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DOI
10.1016/j.conbuildmat.2017.03.097

Publication date
2017

Document Version
Final published version

Published in
Construction and Building Materials

Citation (APA)
Borsoi, G., Lubelli, B., van Hees, R., Veiga, R., & Santos Silva, A. (2017). Evaluation of the effectiveness and compatibility of nanolime consolidants with improved properties. *Construction and Building Materials*, *142*, 385-394. https://doi.org/10.1016/j.conbuildmat.2017.03.097

Construction and Building Materials 142 (2017) 385–394

Contents lists available at ScienceDirect

Construction and Building Materials

journal homepage: www.elsevier.com/locate/conbuildmat

Evaluation of the effectiveness and compatibility of nanolime consolidants with improved properties

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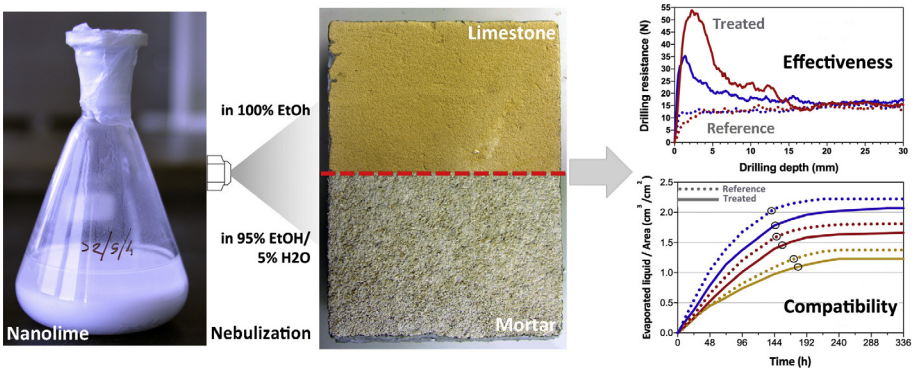
HIGHLIGHTS

- Recover the cohesion loss of limestone and lime-based mortar through compatible nanolime consolidants.
- Synthesis and characterization of new nanolimes, dispersed in different solvents.
- Solvent modification to improve in-depth deposition and effectiveness of nanolimes.
- Evaluation of the mechanical effectiveness and physical compatibility of the nanolime treatment.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 27 November 2016
Received in revised form 2 March 2017
Accepted 11 March 2017
Available online 19 March 2017

Keywords:
Consolidation
Nanolime
Calcareous substrates
Compatibility
Effectiveness

ABSTRACT

Surface consolidation is a common practice in the conservation of the built heritage. However, the effectiveness of consolidation of calcareous materials is often doubtful, due to the lack of effective and compatible consolidation products. Dispersions of calcium hydroxide nanoparticles in alcohol, the so-called *nanolimes*, can recover the superficial consolidation of calcareous substrates. Nevertheless, they are often not able to guarantee an in-depth consolidation.

Previous research by the authors has demonstrated that the effectiveness of nanolime can be improved by fine-tuning the properties and the application protocol of the dispersions, based on the moisture transport properties of the material to be treated.

In this paper, we verify the consolidation effectiveness and physical compatibility of the developed nanolimes, when applied on coarse porous calcareous materials like Maastricht limestone and lime-based mortars. The results show that a suitable mass consolidation can be achieved with nanolimes, while maintaining a good compatibility with the substrate material.

1. Introduction

A significant part of the Built Heritage is constituted by calcareous and lime-based materials, which have demonstrated their durability over the centuries. These materials, however, may be subjected to degradation phenomena (e.g. salt crystallization, frost action, biological growth) that can lead to surface decay [1]. Powdering, sanding and chalking are among the most common decay patterns of calcareous materials [2,3]. This implies the loss of cohesion and thus of mechanical strength [4]. The mechanical properties of deteriorated materials can be recovered through the

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http://dx.doi.org/10.1016/j.conbuildmat.2017.03.097
0950-0618/

application of a consolidation treatment [4]. This intervention is meant to recover the cohesion of the grain structure and so the adhesive forces across the mineral surfaces by introducing a new binding agent and forming organic or inorganic bridges [3,4].

A consolidation treatment should fulfil three main requirements: effectiveness (i.e. improvement of the mechanical strength), compatibility (with the treated substrate) and durability (resistance to different damage mechanisms) [2,4,5]. A treatment can be considered compatible if it does not lead to technical (material) or aesthetic damage to the historical materials and is at the same time as durable as possible [2]. More specifically, the consolidant product should have a short- and long-term stability and decay patterns due to a differential aging between the consolidated and unconsolidated areas of the substrate should be avoided.

Organic consolidant products (e.g. acrylics and epoxy resins) are easy to apply, flexible, and have good adhesion to the substrate, but they often lack physical-chemical compatibility with the substrate [6]. TEOS-based (tetraethyl orthosilicate) and silica-precursor consolidant products (e.g. ethyl silicate), widely used for the consolidation of stone and mortars, can penetrate deeply into porous materials, but have low chemical compatibility with calcareous substrates, showing in some cases also low effectiveness and durability [2,4,5,7]. In fact, they form disordered lattices of tetracoordinated silica, with poor chemical bonding to calcitic substrates and tendency to shrink and crack during drying [8].

Inorganic consolidants (e.g. lime-based or barium-based treatments) are a suitable alternative to organic compounds, thanks to their compatibility with calcareous substrates and good durability [5,9,10]. Limewater is the most traditional consolidant product, with full chemical compatibility with lime-based substrates [11]; however, limewater has low effectiveness and, due to the low solubility of $Ca(OH)_2$ in water [5,9], a large number of applications is necessary. Additionally, limewater has often low penetration and the lime deposited within the treated surface shows sometimes low or incomplete carbonation.

In the last two decades, the progresses in colloid science have introduced new nanostructured materials with improved properties. Among them, the so-called nanolimes, i.e. dispersions of lime nanoparticles in alcohols, have acquired an increasing interest due to their consolidating properties and physical-chemical compatibility with calcareous materials [12]. The consolidation effectiveness and material strengthening is obtained thanks to the penetration of the calcium hydroxide nanoparticles into the treated material and their subsequent carbonation [11].

Nanolime dispersions are opal fluids containing stable calcium hydroxide nanoparticles, with spherical to hexagonal shape and a size ranging from 50 to 600 nm, dispersed in an alcoholic medium [12–15]. The high active surface of the nanoparticles ensures a high reactivity, and the alcoholic solvent a high stability and lime concentration, thus providing a proper consolidating action [16].

Nanolimes have proven to recover the superficial cohesion of many different materials [12,13,16,17], but they often show a poor effectiveness when mass consolidation is required, like for example in the case of decayed plasters, renders or lithotypes [1,17,18]. In fact, lime nanoparticles may sometimes deposit or partially migrate back towards the surface during drying, resulting in a poor consolidating effect in depth [1].

Previous research by the authors [19,20] suggests that the use of binary solvent mixtures (e.g. ethanol and water) can enhance a more homogeneous nanoparticles in-depth deposition in highly and coarse porous calcareous substrates. Nanolimes can thus be tailored for a specific substrate by fine-tuning their solvent. According to this approach, dispersions with lower stability and higher drying rate should be preferred for application on substrates with very fast moisture transport properties (and thus with higher total porosity and coarse pore size distribution), in order to improve in-depth deposition. The application procedure is another crucial factor that has been previously studied [21] and that should be taken in account for an optimal result.

In this paper, we verified the effectiveness and compatibility of freshly synthetized nanolimes (Section 2.2) when applied on highly porous calcareous substrates: Maastricht limestone (sound and weathered) and a lime-based mortar (Sections 2.1 and 3.1). Based on previous research [19–21], pure ethanol was selected as solvent for the nanolime to be applied on specimens of sound and weathered Maastricht limestone, and a binary mixture of solvents (95% ethanol-5% water) was used in the case of application on lime-based mortars (Section 4.1). Both nanolime dispersions were applied by nebulization, a methodology widely used in practice (Section 3.2).

The mechanical effectiveness of the consolidation action in depth was assessed by measuring the hardness of the substrate, before and after consolidation, by means of Drilling Resistance Measurement System (DRMS) (Sections 3.4 and 4.3). The compatibility of the treatment was evaluated by measuring the effect of the consolidant on the moisture transport properties (water absorption and drying kinetics, Sections 3.5 and 4.4), on the total porosity by immersion (or open porosity, Sections 3.3 and 4.2) and on the aesthetic properties of the substrates (macro-evaluation by NCS scale, Sections 3.6 and 4.5).

2. Materials

2.1. Substrates

Nanolime consolidants have been tested on both sound and weathered Maastricht limestone and on lime based mortar.

2.1.1. Maastricht limestone

Maastricht limestone is a building material quarried and mainly used in the Belgian and Dutch provinces of Limburg. It is a soft, highly pure (≈95% $CaCO_3$) limestone, with high-porosity (50%) and a unimodal pore size distribution (35–40 μm) [21–23]. Despite its good durability, it may in some cases show decay in the form of loss of cohesion at the surface (e.g. powdering) [24]. The Maastricht limestone used in this research comes from the quarry of Sibbe, in the Netherlands.

The effectiveness of the nanolimes was verified also on weathered Maastricht limestone, from the medieval Castle of Keverberg, situated in the village of Kessel (North Limburg, Netherlands). These blocks, which show a severe weathering of the surface (i.e. powdering), were recently removed from the external façade of the castle during a restoration campaign. The porosity of this weathered limestone was investigated as reported in Section 3.3.

2.1.2. Lime-based mortar

Lime-based mortar specimens were prepared using a commercial CL90 hydrated lime (H100 by Lusical, Portugal) and a siliceous sand. The sand used was a mixture of three different, calibrated sands (by Areipor, Portugal), in proportion 0.66:1:1 (in volume), as presented in Ref. [6]. A binder/aggregate ratio 1:4 in volume was chosen in order to obtain a weak mortar with a high porosity, similar to an old render needing consolidation [6,25]. A water:binder ratio of 2:1 (in mass) was adopted for this mortar in order to obtain an optimal workability, in accordance with EN 1015-3 [26]. The lime-based mortar has a high porosity (29%), with a heterogeneous pore size distribution, including meso (0.2–1 μm), macro (20–100 μm) and coarse pores (100–400 μm). The high total porosity and the presence of a large volume of coarse pores (≈20% of the pores >100 μm) indicates that this mortar can simulate an altered and decayed plaster or render [21].

Table 1
Overview on the tests performed on different specimen types and number of replicates.

Test procedure	Material, number and size of specimen	
	Sound and Weathered Maastricht limestone	Lime-based mortar
Open porosity	3 (samples with size 2 × 1 cm)	3 (samples with size 2 × 1 cm
DRMS	10 measurements on 1 block (size 15 × 15 × 4 cm)	10 measurements on 1 mortar applied on brick (size 29 × 17 × 2 cm)
Absorption and drying kinetics	3 (core specimens size 4 × 4 cm)	3 (prismatic specimens size 4 × 4 cm)
NCS Scale	10 measurements on 1 on block (size 15x15x4 cm)	10 measurements on 1 mortar applied on brick with size 29x17x2 cm
Optical microscopy	10 observations on 1 on block (size 15 × 15 × 4 cm)	10 observations on 1 mortar applied on brick with size 29 × 17 × 2 cm

2.2. Synthesis and solvent selection of nanolime

Lime nanoparticles were synthetized, as described in Refs. [19,20]. Ethanol (p.a. 99.5% by Sigma-Aldrich) and distilled water (conductivity < 2 μs/cm) were selected as solvents, based on the results obtained in previous works [1,21]. Ethanol is a highly volatile solvent and can guarantee a high kinetic stability to the dispersion, whereas water has a higher boiling point and higher surface tension, which results in a low kinetic stability.

Based on results obtained in previous research [19–21], two nanolime consolidants were selected: a nanolime dispersed in pure ethanol (identified as E100) for the treatment of the sound and weathered limestone, and a nanolime dispersed in an ethanol (95%)–water (5%) mixture, identified as E95H5, for application on lime-based mortars specimens. In the latter case, the addition of small amount of water is known to guarantee a moderate kinetic stability, sufficient for the nanolime to be properly absorbed. Thus, when the necessary absorption depth is reached, the decreased kinetic stability can favour nanolime precipitation in depth and avoid back transport to the drying surface [20].

3. Methods

3.1. Specimen preparation

Cylindrical specimens (diameter: 4 cm, height: 4 cm) and prismatic blocks (15 cm side, 4 cm height) were drilled or cut from sound Maastricht limestone blocks. Cubic specimens (diameter: 4 cm, height: 4 cm) and prismatic blocks (15 cm side, 4 cm height) were cut from bigger blocks of weathered Maastricht limestone. Both the sound and weathered limestone blocks were covered on the lateral sides with an epoxy resin (Wapex 105 by Sikkens, The Netherlands), in order to avoid any percolation of the dispersion or evaporation of the solvent from the lateral sides.

Prismatic mortar specimens (16 × 4 × 4 cm) of lime-based mortars were produced and cut in cubes of 4 cm side. In addition, a single mortar layer of 1.5 cm thickness was applied on fired-clay bricks (28 × 19 × 4 cm). All specimens were stored under controlled conditions (T = 20 °C, 65% RH) for more than 1 year.

The type of specimens and number of replicas used in the different tests (described in the next sections) is resumed in Table 1.

3.2. Application of nanolime

Nanolimes were applied by nebulization, an application method commonly adopted in the practice of conservation [9]. The application protocol was optimized in order to reach a good penetration and deposition in depth, as described in Ref. [21].

Application by nebulization was carried out with a trigger spray nozzle, calibrating the nanolime necessary depending on the substrate. The amount of nanolime used for a single nebulization application was 0.787 ± 0.052 L/m^2 for sound and weathered limestone and 0.779 ± 0.022 L/m^2 for mortar respectively. The nebulization was repeated up to 10 consecutive applications, in order to improve the consolidation effect. The interval between consecutive applications was defined at 48 h, as within this interval an almost complete evaporation of the alcoholic solvent is achieved [1,21]. This timespan can guarantee a deposition of the nanoparticles within the porous network and so avoid that the excess of solvent between consecutive applications would influence the deposition of the nanoparticles.

The applications were performed under controlled conditions (50% RH, T = 20 °C, air speed <0.1 m/s). The treated specimens were then stored at 65% RH, T = 20 °C, air speed <0.1 m/s for over 3 months, in order to enhance the carbonation of the nanoparticles. In fact, the carbonation of the $Ca(OH)_2$ nanoparticles and thus the strengthening effect on the treated substrates is speeded up at RH > 50% [27]; higher RH conditions give rise also to the formation of $CaCO_3$ polymorphs (e.g. vaterite, aragonite, calcite and monohydrocalcite – MHC or amorphous calcium carbonate – ACC) with higher crystallinity and particle size [28–30], when compared to the polymorphs obtained at lower RH (<50%).

3.3. Measurement of the pore filling

The degree of pore filling due to consolidation influences the moisture transport behaviour of the treated material and it may thus negatively affect damage processes like salt crystallization and freeze-thaw.

A first, indicative degree of pore filling was calculated based on the following assumptions:

- at the used T and RH of curing of the treated specimens (20 °C/65% RH), stored for over 3 months, the formation of mainly of calcite is expected, as well as other anhydrous (aragonite and vaterite) and hydrated (MHC and ACC) polymorphs of $CaCO_3$ [29–31]. However, ACC is an instable and transition phase [30] and it will be converted into anhydrous polymorphs.
- the density of calcite (2711 g/cm^3) and that of vaterite (2645 g/cm^3) are comparable, whereas aragonite (2944 g/cm^3) and MHC (2241 g/cm^3) have different values. Thus, the degree of pore filling in the treated substrate was obtained by considering the polymorph with the lower density (MHC) and that with the higher density (aragonite). This range of values can be representative of all the possible polymorph formations.
- All the nanolime particles deposit in the outer 20 mm of the specimen.

The calculated values were then compared to the measured values in order to assess the degree of pore filling due to consolidation. Open porosity tests were thus carried out on the substrates before and after consolidation was measured, according to [31].

Samples were dried in an oven at 60 ± 5 °C for 24 h, till constant mass. After drying to constant mass (M1), the samples were put within an evacuation vessel, applying a pressure of 400 mbar for 24 h, in order to eliminate the air contained in the pores of the samples. Distilled water (at T = 20 °C) was then slowly introduced into the vessel, maintaining afterwards the vacuum for additional

24 h. The samples were then stabilized and maintained at atmospheric pressure for additional 24 h. Finally, the samples were weighed immersed in water (hydrostatic weighting, M2), and, after a quick wipe with a shammy cloth, in air (M3).

The open porosity values (vol %) of the treated and untreated substrates were calculated (in %), using the following equation:

$$\text{Open Porosity}\,(\%) = \frac{M3 - M1}{M3 - M2} \times 100 \quad (1)$$

Measurements were carried out in threefold. In the case of the treated substrates, samples were collected in the outer layer of the specimens (0–20 mm from the treated surface), in order to be representative of the treated area.

3.4. Assessment of the consolidation effectiveness by DRMS

The consolidation action in terms of in-depth strength increase was assessed by Drilling Resistance Measurement System (DRMS). This method is generally considered suitable for evaluating the consolidation performance, particularly in soft stones [32–34].

The test consists of drilling a hole at a defined constant revolution speed x (rpm) and constant penetration rate v (mm/min), and measuring the penetration force needed as function of depth [32,33].

Drilling tests were performed with the drilling device DRMS Cordless, developed bySINT Technology (Italy) [35]. The drilling machine is equipped with two precision motors able to keep a predefined rotation speed and to guarantee a predefined penetration rate [34]. The force, F_d (N), which corresponds to the thrust to be exerted on the drill to drive the bit [33], is measured continuously by a load cell and a graph showing the force versus depth is displayed after the test [35].

A drill bit of 5 mm diameter and made with the application of a polycrystalline diamond plaque was adopted [35]. All acquired data are memorized and can be processed with a dedicated software.

All tests were performed on both limestone and lime-based mortars with the same drilling parameters (v/ω = 40/40 mm/min/rpm), which were defined by previous tests [23]. Holes were drilled up to 30 mm in the case of the Maastricht limestone, 16 mm for the lime-based mortars, thus over the penetration depth of the nanolime and the depth where consolidation effect of the treatment might be expected.

DRMS measurements were carried out on twofold in all the treated and untreated substrates (sound and weathered limestone, mortar) performing 10 drillings in every specimen. In the case of the Maastricht limestone, the average of these measurements was used as criterion to assess the mechanical strength improvement (Table 2). The increase of the drilling resistance can be easily analyzed by comparing the resistance profiles before and after treatment [32]. Besides, DRMS measurements on weathered Maastricht limestone specimens from the site, before and after treatment, allowed to verify the penetration depth of the consolidant on weathered stone but also to assess the compatibility of the consolidation effect. The consolidation effect can be defined as optimal (the consolidated weathered material has a strength, F_{cw}, comparable to that of the sound stone, F_s), insufficient ($F_{cw} \ll F_s$) or excessive ($F_{cw} \gg F_s$) [2].

In the case of the mortar, the use of DRMS poses some problems in relation to the interpretation of the data. In fact, lime-based mortars are materials composed of aggregates (usually harder than the paste), paste (which includes binder crystals and voids) and the interface between aggregates and paste (usually called the interfacial transition zone, ITZ) [33]. The high heterogeneity of the mortars and the systematic presence of abrasive components (especially quartzite aggregates) complicate the interpretation of the DRMS data. Thus, a direct comparison of DRMS profiles before and after consolidation can hardly be done, given the extreme background noise introduced by the high resistance peaks of the quartz aggregate particles [36].

A typical profile of a soft mortar has a baseline with forces varying within a more or less narrow band and a series of intercalated peaks with significantly higher values: the baseline can be attributed to the binding matrix, while the peaks are due to the presence of the aggregate [36]. A method for the elaboration of DRMS data measured on mortar has been recently proposed by Delgado Rodrigues & Costa [36]. This method splits the drilling profile in several segments, which are then analysed independently. An algorithm, which excludes the high picks that are attributed to the aggregate, is used for the analysis of the consolidated mortars: only the lowest values are considered and averaged. Following this approach, we considered segments of 2 mm, which consist of 20 measurements (one each 0.1 mm) registered by the software. Within this 2 mm segment, the 5 lowest values were selected (25th percentile) and then averaged. Finally, the averages of the lowest picks of every segment are plotted in one graph, allowing the comparison between a treated and an untreated lime-based mortar. In addition, we considered 10 different drilling measurements and averaged the force values obtained from the lowest peaks of every segment of every drilling measurement, in order to evaluate the consolidation action on a wider scale.

3.5. Measurement of the water absorption and drying

The water absorption and drying kinetics of the sound and weathered Maastricht limestone and of the lime-based mortar specimens were measured before and after the treatment with nanolime, in order to assess the compatibility of the treatments.

The capillary absorption of water in the sound (core specimens 4 cm diameter and 4 cm height) and weathered (cubic specimens of 4 cm side) Maastricht limestone, and in the lime-based mortar specimens (cubic specimens of 4 cm side) was measured; the water absorption coefficient (WAC) was calculated according to EN 15801 [37]. The specimens, sealed with Parafilm M (by Bemis NA, USA) on the lateral sides, were partially immersed with their

Table 2
Properties of the substrates and details of the relative DRMS measurements.

Substrate	Properties	Consolidation	DRMS parameters	Type of DRMS analysis
Sound Maastricht limestone	Undamaged blocks (15 × 15 × 4 cm) from quarry	Untreated block Block treated with E100	v/ω = 40/40 mm/min/rpm, 30 mm in depth	Average of 10 drilling measurements (on the same block)
Weathered Maastricht limestone	Blocks with weathered surface (15 × 15 × 4 cm), from Keverberg Castle	Untreated block Block treated with E100		
Lime-based mortar	Mortar layer (29 × 17 × 1.5 cm) applied on brick substrate	Untreated specimen Specimen treated with E95H5	v/ω = 40/40 mm/min/rpm, 16 mm in depth	Average of the lowest values of every 2 mm segment of 10 drilling measurements (on the same block)

Table 3
Total amount of nanolime dispersion and nanoparticle content absorbed, and foreseen porosity reduction in the treated part of the substrates.

Substrate	Nanolime	Nanolime dispersion absorbed ± standard deviation (L/m^2)	Lime nanoparticle content* (kg/m^3)
Sound Maastricht limestone	E100	5.516 ± 0.223 (7 applications)	0.689 (7 applications)
Weathered Maastricht limestone	E100	7.548 ± 0.201 (10 applications)	0.924 10 applications)
Lime-based mortar	E95H5	7.797 ± 0.216 (10 applications)	0.981 (10 applications)

* This amount has been calculated considering the penetration depth of the nanolime (20 mm in all the substrates).

treated side in a petri dish, filled with water and with a grid on the bottom. During the absorption process, the specimen weight was measured until saturation was reached.

Once saturated, the specimens were allowed dry through the treated surface; the drying rate was evaluated by measuring the weight loss over time, in accordance with EN 16322 [38].

The absorption and drying tests were carried out in threefold and performed under controlled conditions (50% RH, T = 20 °C, air speed < 0.1 m/s).

3.6. Evaluation of chromatic alteration

In order to assess any possible chromatic alteration (e.g. whitening) due to the nanolime treatment, treated and untreated specimens were visually observed and photographs were taken, using a WX220 Compact Camera (by Sony, Japan). Chromatic variations on the treated specimens were evaluated with the NCS (Natural colour System) Scale [NCS].

In addition, the surface of treated and untreated specimens was observed with a stereomicroscope Zeiss Stemi SV 11. Images were recorded with a Zeiss AxioCam MRc5 digital microscopy camera. The AxioVision 4.8 software and its interactive measurement tools were used to record and analyze the specimens.

4. Results and discussion

4.1. Absorption of nanolime dispersions

The nanolime dispersions were nebulized till any white haze was macroscopically visible on the treated surface, up to maximum 10× applications. In the case of the sound limestone, 7 applications were performed, as after this number of applications a white haze appeared on the treated surface. In the case of the weathered limestone and of the lime-based mortar, 10 nanolime applications were performed, and no whitening was macroscopically observed on the treated substrates.

The optimal interval between application by nebulization was defined at 48 h, as an almost complete evaporation of the alcoholic solvent (≈90%, in volume) is achieved within this timespan. This procedure can avoid that the excess of solvent from previous applications would favour the migration of the nanoparticles back towards the surface during drying [1].

The amount of E100 and E95H5 nanolime dispersions (L/m^2) absorbed at each application by specimens of Maastricht limestone (both sound and weathered from Kessel) and of lime-based mortar is given in Table 3.

A similar amount of nanolime dispersion was absorbed at each application by the specimens.

In the case of the sound Maastricht limestone (7 applications), the specimens absorbed between 8.21 L/m^2 (1st application) and 7.42 L/m^2 (7th application) of E100 nanolime. The calculated content of lime nanoparticles, expressed as the weight of product per volume (kg/m^3), after 7 applications is 0.689 kg/m^3 (Table 3).

The weathered limestone specimens (10 applications) absorbed between 7.81 L/m^2 (1st application) and 7.23 L/m^2 (10th application) of E100 nanolime dispersion. The final content of lime nanoparticles deposited in the stone is considerably higher (0.924 kg/m^3) when compared to that of the sound limestone, due to the higher number of applications.

Lime-based mortars (10 applications) absorbed between 8.11 L/m^2 (1st application) and 7.54 L/m^2 (7th application) of E95H5 nanolime, resulting in a lime nanoparticle content of 0.981 kg/m^3.

4.2. Pore filling

Nanolime, like other consolidation treatments, is expected to partially fill the pores of a material and lead thereby to a small reduction of its porosity. First, an indicative measure of the degree of pore filling has been calculated, based on the assumptions mentioned in Section 3.3. Then the actual degree of pore filling has been experimentally assessed by means of open porosity tests. Calculated and measured data are reported in Table 4.

It can be observed that for all substrates the calculated pore filling is higher than the actual pore filling measured in the specimens. This difference might be due to the nanolime penetration also partially deeper than the outer 20 mm (layer considered in the calculation).

When considering the measured data, it can be observed that:

- the open porosity of the untreated sound limestone (around 47%) is higher than that of the untreated weathered limestone (44.7%). This can be justified either by natural differences between Maastricht stone quarried in different times or by the partial occlusion of the pores at the very surface of the weathered limestone due to calcite dissolution/re-precipitation processes, typically found with this coarse porous limestone [24], especially when exposed to weathering.
- both the treated sound and weathered limestone show a small reduction of the total porosity (respectively around 2% and 3%). In the case of the lime-based mortar specimens, the reduction of the total porosity is higher (4.6%) than that of the treated limestone specimens.

4.3. Effectiveness of consolidation – DRMS results

When analysing the sound Maastricht limestone, the untreated specimen has a homogeneous matrix with strength values of 12–15 N (Fig. 1).

The block treated with E100 shows a remarkable increase of the mechanical strength (varying between 20 and 80%) in the treated layer. The penetration depth of the treatment is about 18 mm. The highest strength values were measured in the outer 2–4 mm, showing an over-strengthening at this depth.

When analysing the untreated weathered Maastricht limestone block (Fig. 1), it is possible to observe that the outer 4 mm show a lower strength, due to weathering.

Table 4
Open porosity (%) of treated and untreated substrates and comparison measured/calculated pore filling.

Substrate	Mean Open porosity ± standard deviation (%)	Measured pore filling (porosity untreated – porosity treated) (%)	Calculated pore filling (%) due to treatment*
Untreated sound Maastricht limestone	47.02 ± 0.08	+2.16	+2.64/3.74
Treated sound Maastricht limestone	44.86 ± 0.24		
Untreated weathered Maastricht limestone	44.71 ± 0.25	+3.03	+3.43/4.51
Treated weathered Maastricht limestone	41.68 ± 0.59		
Untreated lime-based mortar	30.57 ± 0.21	+4.62	+5.51/6.71
Treated lime-based mortar	25.94 ± 0.04		

* This range of value has been calculated by considering the nanoparticle content in the treated layer, the porosity of the substrates, the carbonation of calcium hydroxide (which implied a volume improvement of around 37%) and the density of the $CaCO_3$ polymorph with the lower density (MHC, 2241 g/cm^3) and that with the higher density (aragonite, 2944 g/cm^3).

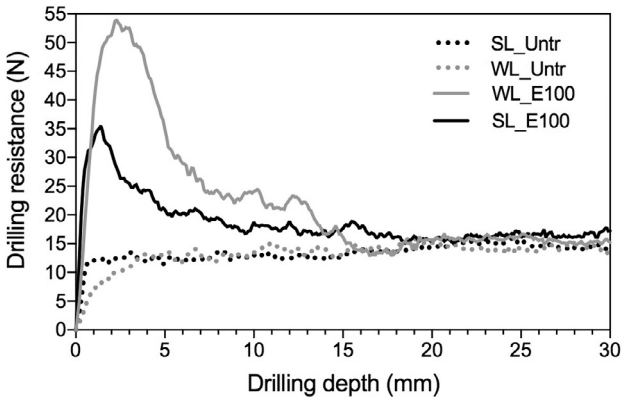

Fig. 1. Drilling resistance profile of sound and weathered Maastricht limestone, untreated (dashed line) and treated with E100 (solid line). All profiles are an average of 10 measurements.

E100 treatment (10×) results in a notable consolidation effect within the weathered limestone, up to 15 mm in depth. Also in this case the highest increase in strength is measured in the outer layer (6 mm).

When comparing the strength of the weathered layer after consolidation with the strength of the not weathered stone (in the depth of the same block), it is possible to conclude that the nanolime treatments, although very effective, has strengthened too much the outer layer of the stone. In this case a lower number of applications would have led to a more compatible consolidation effect.

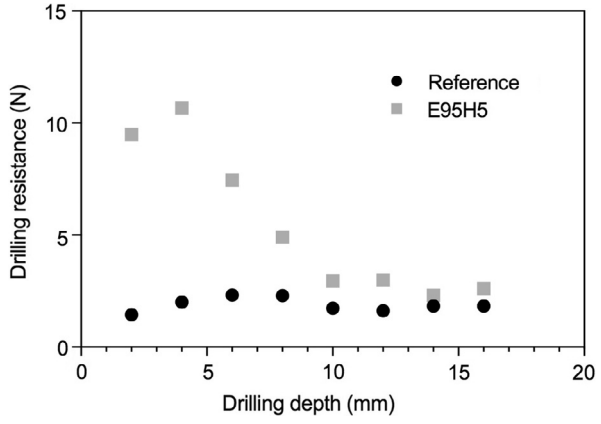

Fig. 2. Drilling resistance profile of untreated and treated (with nanolime E95H5) lime-based mortar specimens. Markers represent average (10 measurements) of the arithmetic mean of the lowest values of every 2 mm segment.

Analysing the two treated limestones, in the weathered limestone a more heterogeneous in-depth distribution of the lime nanoparticles and a higher strength increase at the absorption surface can be observed. This difference can be attributed to the different absorption behavior of the weathered stone, (decohesion of the outer, weathered layer) and the higher number of nanolime applications.

The methodology described in Section 3.3 was adopted in order to examine the DRMS profiles of the treated and untreated mortars. The obtained data confirmed a consolidation action within the treated specimen, mostly up to 8–10 mm in depth (Fig. 2): an increase of the mechanical strength was observed (with values ranging 5–11 N), compared to the untreated specimen (1.5–2.5 N). The consolidation action is confined mostly in the outer 6–8 mm.

4.4. Effect of treatment on water absorption and drying

The moisture transport properties of treated and untreated core specimens were assessed in order to evaluate the compatibility of the nanolime consolidant with the substrates (Fig. 3).

The total water amount absorbed within the weathered limestone is considerably lower (around 20% in volume) than that absorbed within the sound limestone. This difference can be attributed to lower open porosity of the stone from Kessel in comparison to that from the quarry (as seen in Section 4.3). Such differences in porosity have been observed in Maastricht limestone before [24] due to natural variations.

When comparing the untreated with the treated specimens, the results show that water absorption by capillarity of sound Maastricht limestone specimens treated with E100 is slower than that of the untreated specimen. The treated specimen takes around 3 min to be completely saturated with water, whereas 1 min is necessary for the untreated specimens. A similar trend is observed with the weathered limestone: the specimens treated with nanolime E100 are completely saturated in slightly more than 4 min, while the untreated specimens are saturated in about 90 s.

Also in the case of the lime-based mortar, the nanolime treatment induced a delay of the water absorption; the specimens treated with nanolime E95H5 are completely saturated within 5 min, whereas it takes about 2 min for the untreated specimens to be saturated.

Additionally, it can be observed that a slightly smaller amount of water was absorbed within all the treated substrates, due to the pore filling induced by the nanolime treatments, in accordance with the results of Section 4.2.

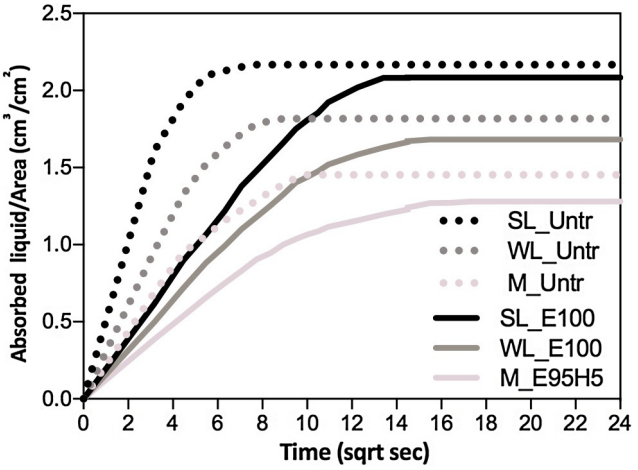

Fig. 3. Comparison of the capillary absorption curves (in volume) of water of treated (solid line) and untreated (dashed line) specimens of sound Maastricht limestone (SL, black line), weathered Maastricht limestone (WL, dark grey line) and lime-based mortar (M, light grey line).

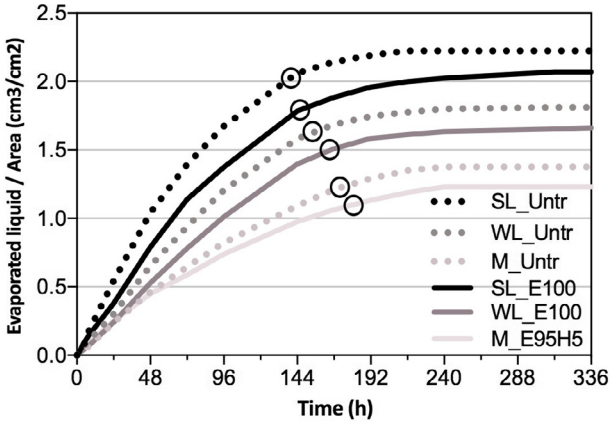

Fig. 4. Drying curves (in volume) of water of treated (solid line) and untreated (dotted line) specimens of sound Maastricht limestone (blue line), weathered Maastricht limestone (yellow) and lime-based mortar (red line). The black circles indicate the critical liquid content and the end of the first step of drying. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 5
Water absorption coefficient (WAC) of treated and untreated substrates.

Material	WAC (kg/m² h$^{1/2}$)
Untreated sound limestone	2.482 ± 0.067
Treated sound limestone	1.577 ± 0.156
Untreated weathered limestone	2.207 ± 0.183
Treated weathered limestone	1.275 ± 0.199
Untreated mortar	1.753 ± 0.187
Treated mortar	1.048 ± 0.264

The water absorption coefficient (WAC) of treated and untreated specimens is presented in Table 5. It can be seen that the WAC of the treated sound limestone has a reduction of around 36% when compared to the untreated specimens; a slightly higher reduction is observed in the case of the weathered limestone (44%), due to the higher number of applications (10). In the case of the lime-based mortar, the reduction is around 40%.

In order to assess compatibility, the following criterion can be considered: after treatment the WAC should not increase and not differ too much from that of the untreated material [2,39]. Nanolime treatment fulfills the first requirement, as they do no increase the WAC; in fact, a moderate reduction of the WAC (around 40% of the original value for all the 3 substrates) was measured.

The drying curves (Fig. 4) show that the water absorbed by treated and untreated, sound limestone specimens evaporates within about the same time span. In the drying curves, two stages can be observed: in the 1st stage of drying, called the constant drying period, the drying front is at the surface and the drying rate is relatively constant and controlled by the external conditions [40]. This first phase ended in around 144 h in the case of both the treated and untreated sound limestone. In the 2nd stage of drying, identified by the change in the slope of the drying curve, the liquid water content can no longer support the demands of the evaporation flux. The drying front recedes progressively into the material and the properties of the substrate control the rate of drying [40]. In this second stage of drying, where drying occurs in the vapor phase, most of the water has already evaporated. In this step, some delay can be observed in the case of the treated limestone. Untreated sound limestone specimens completely dried in about 8 days, whereas the treated specimens need up to 10 days.

A similar trend is observed in the case of the weathered limestone.

In the case of the mortar specimens, no significant differences in the drying rate are observed between treated and untreated specimens, which completely dried in 9–10 days.

Summarizing, it can be concluded that nanolime treatments do not cause drastic alteration of water transport properties in the studied substrates. Therefore, the risk of harmful consequences and future decay of the substrate caused by differential moisture transport properties between treated and untreated layer is low [41].

4.5. Influence of the treatments on the aesthetical aspect

The sound and weathered limestone blocks and the lime-based mortar were observed macroscopically, before and after the treatment with nanolime. NCS indexes measurements were considered to evaluate any possible macroscopical chromatic alteration of the treated specimens.

In the case of the sound limestone (Fig. 5a), identified with the NCS indexes S0530-G80Y and S0540-G80Y, no white patina was observed at the drying surface after 6 applications of nanolime E100 (Fig. 5c); some whitish haze was visible only after the 7th application (Fig. 5b), when compared to the untreated specimen, being the specimen identified with the NCS indexes S0530-G80Y, S0520-G80Y and S0510-Y. This slight whitening is due to lime nanoparticles accumulated nearby the surface. This white patina is not homogeneously distributed on the surface, and an accumulation is visible in the center of the specimen (Fig. 5d).

When considering the weathered limestone (NCS indexes: S0530-G80Y and S0540-G80Y), the surface is more irregular than that of the sound limestone, and it shows powdering and loss of cohesion (Fig. 6a, c). After 10x treatment with nanolime E100, the specimen shows a more homogeneous surface (Fig. 6b) and no significant chromatic alteration (NCS indexes: S0530-G80Y and S0520-G80Y). In fact, even if a higher number of applications was performed compared to the sound limestone (10 instead of 7), no white patina is observed at the surface (Fig. 6d).

The untreated mortar specimen, identified by the NCS indexes S0500-N and S0502-Y, presents a whitish, highly porous surface (Fig. 7a, c). The treated specimen shows a more homogeneous surface and no chromatic alteration or white patina is macroscopically visible (Fig. 7b) (NCS index: S0500-N). Looking more in detail to the microstructure, it can be observed that lime nanoparticles partially filled the superficial pores and enriched the binder of the original matrix (Fig. 7d) [6].

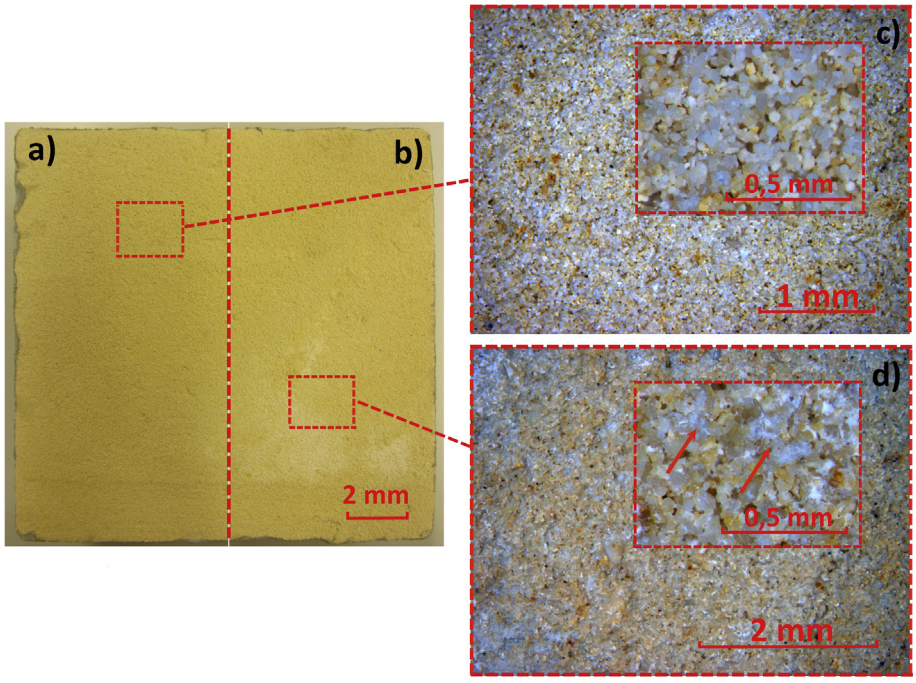

Fig. 5. Pictures of the drying surface of a) untreated and b) treated (7 applications with E100) blocks (15 × 15 × 4 cm) of sound Maastricht limestone; c, d) relative microphotos on the most significant spots. The arrows indicate the deposits of lime nanoparticles.

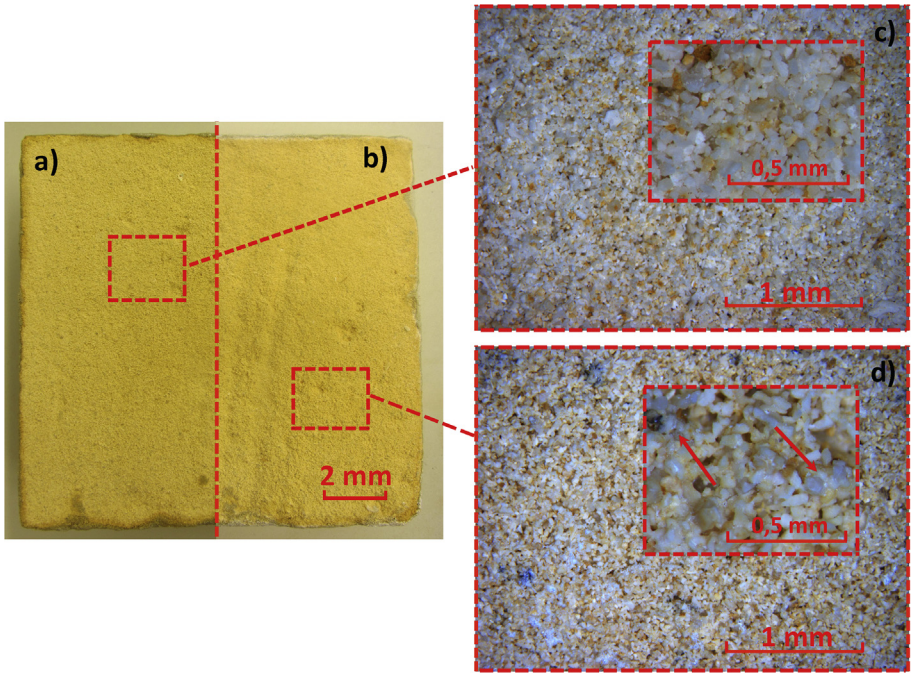

Fig. 6. Pictures of the drying surface of a) untreated and b) treated (10 applications with E100) blocks (13 × 13 × 4 cm) of weathered Maastricht limestone; c, d) relative microphotos on the most significant spots. The arrows indicate the deposits of lime nanoparticles.

In the case of the weathered limestone and of the lime-based mortar, the variations observed in the treated specimens are not macroscopically perceptible and thus the treatments demonstrate to respect the chromatic parameters of the substrates.

5. Conclusions

In this research the effectiveness and compatibility of freshly synthesized nanolimes with fine-tuned solvent [19,20] and applied according to an optimized protocol [21], was assessed on Maastricht limestone (both sound and weathered) and on lime-based mortar.

In the case of the sound and weathered Maastricht limestone, the results showed that nanolime E100 (dispersed in 100% ethanol) can guarantee a consolidation action up to ca. 16 mm in depth, with a maximum effect in the outer 5–6 mm.

The de-cohesion of the outer layer of the weathered stone allowed for a higher number of applications when compared to the sound limestone, without any whitish patina appearing at the drying surface.

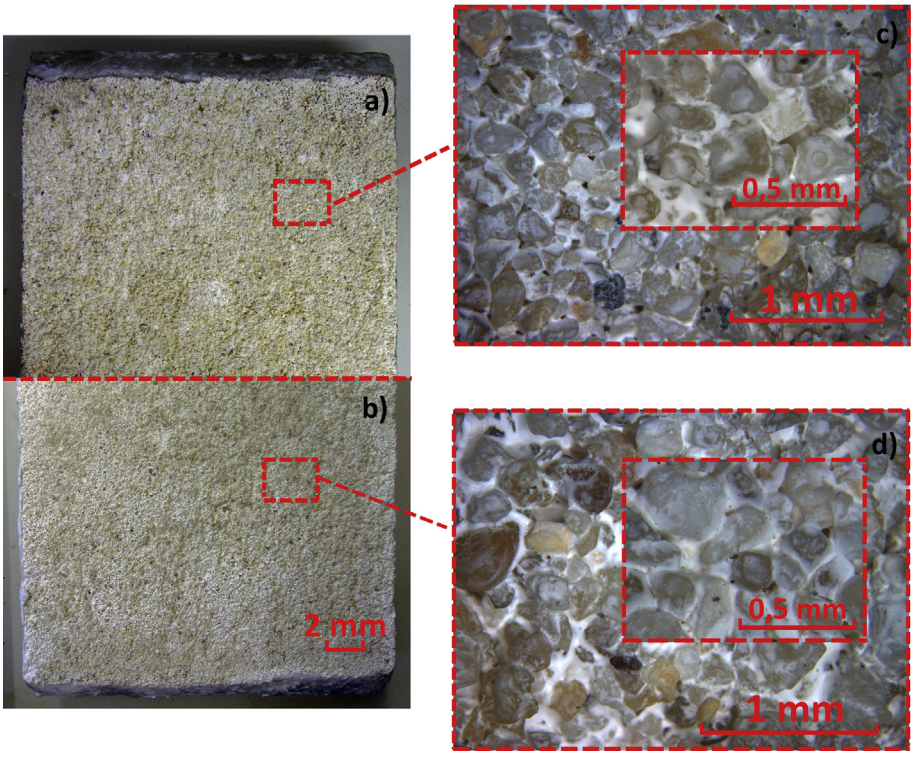

Fig. 7. Pictures of the drying surface of a) untreated and b) treated (10 applications with E95H5) lime-based mortar layer applied on a brick (29 × 17 cm); c, d) relative microphotos on the most significant spots.

Also in the case of lime-based mortar specimens, treated with nanolime E95H5 (nanoparticles dispersed in a binary mixture of 95% ethanol-5% water), a considerable consolidation was observed, which led to an increase of the mechanical strength up to 8–10 mm in depth.

Based on these results, it can be concluded that a significant strengthening effect can be obtained by the use of the developed nanolime dispersions on coarse porous lime-based substrates. A higher strengthening effect measured at the very surface of the specimens might be necessary to compensate for the weakness of strongly weathered substrates. The strengthening effect may be adapted to the de-cohesion of the substrate by adjusting the number of nanolime applications.

In spite of the considerable strengthening effect, the treatment only moderately altered the total porosity and the moisture transport properties of the investigated substrates.

The nanolime treatments tested in this work showed to have a good effectiveness and compatibility when applied for consolidation of highly porous, calcareous substrates like Maastricht limestone and lime mortar.

Future research should evaluate the effect of the treatment on the durability related to decay processes (e.g. salt crystallization and freeze-thaw resistance) of the treated materials.

Acknowledgements

The authors acknowledge TNO (Delft, The Netherlands) and Delft University of Technology (Delft, The Netherlands) for the financial support.

References

[1] G. Borsoi, B. Lubelli, R. van Hees, R. Veiga, A. Santos Silva, Understanding the transport of nanolime consolidants within Maastricht limestone, J. Cult. Herit. 18 (2016) (2016) 242–249.

[2] R.P.J. van Hees, B. Lubelli, T. Nijland, A. Bernardi, Compatibility and performance criteria for nano-lime consolidants, in: Proceedings of the 9th International Symposium on the Conservation of Monuments in the Mediterranean Basin Monubasin 2014, Ankara, 3–5 June, 2014.

[3] R. van Hees, R. Veiga, Z. Slížková, Consolidation of renders and plasters, Mater. Struct. 50 (12) (2017) 65.

[4] L. Toniolo, A. Paradisi, S. Goidanich, G. Pennati, Mechanical behavior of lime-based mortars after surface consolidation, Constr. Build. Mater. 25 (4) (2010) 1553–1559.

[5] E. Hansen, E. Doehne, J. Fidler, J. Larson, B. Martin, M. Matteini, C. Rodrigues-Navarro, E. Sebastian Pardo, P. Price, A. de Tagle, J.M. Teutonico, N. Weiss, A review of selected inorganic consolidants and protective treatment for porous calcareous materials, Rev. Conserv. 4 (2003) 13–25.

[6] G. Borsoi, M. Tavares, R. Veiga, A. Santos Silva, Microstructural characterization of consolidant products for historical renders: an innovative nanostructured lime dispersion and a more traditional ethyl silicate limewater solution, Microsc. Microanal. 18 (2012) 1181–1189.

[7] A.P. Ferreira Pinto, J. Delgado Rodrigues, Impacts of consolidation procedures on colour and absorption kinetics of carbonate stones, Stud. Conserv. 59 (2) (2012) 79–90.

[8] G. Wheeler, Alkoxysilanes and the Consolidation of Stone, The Getty Conservation Institute, Los Angeles, 2005.

[9] E. Doehne, C.A. Price, Stone Conservation – An Overview of Current Research, second ed., The Getty Conservation Institute, Los Angeles, 2010.

[10] J. Delgado Rodrigues, A.P. Ferreira Pinto, Laboratory and onsite study of barium hydroxide as a consolidant for high porosity limestones, J. Cult. Herit. 19 (2016) 467–476.

[11] M. Drdácký, Z. Slízkova, Calcium hydroxide based consolidation of lime mortars and stone, in: Proceedings of 1st Historical Mortars Conference HMC08 – Characterization, Diagnosis, Conservation, Repair and Compatibility, Lisbon, LNEC, May 2008, pp. 299–308.

[12] R. Giorgi, L. Dei, P. Baglioni, A new method for consolidating wall paintings based on dispersions of lime in alcohol, Stud. Conserv. 45 (2000) 154–161.

[13] L. Dei, B. Salvadori, Nanotechnology in cultural heritage conservation: nanometric slaked lime saves architectonic and artistic surface from decay, J. Cult. Herit. 7 (2006) 110–115.

[14] D. Chelazzi, G. Poggi, Y. Jaidar, N. Toccafondi, R. Giorgi, P. Baglioni, Hydroxide nanoparticles for cultural heritage: consolidation and protection of wall paintings and carbonate materials, J. Colloid Interface Sci. 392 (2013) 42–49.

[15] G. Ziegenbalg, K. Brummer, J. Pianski, Nano-Lime – a new material for the consolidation and conservation of historic mortars, in: J. Válek, C. Groot, J.J. Hughes (Eds.), Proceedings of 2nd Historic Mortars Conference And RILEM TC 203-RHM Final Workshop – HMC10, Prague, September 11–14, RILEM Publications, 2010, pp. 1301–1309.

[16] C. Rodriguez-Navarro, A. Suzuki, E. Ruiz-Agudo, Alcohol dispersions of calcium hydroxide nanoparticles for stone conservation, Langmuir 29 (36) (2013) 11457–11470.
[17] A. Campbell, A. Hamilton, T. Stratford, S. Modestou, I. Ioannou, Calcium hydroxide nanoparticles for limestone conservation: imbibition and adhesion, in: Proceedings of Symposium Adhesive and Consolidants for Conservation: Research and Applications, ICC, Ottawa, October 17–21, 2011, pp. 1–16.
[18] D. Costa, J. Delgado Rodrigues, Consolidation of a porous limestone with nanolime, in: Proceeding of 12th International Congress on Deterioration and Conservation of Stone, Columbia University, New York, October 22–26, 2012, pp. 9–20.
[19] G. Borsoi, B. Lubelli, R. van Hees, R. Veiga, A. Santos Silva, L. Colla, L. Fedele, P. Tomasin, Effect of solvent on nanolime transport within limestone: how to improve in-depth deposition, Colloids Surf., A 497 (2016) 171–181.
[20] G. Borsoi, B. Lubelli, R. van Hees, R. Veiga, A. Santos Silva, Optimization of nanolime solvent for the consolidation of coarse porous limestone, Appl. Phys. A 122 (2016) 846–857.
[21] G. Borsoi, B. Lubelli, R. van Hees, R. Veiga, A. Santos Silva, Application protocol of nanolimes for the consolidation of calcareous substrates: the step from research to practice, Restor. Build .Monuments (2016) (accepted for publication).
[22] T.G. Nijland, C.W. Dubelaar, H.J. Tolboom, R.P.J. van Hees, Building stones from a muddy delt: native natural stone from the Netherlands, in: Proceedings of Heritage, Weathering and Conservation Conference – HWC 2006, Madrid, June 21–24, CRC Press/Taylor & Francis group, London, 2006, pp. 15–21.
[23] B. Lubelli, R. van Hees, T. Nijland, J. Bolhuis, A new method for making artificially weathered stone specimens for testing of conservation treatments, J. Cult. Herit. 16 (2015) 698–704.
[24] R.P.J. van Hees, T. Nijland, Assessment of the state of conservation of a Middle Neolithic flint mine in Maastricht limestone, Heron 54 (4) (2009) 227–250.
[25] P. Pascoal, G. Borsoi, R. Veiga, P. Faria, A. Santos Silva, Consolidation and chromatic reintegration of historical renders with lime-based pozzolanic products, Stud. Conserv. 60 (5) (2015) 321–332.
[26] EN 1015-3, European Standard, Methods of Test for Mortar for Masonry - Part 3: Determination of Consistence of Fresh Mortar (by Flow Table), European Committee for Standardization (CEN), 1999.
[27] V. Daniele, G. Taglieri, R. Quaresima, The nanolimes in Cultural Heritage conservation: characterisation and analysis of the carbonatation process, J. Cult. Herit. 9 (2008) 294–301.
[28] P. López-Arce, L.S. Gomez-Villalba, S. Martinez-Ramirez, M. Alvarez de Buergo, R. Fort, Influence of relative humidity on the carbonation of calcium hydroxide nanoparticles and the formation of calcium carbonate polymorphs, Powder Technol. 205 (1) (2011) 263–269.
[29] P. López-Arce, A. Zornoza-Indart, L. Gomez-Villalba, R. Fort, Short- and longer-term consolidation effects of portlandite $CaOH_2$ nanoparticles in carbonate stones, J. Mater. Civ. Eng. 25 (11) (2013) 1655–1665.
[30] M. Saharay, A.O. Yazaydin, R.J. Kirkpatrick, Dehydration-induced amorphous phases of calcium carbonate, J. Phys. Chem. B 117 (2013) 3328–3336.
[31] RILEM Technical Committee 25 PEM, Recommended test to measure the deterioration of stone and to assess the effectiveness of treatment methods, Mater. Struct. 13 (75) (1980) 175–253.
[32] A.P. Ferreira Pinto, J. Delgado Rodrigues, Consolidation of carbonate stones: Influence of treatment procedures on the strengthening action of consolidants, J. Cult. Herit. 16 (13) (2012) 154–166.
[33] R. Nogueira, A.P. Ferreira Pinto, A. Gomes, Assessing mechanical behavior and heterogeneity of low-strength mortars by the drilling resistance method, Constr. Build. Mater. 68 (2014) 757–768.
[34] A.P. Ferreira Pinto, J. Delgado Rodrigues, Study of consolidation effects in carbonate stones by means of drilling resistance, in: 6th International Symposium on the Conservation of Monuments in the Mediterranean Basin, Lisbon, Portugal, April 7–10, 2004.
[35] E. Valentini, A. Benincasa, P. Tiano, F. Fratini, S. Rescic, On site drilling resistance profiles of natural stones, Personal communication.
[36] J. Delgado Rodrigues, D. Costa, A new interpretation methodology for microdrilling data from soft mortars, J. Cult. Herit. 22 (2016) 951–955.
[37] EN 15801, European Standard, Conservation of Cultural Heritage – Test Methods – Determination of Water Absorption by Capillarity, European Committee for Standardization (CEN), 2009.
[38] EN 16322, European Standard, Conservation of Cultural Heritage – Test Methods – Determination of Drying Properties, European Committee for Standardization (CEN), 2013.
[39] R. Snethlage, M. Pfanner, Leitfaden Steinkonservierung - Planung von Untersuchungen und Maßnahmen zur Erhaltung von Denkmälern aus Naturstein, 4th rev. ed., Fraunhofer IRB Verlag, Stuttgart, 2013.
[40] C. Hall, W.D. Hoff, Water Transport in Brick, Stone and Concrete, Spon Press, Taylor & Francis Group, New York, 2012.
[41] A. Zornoza-Indart, P. Lopez-Arce, N. Leal, J. Simão, K. Zoghlami, Consolidation of a Tunisian bioclastic calcarenite: from conventional ethyl silicate products to nanostructured and nanoparticle based consolidants, Constr. Build. Mater. 116 (2016) 188–202.