TEOS-based treatments for stone consolidation: acceleration of hydrolysis–condensation reactions by poulticing. J Sol-Gel Sci Technol 74(2):44–78
23. De Rosario I, Elhaddad F, Pan A, Benavides R, Rivas T, Mosquera MJ (2011) Effectiveness of a novel consolidant on granite: laboratory and in situ results. Constr Build Mater 76:140–149
24. Liu R, Han X, Huang X, Li W, Luo H (2013) Preparation of three-component TEOS-based composites for stone conservation by sol–gel processes. J Sol-Gel Sci Technol 68:19–30
25. Ferreira-Pinto AP, Delgado-Rodrigues J (2008) Hydroxylating conversion treatment and alkoxysilane coupling agent as pre-treatment for the consolidation of limestones with

ethyl silicate. In: Delgado-Rodriguez J, Mimoso JM (eds) Stone consolidation in cultural heritage: research and practice; proceedings of the international symposium, Lisbon. LNEC (Laboratorio National de Engenheria Civil), Lisbon, pp 41–52

26. Franzoni E, Gabriela Graziani G, Sassoni E, Bacilieri G, Lura M, Griffa O (2014) Solvent based Ethyl Silicate for stone consolidation: influence in the application technique on penetration depth, efficacy and pore occlusion. Mater Struct 248:3503–3515
27. Pinna D, Salvadori B, Porcinai S (2011) Evaluation of the application conditions of artificial protection treatments on salt-laden limestones and marble. Constr Build Mater 25:2723–2732
28. Snethlage R, Wendler E, Sattler L (1990) The application of laboratory processes and studies to real structures. In: Proceedings of the workshop analytical methodologies for the investigation of damaged stones, Pavia
29. Maravelaki-Kalaitzaki P, Kallithrakas-Kontos N, Agioutantis Z, Maurigiannakis S, Korakaki DA (2008) Comparative study of porous limestones treated with silicon-based strengthening agents. Prog Org Coat 62:49–60
30. Tulliani JM, Formia A, Sangermano M (2011) Organic-inorganic material for the consolidation of plaster. J Cult Herit 12:364–371
31. Mundronja D, Vanmeert F, Hellemans K, Fazinic S, Janssens K, Tibljas D, Rogosic M, Jakovljevic S (2013) Efficiency of applying ammonium oxalate for protection of monumental limestone by poultice, immersion and brushing methods. Appl Phys A 111:109–119
32. Franzoni E, Pigino B, Leemann A, Lura P (2014) Use of TEOS for fired-clay bricks consolidation. Mater Struct 47(7):1175–1184
33. Drdácký M, Slížková Z, Ziegenbalg G (2009) A nano approach to consolidation of degraded historic lime mortars. J Nano Res 8:13–19
34. Arizzi A, Gomez-Villalba LS, Lopez-Arce P et al (2015) Lime mortar consolidation with nanostructured calcium hydroxide dispersions: the efficacy of different consolidating products for heritage conservation. Eur J Miner 27(3):311–323
35. Slizková Z, Frankeová D (2012) Consolidation of porous limestone with nanolime laboratory study. In: 12th International congress deterioration and conservation of stone. New York, 2012. http://iscs.icomos.org/cong-12.html
36. Otero J, Starinieri V, Charola AE (2019) Influence of substrate pore structure and nanolime particle size on the effectiveness of nanolime treatments. J Constr Build Mater 209:701–708
37. Taglieri G, Daniele V, Del Re G, Volpe R (2015) A new and original method to produce $Ca(OH)_2$ nanoparticles by using an anion exchange resin. Adv Nanopart 4:17–24
38. Daniele V, Taglieri G, Macera L et al (2018) Green approach for an eco-compatible consolidation of the agrigento biocalcarenites surface. Constr Build Mater 186:1188–1199
39. Otero J, Starinieri V, Charola AE (2018) Nanolime for the consolidation of lime mortars: a comparison of three available products. J Constr Build Mater 181:394–407
40. Otero J, Starinieri V, Charola AE, Taglieri G (2020) Influence of different types of solvent on the effectiveness of nanolime treatments on highly porous mortar substrates. Constr Build Mater 230:117112
41. Otero J, Charola AE, Starinieri V (2019) Sticky rice–nanolime as a consolidation treatment for lime mortars. J Mater Sci 54(14):10217–10234
42. Taglieri G, Otero J, Daniele V et al (2017) The biocalcarenite stone of agrigento (Italy): preliminary investigations of compatible nanolime treatments. J Cult Herit 30:92–99
43. Gherardi F, Otero J, Blakeley J, Colston B, (2019) Application of nanolimes for the consolidation of Limestone from the Lincoln Medieval Bishop’s Palace. Studies in Conservation. IIC 2020 Edinburgh Congress special issue (in-press)
44. Rodriguez-Navarro C, Bettori I, Ruiz-Agudo E (2016) Kinetics and mechanism of calcium hydroxide conversion into calcium alkoxides: implications in heritage conservation using nanolimes. Langmuir 32(20):5183–5194
45. Taglieri G, Daniele V, Macera L, Mondelli C (2017) Nano $Ca(OH)_2$ synthesis using a cost-effective and innovative method: reactivity study. J Am Ceram Soc 100:5766–5778
46. UNE-EN 15801 (2009) Conservation of cultural property—test methods—determination of water absorption by capillarity
47. Greenspan L (1977) Humidity fixed points of binary saturated aqueous solutions. J Res Natl Bur Stand 81A:89–96
48. BRE Digest 405, DG405, ISBN 1-86081-015-2, Phenolphthalein test, Carbonation of concrete and its effect on durability
49. UNE-EN 1936 (2007) Natural stone test methods—determination of real density and apparent density, and of total and open porosity
50. ASTM C 67-00: Standard Test Methods for Measuring Apparent Porosity at atmospheric pressure (2000) ASTM
51. EN 13755 (2008) The English Standard for Natural stone test methods. Determination of water absorption at atmospheric pressure
52. Desarnaud J, Kiriyama K, Bicer Simsir B, Wilhelm K, Viles H (2019) A laboratory study of Equotip surface hardness measurements on a range of sandstones: what influences the values and what do they mean? Earth Surf Proc Land 44(7):1419–1429
53. ASTM D3359-02: Standard Test Methods for Measuring Adhesion by Tape Test (2002), ASTM International, 10 August
54. Drdácký M, Lesák J, Rescic S et al (2012) Standardization of peeling tests for assessing the cohesion and consolidation characteristics of historic stone surfaces. Mater Struct 45:505–520. https://doi.org/10.1617/s11527-011-9778-x
55. CIE Publication 15-2, Colorimetry CIE Central Bureau, Vienna (1986)
56. CIE S014–4, E:2007Colorimetry Part 4: CIE (1976) L*a*b* Colour Space, Commission Internationale de l’eclairage. CIE Central Bureau, Vienna, p 2007
57. Sanmartín P, Ferrer P, Cárdenes V, Martínez-Verdú F, Silva B, Prieto B (2010) El color de las rocas ornamentales: comparación de las metodologías de determinación en granitos y pizarras (The colour of ornamental rocks: comparison of determination methodologies in granites and slates). In: IX Congreso Nacional del Color: Alicante, 29–30 June, 1–2 July 2010. San Vicente del Raspeig:

Publicaciones de la Universidad de Alicante, pp 433–436. ISBN: 978-84-9717-144-1

58. Rivas T, Matías JM, Taboada J, Ordóñez C (2011) Functional experiment design for the analysis of colour changes in granite using new L*a*b* functional colour coordinates. J Comput Appl Math 235(16):4701–4716. https://doi.org/10.1016/j.cam.2010.08.005
59. Borsoi G, Lubelli B, van Hees R et al (2016) Optimization of nanolime solvent for the consolidation of coarse porous limestone. Appl Phys A 122:846–859. https://doi.org/10.1007/s00339-016-0382-3
60. Pesce C, Moretto LM, Orsega EF, Pesce GL, Corradi M, Weber J (2019) Settings open access article effectiveness and compatibility of a novel sustainable method for stone consolidation based on di-ammonium phosphate and calcium-based nanomaterials. Materials 12(18):3025. https://doi.org/10.3390/ma12183025
61. Charola AE, Wendler E (2015) An overview of the water-porous building materials interactions. Restor Build Monum J 21(2–3):55–63
62. Borsoi G, Lubelli B, Van Hees RPJ et al (2015) Understanding the transport of nanolime consolidants within Maastricht limestone. J Cult Herit. https://doi.org/10.1016/j.culher.2015.07.014
63. Mokrzycki W, Tatol M (2011) Colour difference dE—a survey. Mach Graph Vis 20:383–411
64. Rodrigues JD, Grossi A (2007) Indicators and ratings for the compatibility assessment of conservation actions. J Cult Herit 8:32–43