Air lime mortar consolidation by nanolimes and ammonium phosphate: Compatibility, effectiveness and durability

AIR LIME MORTAR CONSOLIDATION BY NANOLIMES AND AMMONIUM PHOSPHATE: COMPATIBILITY, EFFECTIVENESS AND DURABILITY

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ABSTRACT

In this study, a systematic comparison is presented between a commercial dispersion of $Ca(OH)_2$ nanoparticles (so-called nanolimes) and aqueous solutions of diammonium hydrogen phosphate (DAP) for consolidation of air lime mortars. The effects were evaluated in terms of compatibility (composition and morphology of the new phases, changes in color, porosity and water absorption), effectiveness (product uptake, dynamic elastic modulus, scotch tape test) and durability (permanence of the consolidating action after accelerated ageing). While both consolidants proved to be compatible, DAP solutions outperformed nanolimes in terms of effectiveness and durability, especially when highly concentrated DAP solutions were used.

KEYWORDS

Inorganic consolidants; Nanodispersion; Nanotechnology; Nanoparticle; Hydroxyapatite; Calcium phosphate; Plaster; Render; Accelerated ageing; Scotch tape test

HIGHLIGHTS

- Consolidation of lime mortars by innovative inorganic treatments was investigated
- Nanolimes (NL) and diammonium hydrogen phosphate (DAP) were compared
- Compatibility, effectiveness and durability after accelerated ageing were evaluated
- Neither consolidant significantly altered color, open porosity or water absorption
- DAP outperformed NL in terms of effectiveness and durability to accelerated ageing

1. INTRODUCTION

Consolidation of weathered air lime mortars (used as renders, plasters or bedding mortars) is a complex task, especially if pigments are present, like in the case of frescoes and wall paintings. For this reason, many consolidants have been proposed and tested through the years, including both organic (e.g. acrylic resin [1]) and inorganic treatments (e.g. calcium hydroxide [2-8], barium hydroxide [1], ethyl silicate [1,9], ammonium phosphate [10-13]). Because organic treatments applied in the past decades have shown severe compatibility and durability issues in the long term [14], attention has recently focused mainly on inorganic treatments.

Among inorganic consolidants, dispersions of $Ca(OH)_2$ nanoparticles (the so-called nanolimes) have been extensively tested, in the light of their ideal mineralogical compatibility with air lime-based substrates [15]. Indeed, $Ca(OH)_2$ nanoparticles convert to $CaCO_3$ upon carbonation, thus forming the same mineral constituting lime-based mortars and carbonate stones. Nanolimes have generally shown good compatibility also in terms of color change [4] (although some cases of visible whitening have been reported [6,8]), as well as alterations in the pore system [8] and water transport properties [6,8]. In studies evaluating lime mortars consolidation by nanolimes, a suitable consolidating effectiveness has been assessed by microdrilling resistance [6,8], ultrasonic pulse velocity [5], peeling resistance [8] and compressive strength [9]. However, cases of either insufficient [12] or excessive strengthening [6] have also been reported. As for durability, systematic studies on the salt and frost resistance of nanolime-consolidated mortars are still missing, but increases in the resistance to salt weathering have been reported for nanolime-consolidated stones [16-18]. However, literature studies have pointed out that nanolimes cause alterations in the pore size distribution that may actually increase the crystallization pressure and thus decrease the salt resistance of the substrate [18].

As an alternative to traditional inorganic consolidants, ammonium phosphate solutions have been proposed for consolidation of carbonate substrates [19,20], also including lime mortars [10-13]. The idea is to form new calcium phosphates (CaP) with binding action, by treating the substrate with an aqueous solution of diammonium hydrogen phosphate (DAP, $(NH_4)_2HPO_4$) [19]. While the phosphate ions necessary to form new CaP have to be externally provided, the calcium ions can either come from the substrate [19] or be externally supplied. In this latter case, a calcium source can be added directly into the DAP solution [21] or the substrate can be pre-treated with a calcium source (such as nanolimes [22-24]) before DAP application. By adding a calcium source directly into the DAP solution, a significant consolidating action has been registered not only on lime-based mortars [10-12] (where Ca^{2+} ion availability is high), but also on mortars based on hydraulic lime and cement [11] (where Ca^{2+} ion availability is lower). The strengthening effectiveness of DAP solutions applied on lime mortars has been proven by ultrasonic velocity [11-13], peeling resistance [12-13] and compressive strength [11], the increase in mechanical properties varying as a function of the formulation of the DAP solution. The treatment generally ensures good physical-microstructural compatibility, because changes in pore size distribution and water transport properties are minor [11-13]. In terms of aesthetic compatibility, negligible color alterations have been found on lime-based mortars (initially white), whereas some whitening was observed when highly concentrated DAP solutions were used on mortars containing brick dust (initially pink), hydraulic lime (initially brown) or cement (initially gray) [11]. As for durability, encouraging results have been obtained on porous stones, in terms of resistance to salt crystallization [23,25,26] and freezing-thawing cycles [25,26], but systematic studies are still missing in the specific case of lime mortars.

Therefore, the aim of the present study was to perform a systematic comparison between nanolimes and ammonium phosphate applied onto lime mortars. A few studies comparing the performance of these two consolidants have been reported in the literature on stones [24,26,27] and mortars [12], but in the present study all the main requirements of a

consolidant (namely, compatibility, effectiveness and durability) were systematically evaluated on lime mortars for the first time. In this work, the consolidants were tested on mortar samples applied onto a brick substrate, to resemble the situation of plasters and renders that were traditionally applied onto brick masonry. However, the intended application of these products also includes consolidation of bedding mortars and decorative mortars often used to imitate natural stones (the so-called “artificial stones”).

2. MATERIALS AND METHODS

2.1. Specimens

Multilayer specimens, composed of a layer of air lime mortar over a brick substrate, were used for the tests. It is noteworthy that, in the present case, a single mortar layer was applied onto the substrate, whereas historic plasters and renders were usually composed of multiple layers with different composition and porosity.

First, slabs (5×5×1 cm^3) were sawn from a single brick, to ensure that all the brick substrates have the same porosity and, hence, the same behavior for all the specimens. The brick slabs were let saturate with water for 24 hours before applying the mortar layer, to prevent bricks from absorbing water from the mortar, which would alter the water to binder ratio and the porosity of the mortar [28]. A 1 cm-thick layer of lime mortar, prepared as described in the following, was then applied onto the brick slabs.

The lime mortar was prepared using hydrated lime by Colacem, Italy (CL 70-S according to EN 459-1:2015) and calcareous sand ($CaCO_3$ = 95 ± 1.5 wt%, maximum particle size of 4 mm). A binder-to-aggregate ratio of 1:2 v/v (0.41 w/w) and a water-to-binder ratio of 1:1 v/v (0.45 w/w) were used. The mortar was mixed in a Hobart mixer, then poured onto the brick slabs inside plastic molds and finally manually leveled out. The sandwich specimens (5×5 cm^2 cross section, composed of 1 cm of mortar over 1 cm of brick) were then immediately demolded and left to cure in a climatic chamber (RH = 90 ± 2%, T = 21 ± 2 °C) for 4 months. The adopted RH value was selected considering that, in the case of $Ca(OH)_2$ nanoparticles, faster and more thorough carbonation was systematically observed for RH increasing from 33 % up to 95 % [15]. After curing for 4 months in these conditions, carbonation of the lime mortar specimens could be considered as complete, since no residual portlandite band was detected by FT-IR performed on the lime mortar.

2.2. Consolidants

A commercial product based on nanolimes and two different formulations of the DAP treatment were tested, so that in total 4 conditions were considered:

1) Untreated reference (labelled “UT”).
2) Nanolimes (labelled “NL”). The commercial product Nanorestore Plus® Ethanol 5 by CTS Srl (Italy), consisting in a dispersion of calcium hydroxide nanoparticles in

ethanol with a concentration of 5 g/L, was used. As recommended by the producer to prevent whitening, a sheet of Japanese paper was first applied onto the surface to be treated (i.e. the 5×5 cm^2 face of the mortar specimens) and then the nanodispersion was applied by brushing 10 times, waiting for the product to be absorbed between subsequent brush strokes. As recommended in the product's technical data sheet, immediately at the end of the brush application, a poultice of cellulose pulp imbibed with deionized water (1:4 weight ratio) was applied over the sheet of Japanese paper, to favor carbonation and to prevent white haze formation. The presence of water favors carbonation because atmospheric CO_2 and $Ca(OH)_2$ both need to dissolve in water (in bulk or adsorbed onto the nanoparticles) for the carbonation reaction to take place [15]. The poultice was left to dry in contact with the specimens for 3 days and finally removed.

3) Aqueous solution containing 1 M DAP + 1 mM $CaCl_2$ (labelled "D1"). This formulation, first proposed for marble protection [21], was here selected as it has shown also significant consolidating effectiveness on different types of substrate [12,20,29]. The addition of $CaCl_2$ as a calcium source has the effect of promoting and accelerating formation of new CaP [21], also on substrates where the availability of calcium ions from the substrate would be limited [11]. The solution (prepared using chemicals supplied by Sigma-Aldrich) was applied by brushing 10 times over the 5×5 cm^2 face of the mortar specimens. Then, the specimens were wrapped in a plastic film to prevent evaporation of the consolidating solution. After 24 hours, the specimens were unwrapped, rinsed with deionized water and left to dry at room temperature until constant weight.

4) Aqueous solution containing 3 M DAP (labelled "D3"). This alternative formulation of the DAP treatment was selected because it has shown a significant consolidating effectiveness, even on highly deteriorated substrates, thanks to the high concentration of phosphate ions available to form new CaP [13,20,30,31]. The solution was applied by brushing 10 times over the 5×5 cm^2 face of the mortar specimens. Similar to the case of the D1 treatment, after application of the DAP solution the specimens were wrapped in a plastic film for 24 hours, then the film was removed, the specimens rinsed with water and dried at room temperature until constant weight. Finally, to ensure that no unreacted DAP remain in the mortar, a poultice of cellulose pulp and limewater (i.e. a saturated solution of calcium hydroxide, 1.7 g/L, supplied by Sigma-Aldrich) with a 1:4 weight ratio was applied onto the treated surface, interposing a sheet of Japanese paper to avoid sticking. The specimens were again wrapped in a plastic film for 24 hours (so that calcium ions contained in limewater could penetrate into the mortar and react with possible unreacted DAP [31]), then the specimens were unwrapped and finally left to dry while still covered with the poultice (so that all the soluble fractions could be extracted from the mortar and transported into the poultice [31]).

Before testing, all the specimens were left to cure for 4 weeks in a climatic chamber (RH = 90 ± 2%, T = 21 ± 2 °C). The RH value was selected to promote nanolime carbonation, for the reasons discussed above [15]. The duration was selected as the nanolime technical data sheet recommends curing for 2-4 weeks, while curing for a much shorter time would

be sufficient for the DAP treatments (namely 24 hours for D1 and about 1 week for D3, which also involves drying and application of limewater).

2.3. Characterization

2.3.1. Compatibility

Composition and morphology of the new phases. The composition of the new phases was investigated by Fourier Transform Infrared Spectrometry (FT-IR), on powdered samples obtained from the specimen surface using a spatula. A Perkin Elmer Spectrum Two instrument (ATR mode, 2000-500 cm^{-1} range, spectral resolution 2 cm^{-1}, 32 scans, data interval 1 cm^{-1}) was used. To allow for a qualitative comparison between the amounts of new phases formed after treatment, the FT-IR spectra were normalized with respect to the calcite band at 872 cm^{-1}. The morphology of the new phases was analyzed by scanning electron microscopy (SEM), using a Field Emission Gun (FEG) instrument (Tescan Mira3) equipped with energy dispersive spectrometry (EDS, Bruker probe). Two types of samples were observed by FEG-SEM: fracture surfaces and polished cross sections. Fracture surfaces were observed on samples (~1 cm^3) collected by chisel after mechanical testing (cf. § 2.3.2). Cross sections were prepared by encapsulating other samples (containing the original treated surface) in epoxy resin and then polishing the encapsulated samples to expose the cross section. All the FEG-SEM samples were made conductive by evaporation of graphite before observation (Quorum Q150R ES+ coater).

Aesthetic compatibility. The color difference after consolidation was evaluated by measuring the CIE Lab color parameters (L* = black-white, a* = green-red, b* = blue-yellow) of untreated and treated specimens, using a NH310 colorimeter. For each condition, three specimens were analyzed and, for each specimen, colorimetric measurements were performed in three different spots. The average CIE Lab color parameters were then calculated for each condition and the resulting color difference ΔE* between treated and untreated samples was determined as $\Delta E^* = (\Delta a^{*2} + \Delta b^{*2} + \Delta c^{*2})^{1/2}$.

Physical compatibility. The alterations in open porosity and pore size distribution were evaluated by mercury intrusion porosimetry (MIP) using a Pascal 140 and 240 instrument (minimum pressure 0.0125 MPa, maximum pressure 200 MPa). The MIP samples (~1 cm^3) were collected by chisel after mechanical testing (cf. § 2.3.2). The alteration in water sorptivity was determined according to the European Standard EN 15801 [32]. Water was let penetrate the samples through the 5×5 cm^2 mortar face (hence with the brick slab upwards), until saturation was reached after about 6 hours. Three replicates were tested for each condition.

2.3.2. Effectiveness

Product uptake. The amount of liquid consolidant absorbed by the specimens was determined by weighing the specimens before and right after the consolidant application.

Dynamic elastic modulus (E_d). The increase in cohesion after consolidation was evaluated by determining the E_d on each specimen, before and after treatment, according to the

formula $E_d = \rho \times UPV^2$, where ρ is the density and UPV is the ultrasonic pulse velocity. UPV can be measured non-destructively and has been shown to be strongly correlated with porosity and mechanical properties in natural stones (especially marbles [33]), so UPV and E_d are commonly used to assess the consolidation effectiveness also on lime mortars [5,11-13]. The UPV was measured using a Pundit instrument with 55 kHz transducers. To ensure that the ultrasonic pulse travel only through the 1-cm thick mortar layer (and not through the adjacent 1-cm thick brick layer), 0.8×5 cm^2 rubber pieces were used between the transducers and the specimens, thus also improving the contact between the two. For each condition, three replicate specimens were tested.

Scotch tape test (STT). An indication about the ability of the consolidants to increase the mortar resistance to material loss was obtained by STT [34]. The test was performed by first applying a piece of adhesive tape onto the specimens and making it adhere uniformly. The scotch tape measured 6×2.5 cm^2, equivalent to half of the mortar face (5×5 cm^2), plus an extra 1 cm to allow for the tape removal. The tape was then manually removed, always adopting the same speed and angle of removal. The amount of mortar detached from the specimen and attached to the scotch tape was determined by weighing the tape before and after the test. To evaluate the consistency with depth of the consolidating action, on each specimen the STT was repeated 10 times in the same position. For each condition, three replicate specimens were tested.

2.3.3. Durability

The permanence of the consolidating action after accelerated ageing was assessed by subjecting the specimens to freezing-thawing cycles and then repeating the characterization tests described above. Freezing-thawing cycles were preferred over salt crystallization cycles because both deterioration processes cause stress in the pores and a decrease in mechanical properties, but salt crystallization cycles also induce contamination of the specimens and formation of efflorescence, which would make it impossible to repeat the STT after ageing. The freezing-thawing cycles were performed by partly modifying the European Standard EN 12371 [35]: after being preliminarily saturated with deionized water by immersion for 3 days, the specimens were subjected to cycles of freezing at -20±2 °C for 2 h, followed by thawing in water at +20±2 °C for 2 h. After 10 cycles, the specimens were dried in an oven at 50 °C for 3 days. The effects of accelerated ageing were then assessed by measuring the weight loss and by repeating SEM observation, E_d measurement and STT after the cycles, following the same procedures described above.

3. RESULTS AND DISCUSSION

3.3.1. Compatibility

In terms of composition of the new phases, nanolimes and DAP can both be considered as suitably compatible. Indeed, nanolimes caused formation of calcite (i.e. the same mineral constituting the substrate), while no metastable $CaCO_3$ minerals (e.g. vaterite or aragonite, which can result from nanolime carbonation [15]) were detected by FT-IR (Figure 1). In the

case of the DAP-based treatments, FT-IR spectra suggest that, in the "D1" sample, octacalcium phosphate (OCP, $Ca_8(HPO_4)_2(PO_4)_4 \cdot 5H_2O$) was formed (OCP having bands at 1038, 961, 602, 560 cm^{-1} [36]). In the D3 sample, hydroxyapatite (HAP, $Ca_{10}(PO_4)_6(OH)_2$) seems to have formed (HAP having bands at 1031, 962, 604, 563 cm^{-1} [36]), although the presence of OCP cannot be completely excluded. HAP, being the least soluble CaP at pH>4, is the ideal mineral to form, but OCP is not undesirable, considering that it is significantly less soluble than calcite [21]. The present findings are consistent with previous results reported in the literature, pointing out that OCP formation is favored by addition of $CaCl_2$ to the DAP solution (like in treatment "D1"), while HAP is formed when only DAP is used (like in treatment "D3") [21]. In the case of the "D3" sample, the increase in the height of the calcite band at 712 cm^{-1} suggests that carbonate ions (coming from the mortar substrate and/or from the atmosphere) were likely incorporated into the HAP lattice, thus leading to formation of carbonated HAP [19]. However, phase identification is very challenging, because of the similarity in the crystal structure of different CaP minerals, so a multiplicity of analytical techniques (ideally also including synchrotron analyses) would be necessary for a conclusive phase identification [37,38]. Notably, the amount of new CaP phases formed after the "D3" treatment appears considerably higher than that formed using the "D1" formulation, in agreement with previous results [30]. HAP and OCP can be regarded as fully compatible minerals, considering that (although not originally present in lime mortars or carbonate stones) they have been found in natural patinas formed through the centuries over historic monuments [39]. Such patinas do not cause deterioration of the substrate, but on the contrary exert a significant protective action, so that during cleaning interventions it is nowadays usually recommended that such patinas be preserved.

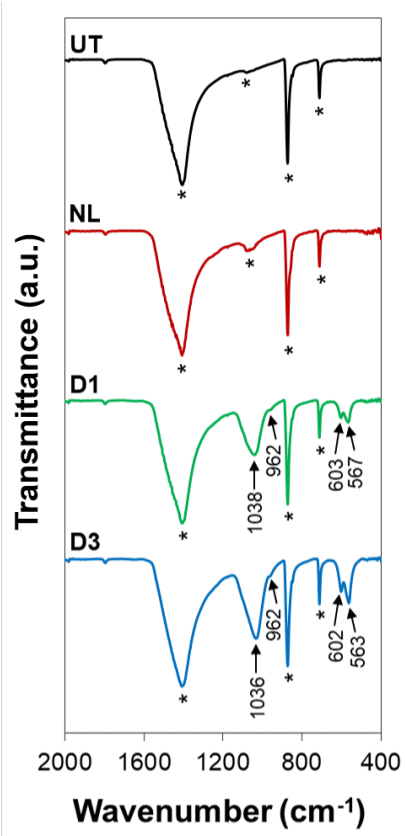

Figure 1. FT-IR spectra of untreated and treated specimens (bands attributed to the substrate are marked with a *, while the position of new bands is reported).

SEM observation of fracture surfaces (Figure 2 and Figure 3) and polished cross sections (Figure 4) revealed that in no case was a clear superficial crust formed after treatment. While in the case of nanolimes the elemental composition of the substrate and the consolidant is the same, so that the consolidant presence cannot be traced by chemical analysis, in the case of the DAP-treatments EDS provided useful information about the penetration depth. Starting from the treated surface, phosphorus was detected through all the mortar thickness (1 cm), the signal being higher in the “D3” sample than in the “D1” one (Figure 3). This further confirmed that a higher amount of new CaP phases was formed after the “D3” treatment, in agreement with the FT-IR results. The high penetration depth registered in the present case (at least 1 cm) is consistent with previous results on lime mortars, as DAP solutions have been reported to penetrate from at least 1 cm [13] up to 4 cm [11] from the treated surface. In the case of nanolimes, no clear indication about the penetration depth could be obtained by EDS, nor was morphology observation sufficient to derive conclusive information. According to the literature, depending on the porosity of the substrate, penetration down to 4 cm from the treated surface has been reported [40], but nanoparticle transport back to the surface during drying has been observed, which may be responsible for particle accumulation near the surface [40].

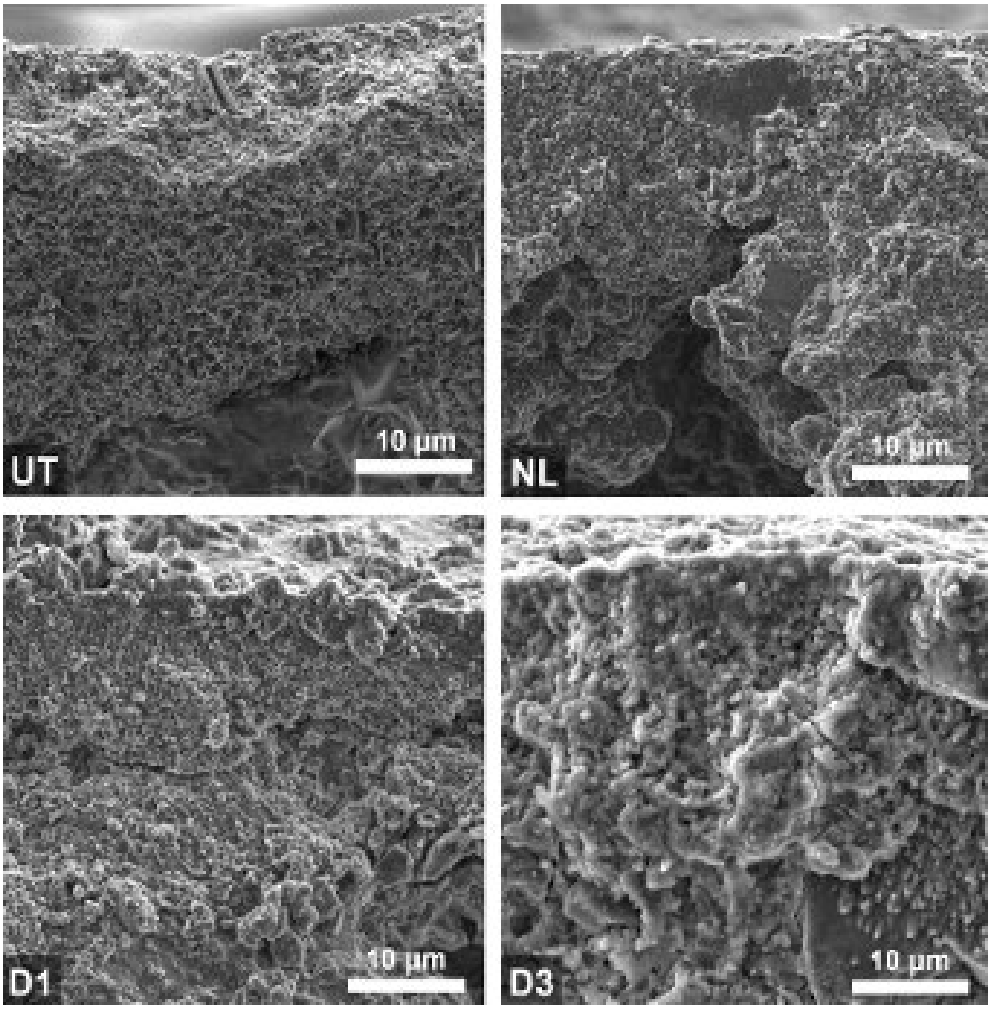

Figure 2. SEM images of fracture surfaces of untreated and treated samples, before accelerated ageing by freezing-thawing cycles.

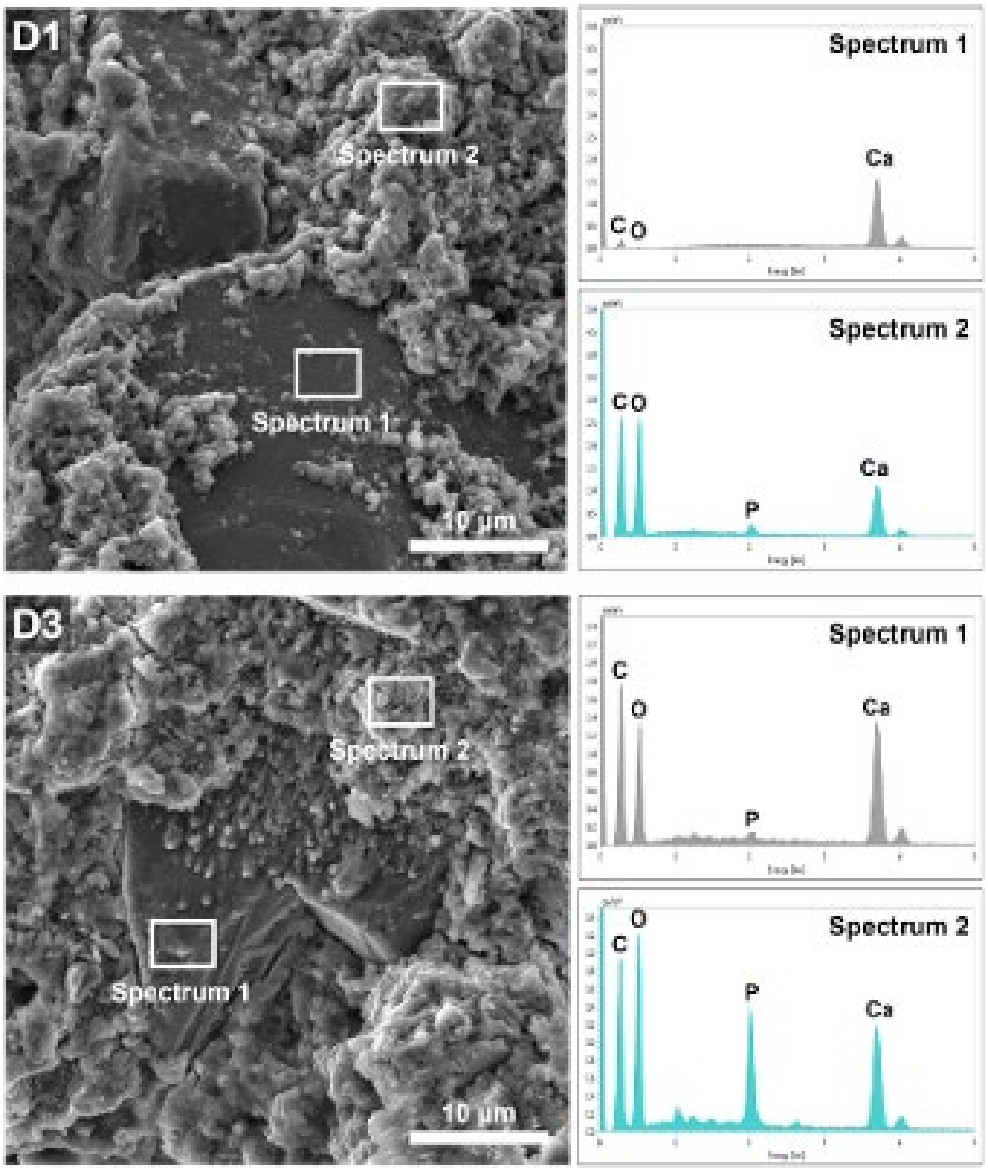

Figure 3. SEM images and EDS spectra of samples treated by DAP (treated surface in the upper part).

The new consolidating phases were responsible for some alterations in the mortar aesthetic appearance (Table 1), but the resulting color change can be considered as always acceptable (Figure 5). The “NL” and “D1” treatments caused color changes (ΔE* = 1.2 and 2.2, respectively) even below the visibility limit (ΔE* = 2.3 [41]). “D3” caused a higher color change (ΔE* = 4.3), mostly owing to a decrease in lightness and a shift towards blue (Table 1), but the color alteration was anyway below the common acceptability limit (ΔE* = 5 [42]). However, in view of the possible application to colored plasters and renders, the color alteration induced by the “D3” treatment should be specifically investigated case by case. All things considered, in the present study none of the consolidants gave rise to aesthetic compatibility issues.

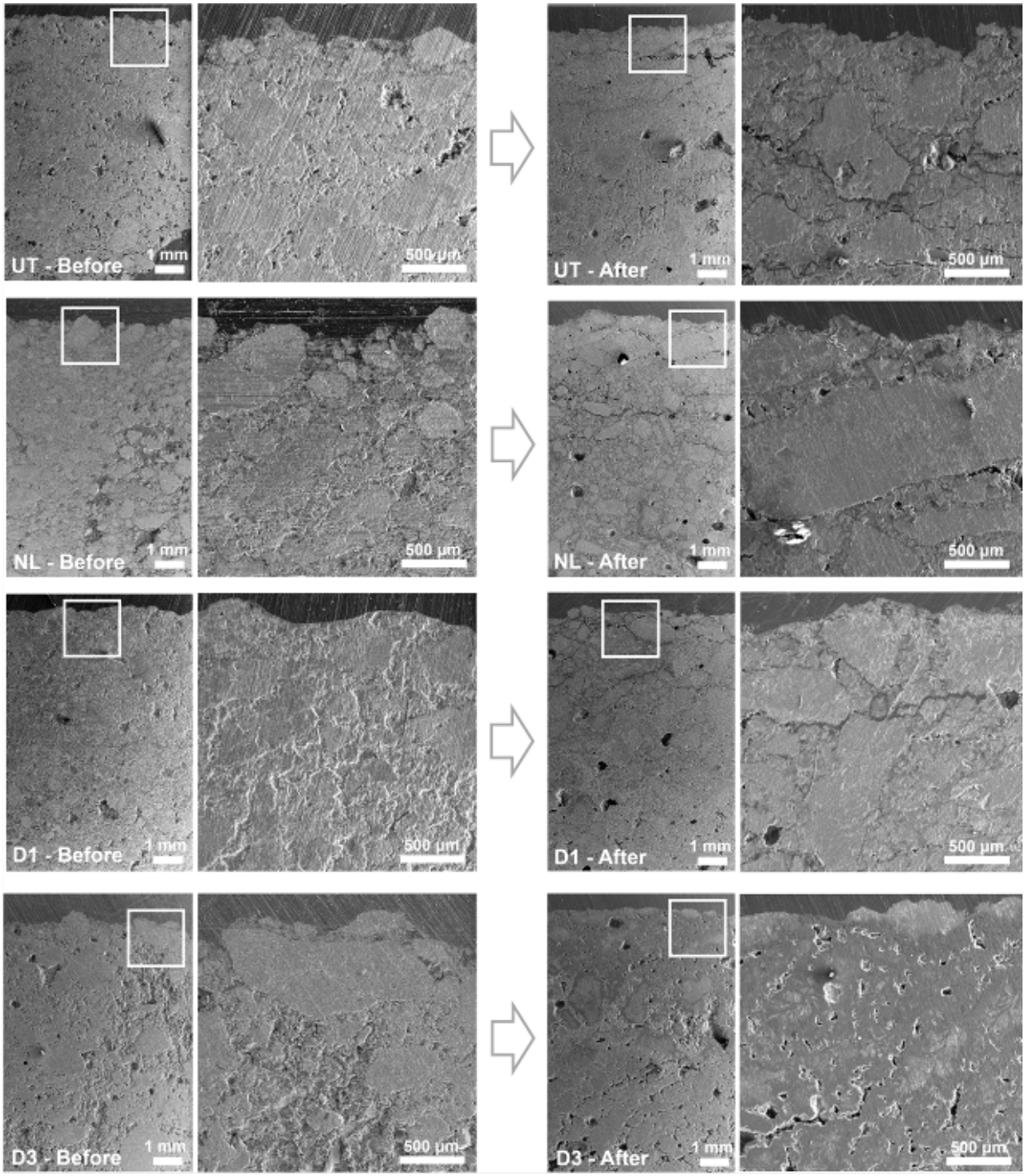

Figure 4. SEM images of polished cross sections of untreated and treated samples, before (left) and after (right) accelerated ageing by freezing-thawing cycles.

Table 1. Color parameters (L* = black-white, a* = green-red, b* = blue-yellow) on untreated and treated specimens and resulting variations ΔL*, Δa*, Δb*, ΔE* (L*, a*, b* are averages for 9 measurements).

	L*	a*	b*	ΔL*	Δa*	Δb*	ΔE*
UT	94.0 ± 0.2	-0.5 ± 0.0	1.8 ± 0.1	-	-	-	-
NL	92.9 ± 0.5	-0.4 ± 0.0	2.4 ± 0.2	-1.1	0.1	0.6	1.2
D1	92.1 ± 0.5	-0.5 ± 0.0	2.7 ± 0.2	-1.9	0.0	1.0	2.2
D3	91.2 ± 0.5	-0.4 ± 0.1	5.0 ± 0.8	-2.7	0.1	3.3	4.3

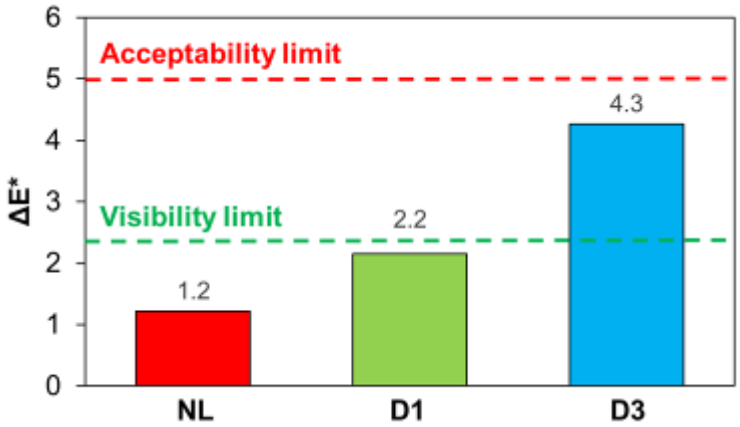

Figure 5. Color change after treatment by the various consolidants.

The new consolidating phases also caused some limited alterations in the mortar pore system, as shown in Figure 6 (solid lines) and Figure 7 (solid bars). In terms of total open porosity (OP), compared to the untreated reference (OP = 26.9%), the "NL" and "D1" treatments caused negligible changes, while the "D3" treatment caused the most pronounced alteration, which was however very limited (OP = 24.7%). In terms of pore size distribution (Figure 7), the "NL" treatment caused basically no alteration, while "D1" and "D3" caused a slight decrease in the amount of bigger pores and a corresponding increase in the amount of smaller pores. This is the effect of the new CaP formation, which partly occluded the bigger pores, thus apparently forming new smaller pores. The limited effect of the DAP-treatments on the pore system, mainly consisting in a slight shift in pore size distribution towards smaller pores, is consistent with previous results on stones [43] and mortars [11].

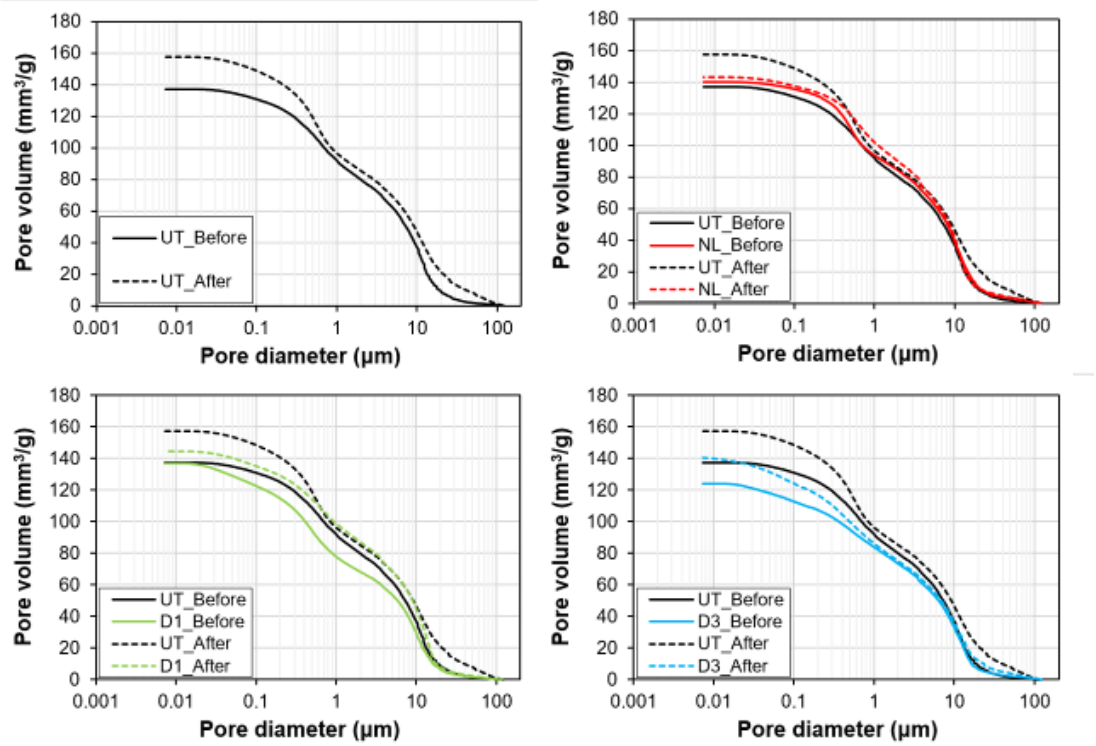

Figure 6. Cumulative pore volume of untreated and treated samples, before (solid lines) and after (dotted lines) accelerated ageing by freezing-thawing cycles.

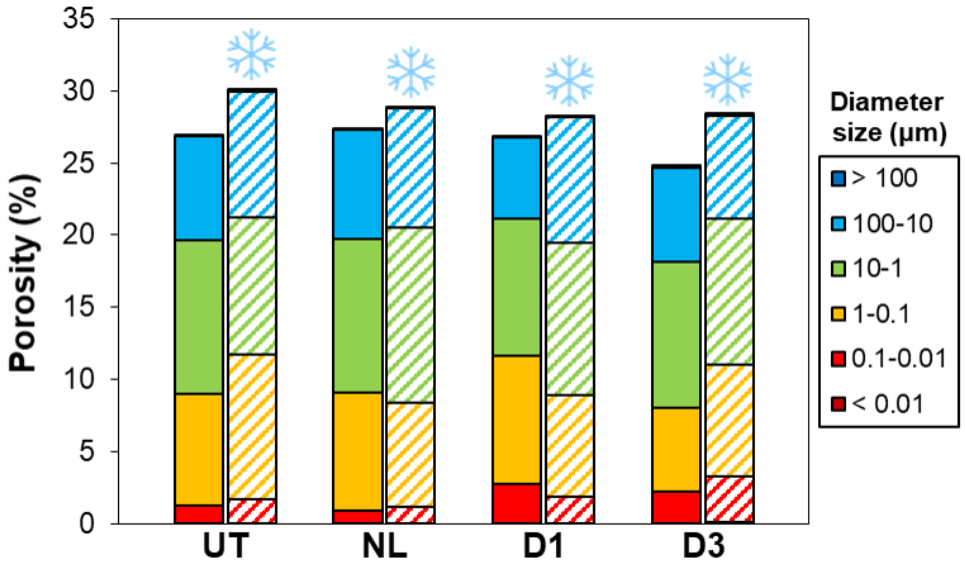

Figure 7. Pore size distribution of untreated and treated samples, before (solid bars) and after (hatched bars) accelerated ageing by freezing-thawing cycles (indicated by the frost symbol).

Consistent with the limited changes in the pore system, none of the consolidants caused significant alterations in water transport properties (Figure 8). Some reduction in the rate of water sorption was registered in all the samples (because water is absorbed more slowly in smaller pores and the treatments caused a slight shift of the pore size distribution towards smaller pores, Figure 6), but the final absorption corresponded to full saturation for all the conditions. It is noteworthy that the "D1" samples apparently experienced some reduction in sorptivity in the middle part of the test (green curve between about 50 and 125 $s^{1/2}$). Considering that the "D1" samples experienced a less pronounced modification in pore size distribution than the "D3" ones and that "D3" samples exhibited a limited alteration in water sorptivity, the slowing down of water absorption registered for the "D1" samples is likely to be ascribed to the experimental conditions during the test. In fact, the water level has to be manually maintained constant during the test by periodically refilling water in the container with the samples. Most likely, the apparent reduction in water sorptivity of the "D1" samples was due to a decrease in the water level in the middle part of the test. A limited alteration in water absorption can be regarded as positive, considering that conservation treatments that cause a strong alteration in water transport properties (e.g. hydrophobic treatments, also including ethyl silicate) may give rise to compatibility issues if a water source is present behind the consolidated layer, which acts as a barrier preventing water from exiting the consolidated material [44].

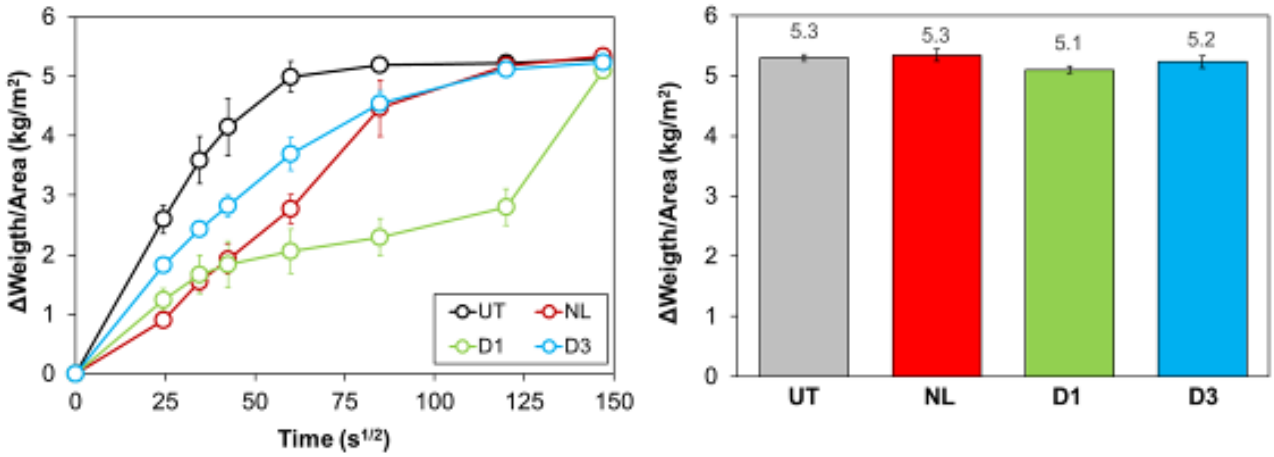

Figure 8. Water sorptivity (left) and total water absorption (right) of untreated and treated specimens.

2.3.4. Effectiveness

The amount of liquid consolidants absorbed by the specimens is reported in Figure 9. In the case of the DAP-treatments, the amounts found in this study for lime mortars (1.6-1.8 kg/m^2) are in good agreement with the values previously reported for porous limestone (1.4-1.5 kg/m^2 [43]), the difference being ascribable to the specific properties of two substrates. In the case of nanolimes, the product uptake (0.5 kg/m^2) was lower compared to the DAP-treatments, which can be explained considering the different concentrations of the consolidants (5 g/L for "NL", 132 g/L for "D1" and 396 g/L for "D3") and the different volatility of the solvents (ethanol, having vapor pressure of 5.8 kPa, for "NL"; water, having vapor pressure of 2.3 kPa, for "D1" and "D3").

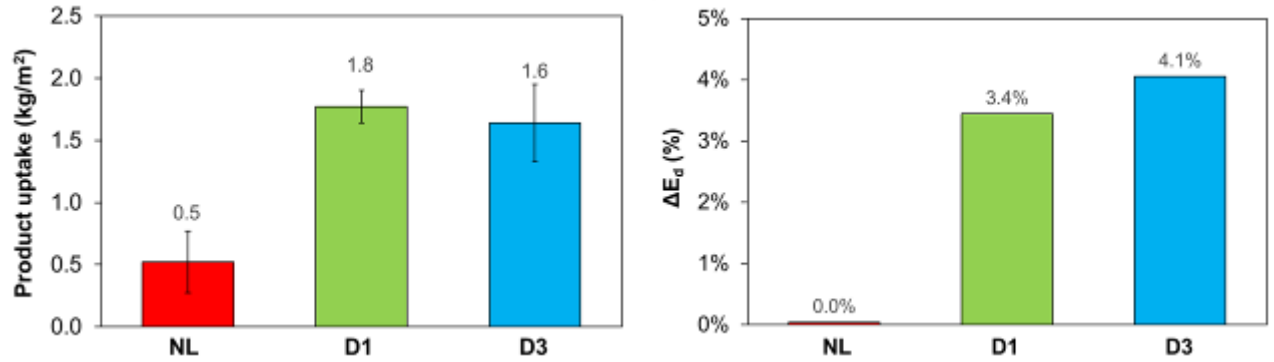

Figure 9. Product uptake (left) and percentage UPV increase (right) after treatment by the various consolidants

After curing, the liquid consolidants formed new CaP binding phases that caused the increases in E_d reported in Figure 9 and the decreases in materials loss after STT reported in Figure 10.

The E_d increases were actually modest (reaching +4.1% for "D3"), which was unexpected considering that E_d increases up to +75% [11] and +100% [13] had been obtained in

previous studies on lime mortar consolidation by similar DAP formulations, while UPV increases up to +10% had been reported for mortars treated with nanolimes [5]. A first reason for such low E_d increases may be that, while in marbles UPV measurements are able to effectively detect the formation of new binding phases in intergranular fissures, in highly porous materials like mortars the bridging effect of the new phases leads to UPV increases much less evident, because the overall porosity of the material is basically unchanged (Figure 6). A second reason for the modest E_d increases may be the specific experimental set-up adopted in this study (i.e. UPV measurements across mortar layers that are attached to brick substrates), which may be altered by the presence of the brick layer. However, in a previous study where the same experimental set-up had been used for a different type of substrate (lime mortars containing siliceous aggregates, instead of calcareous ones), higher improvements (ΔUPV of +5% for "NL", +17% for DAP) had been recorded [12].

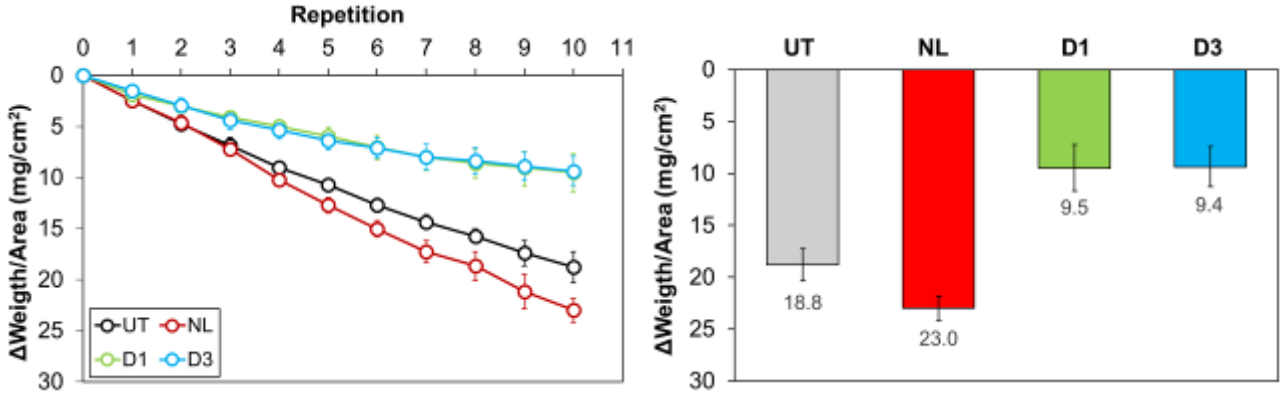

Figure 10. Progressive (left) and cumulative (right) material loss after STT on untreated and treated specimens.

An indication of the actual consolidating ability of the various treatments investigated in this study was obtained by STT. As illustrated in Figure 10, the scarce effectiveness of nanolimes, already suggested by ultrasonic measurements (ΔE_d = 0%), was confirmed, as the cumulative material loss after 10 STT was substantially the same for the "NL" and the "UT" specimens (actually, slightly higher for the former). Even though no clear formation of a surface crust was observed by SEM (Figure 2 and Figure 4), still the lack of consolidating effectiveness is likely due to scarce formation of new binding phases deep in the mortar, resulting in unchanged cohesion after consolidation. The higher weight loss apparently exhibited by the "NL" specimens, compared to the "UT" ones, may actually be due to the easy removal of newly formed calcite crystals deposited mainly near the tested surface. In the case of the DAP-treatments, significant decreases in material loss after STT were registered (about -50% for both "D1" and "D3", Figure 9). Such improvements in resistance to STT are higher than those reported in a previous study, where alternative formulations of the DAP treatment had been tested on lime mortars (decreases in material loss by STT by 35%) [13]. In the present study, the effects of "D1" and "D3" appear similar based on STT results, whereas a higher improvement for "D3" was suggested by E_d measurements (Figure 8).

All things considered, the consolidating effectiveness of the various treatments increased in the order: UT ≈ NL < D1 < D3. A confirmation of such trend was further obtained by the results of the durability tests, described in the following.

2.3.5. Durability

Accelerated ageing by freezing-thawing cycles had a dramatic effect on untreated mortar, which underwent formation of new microcracks clearly visible by SEM (Figure 4 and Figure 11), resulting in increased open porosity and pore size (Figure 7). This led to a significant loss in cohesion after ageing, evidenced by the high weight loss (-1.1%) and high E_d decrease (-52.6%) (Figure 12) after the cycles, as well as dramatic material loss when the STT was repeated (Figure 13). After the freezing-thawing cycles, the cumulative material loss by STT reached 338.5 mg/cm^2, hence almost 20 times more than before accelerated ageing (18.8 mg/cm^2, Figure 10).

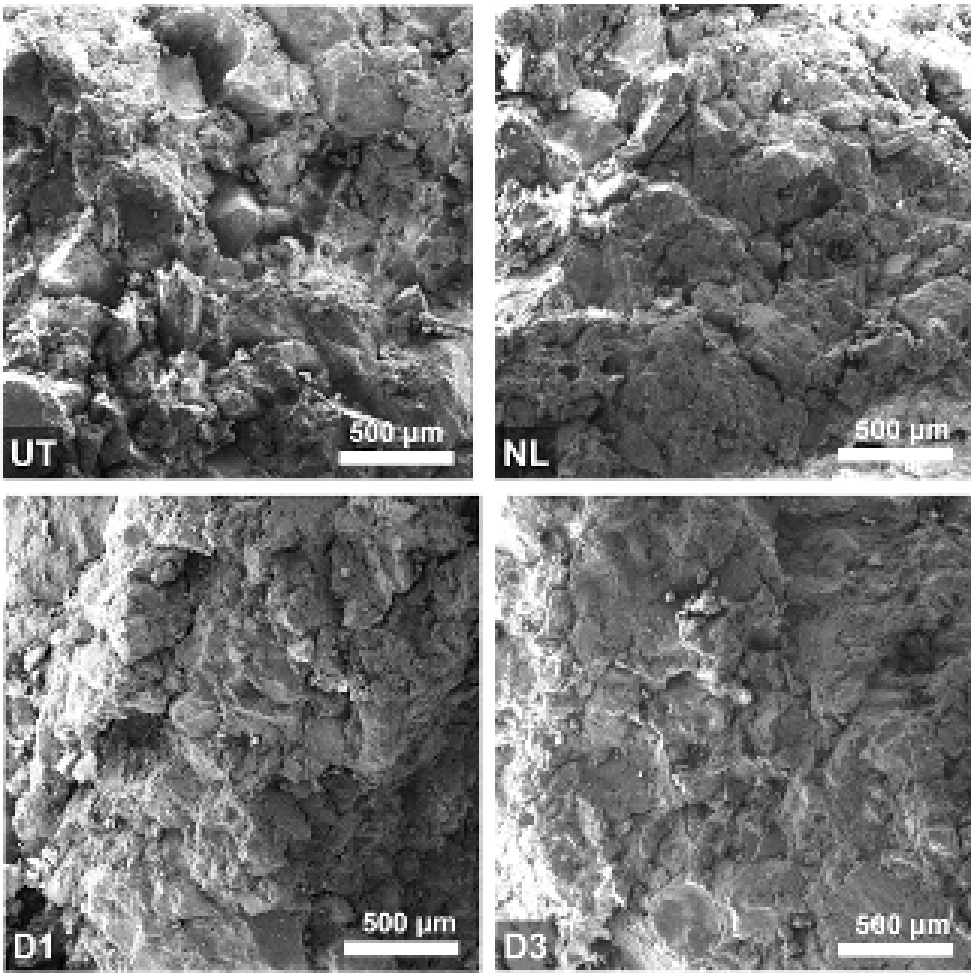

Figure 11. SEM images of fracture surfaces of untreated and treated samples, after accelerated ageing by freezing-thawing cycles.

Specimens treated by nanolimes exhibited similar cracking (Figure 4 and Figure 11) and alterations in open porosity and pore size distribution (Figure 6 and Figure 7) as the

untreated reference. Accordingly, comparable weight loss (-0.9%) and E_d decrease (-53.6%) were registered (Figure 12). Consistently, also the STT pointed out a similar material loss for the two conditions (actually, slightly higher for "NL" than "UT", Figure 12), indicating that no significant consolidation was obtained by nanolimes.

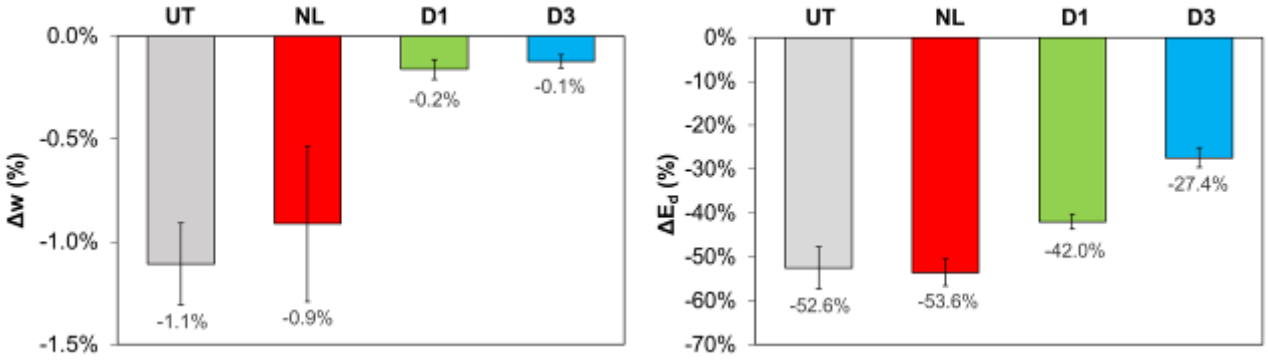

Figure 12. Weight loss (left) and percentage UPV loss (right) of untreated and treated specimens after accelerated ageing by freezing-thawing cycles.

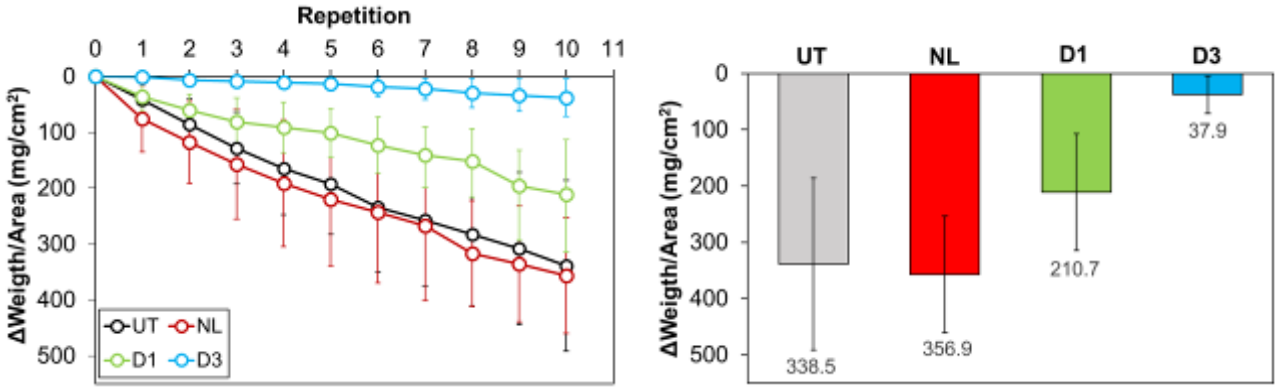

Figure 13. Progressive (left) and cumulative (right) material loss after STT on untreated and treated specimens after accelerated ageing by freezing-thawing cycles.

In the case of the DAP-treatments, less pronounced cracking (Figure 4 and Figure 11) and formation of new voids (Figure 6 and Figure 7) were registered after the freezing-thawing cycles, compared to the "UT" and "NL" conditions. Both DAP treatments also allowed to significantly reduce the weight loss after the freezing-thawing cycles (-0.2% for "D1" and -0.2% for "D3", compared to -1.1% for the "UT" reference, Figure 12). The "D3" treatment proved to be the most effective in reducing damage caused by the ageing cycles, in agreement with the results obtained right after consolidation. Indeed, this formulation caused the lowest E_d decrease (-27.4%, compared to -52.6% for "UT", Figure 11) and the lowest material loss by STT (-37.9 mg/cm^2, compared to -338.5%, Figure 12).

All things considered, the durability tests confirmed and better elucidated the trend in consolidating effectiveness of the various treatments, whose performance improved in the following order: UT ≈ NL < D1 < D3.

4. CONCLUSIONS

The present study aimed at evaluating the compatibility, effectiveness and durability of two different consolidating treatments for lime mortars, namely nanolimes ("NL") and DAP solutions, tested in two formulations ("D1", less concentrated, and "D3", more concentrated). Based on the obtained results, the following conclusions can be derived:

- the "NL" treatment proved to be fully compatible (invisible color change and negligible alteration in open porosity and water absorption), but demonstrated very limited consolidating effectiveness (no decrease in material loss by scotch tape test, STT). When NL-treated specimens were subjected to accelerated ageing by freezing-thawing cycles, the "NL" treatment was not able to provide a significant benefit (no reduction in material loss when STT was repeated after the cycles).
- the DAP-based treatments, especially the more concentrated one "D3", were effective in decreasing the material loss by STT (-50%, compared to the untreated reference) and maintained the consolidating ability also after the freezing-thawing cycles (in the case of "D3", after accelerated ageing material loss was reduced by 10 times, compared to the untreated reference). Such consolidating effectiveness and durability to accelerated ageing were obtained without significant chromatic alterations (invisible color change for "D1", visible but acceptable for "D3") and without significant alterations in open porosity and water absorption.

The results obtained in this study confirm the potential of DAP solutions for consolidation of lime-based mortars, plaster and renders. Compared to nanolimes, DAP solutions proved to be more effective, also after accelerated ageing, with the advantage that the DAP treatment only requires curing for 24 hours, while carbonation of nanolimes requires up to 4 weeks. As the next step, future research will be dedicated to investigate the effects of DAP solutions when applied onto colored plasters and renders (e.g. frescoes and wall paintings). Although SEM observation did not reveal the formation of a clear surface crust in the present study, this possible issue is particularly important in the case of colored plasters, so it will be further specifically investigated in the future.

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