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Comparison between ammonium phosphate and nanolimes for render consolidation

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Abstract. In this study, a systematic comparison is presented between ammonium phosphate and commercial nanolimes for the conservation of lime-based renders. Such comparison is very significant, considering that nanolimes are the most widely used inorganic consolidant commonly applied onto plasters, renders and frescoes. Specimens made of slaked lime and siliceous sand were prepared, by applying the fresh mortar onto a solid brick substrate. After curing for 4 months, samples were consolidated by (i) an aqueous solution of diammonium hydrogen phosphate and (ii) commercial nanolimes. The effects of the treatments were evaluated in terms of composition and morphology of the new phases, effectiveness (ultrasounds and scotch tape test) and compatibility (color change and water absorption). The results of the study confirm the high potential of the phosphate treatment, able to provide higher mechanical consolidation in a shorter time (24 hours, instead of at least 4 weeks for nanolimes), while being equally compatible from the aesthetical and physical point of view.

1. Introduction

Lime mortars and renders exposed outdoors often need consolidation, because weathering processes such as binder dissolution in rain, freeze-thaw cycles and salt crystallization cycles cause pulverization and grain detachment. Several types of organic and inorganic consolidants have bene proposed through the years for lime mortar consolidation, such as acrylic resins [1], ethyl silicate [1,2] and nanolimes [3–6]. However, each of these treatments has shown some limitations, in terms of either effectiveness, compatibility and/or durability. For this reason, the search for alternative consolidants, able to simultaneously meet all these requirements, is still in progress.

Recently, ammonium phosphate solutions have been tested as possible consolidants for lime and cement mortars conservation [7]. Ammonium phosphate was proposed 10 years ago for consolidation of carbonate stones, such as porous limestone and marble [8,9]. By reacting the calcium-rich substrate with aqueous solutions of ammonium phosphate, calcium phosphates (CaP) can be formed inside the stone pores [8]. These new CaP are able to bond stone grains more effectively, which results in improved mechanical properties [8,10,11]. Considering the good results obtained on different types of stones, different formulations of the ammonium phosphate treatment have recently been explored also in the case of mortars with different binder (slaked lime, slaked lime with a pozzolanic addition, natural hydraulic lime, cement) and different aggregate (siliceous or calcareous) [7]. Promising results were obtained, as in all cases the ammonium phosphate treatment was able to improve mechanical properties, without significantly altering the pore system and the water transport properties of mortar [7].

In this study, a comparison is presented between ammonium phosphate and nanolimes for consolidation of lime-based renders. Nanolimes were selected as an alternative to ammonium phosphate, considering that nanolimes were originally proposed for conservation of lime-based wall paintings [12] and that they are currently frequently used for consolidation of lime mortars [3–6]. Mortar specimens made of slaked lime and siliceous sand were produced and applied over a brick substrate. After curing, part of the specimens was consolidated by ammonium phosphate, part by commercial nanolimes and part was left untreated as reference. The performance of the two treatments was then evaluated in terms of effectiveness and compatibility.

2. Materials and methods

2.1. Materials

First, brick specimens (5x5x1 cm^3) were sawn form a single solid brick. Then, mortar specimens (5x5x1 cm^3) were produced and applied onto the brick specimens, so as to obtain 5x5x2 cm^3 sandwich-specimens, resembling renders applied onto solid brick masonry. For mortar preparation, slaked lime and standard siliceous sand were used, adopting a 1:2 binder to aggregate ratio and 1:1 water to binder ratio. Mortars were prepared using a Hobart mixer and then cast into plastic moulds. Specimens were then demoulded and cured in a climatic chamber (RH > 95%, T = 21 ± 2 °C) for 4 months before application of the consolidants.

2.2. Consolidants

The ammonium phosphate treatment (labelled "DAP") consisted in application of an aqueous solution containing 1 M diammonium hydrogen phosphate (DAP) and 1 mM $CaCl_2$. $CaCl_2$ was added to the DAP solution because it promotes formation of the new CaP in a shorter time [13]. This formulation was chosen considering the good performance it has demonstrated for stone consolidation [11] and also considering that a previous study showed that more concentrated DAP solutions may cause overstrengthening of the mortar substrate, while less concentrated solutions exhibited limited strengthening efficacy [7]. The DAP solution was applied by spraying 10 times over the 5x5 cm^2 mortar face, each time waiting for the solution to be absorbed into the mortar before spraying again. At the end of the spray application, the specimens were wrapped in a plastic film for 24 h to avoid evaporation. Then, samples were unwrapped, rinsed with water and stored together with the nanolime-treated specimens until testing, as detailed in the following.

The commercial product Nanorestore Plus Propanol 5 by CTS Srl (Italy) was selected as the nanolime-based consolidant (labelled "NL"). Similarly to the case of DAP, it was applied by spraying 10 times, waiting for the product absorption before successive applications. Following the manufacture's technical data sheet, to avoid possible formation of white hazes over the treated surface, the product was not applied directly onto the mortar surface, but through a sheet of filter paper. At the end of the spraying application, a poultice of cellulose pulp impregnated with deionized water was applied over the treated surface (still covered with filter paper), as suggested by the manufacture's technical data sheet to promote carbonation. When the poultice became dry (after 3 days), the poultice was removed and the specimens were cured in a climatic chamber (RH > 95%, T = 21 ± 2 °C) for 1 month before testing, thus adopting the curing time recommended by the manufacturer.

To avoid any possible interference from different exposure conditions, untreated (labelled "UT") and DAP-treated specimens were stored together with the NL specimens in the climatic chamber. Before testing, all the specimens were dried in an oven at 40 °C for 2 weeks.

2.3. Characterization

The formation of new consolidating phases after treatment was assessed by Fourier Transform Infrared Spectrometry (FT-IR), using a Perkin Elmer Spectrum 2 (ATR mode, 2000-500 cm^{-1} range, spectral resolution 2 cm^{-1}, 32 scans, data interval 1 cm^{-1}). FT-IR spectra were acquired on powder samples obtained by scratching with a spatula.

The increase in cohesion after consolidation was first assessed by ultrasonic testing before and after consolidation, using a Matest instrument with 55 kHz transducers. The ultrasonic pulse velocity (UPV) was measured across the mortar layer, in the two directions parallel to the 5x5 cm^2 face, then averaging the values for the two directions. To avoid any interference from the brick substrate, a suitably sized rubber couplant was used between the 5x1 cm^2 face of the mortar layer and the transducers. Three specimens were tested for each condition.

Then, the increase in cohesion after treatment was assessed by performing the so-called scotch tape test (STT). The test was performed by applying 6x2.5 cm^2 pieces of scotch tape onto the treated surface of the specimens, so that one half of the 5x5 cm^2 mortar face was covered with the scotch tape, with 1 cm

remaining for the scotch tape removal. After uniformly pressing the scotch tape, it was manually removed adopting the same speed and angle for all the specimens. The amount of material removed was determined by weighing the specimens before and after removal of each scotch tape piece. To ascertain the permanence of the consolidating effectiveness also in depth in the sample, the STT was repeated 10 times in the same position. The STT was carried out onto three specimens for each condition.
Specimens were then fractured by chisel to obtain samples for observation by a scanning electron microscope (SEM), using a field emission gun (FEG) SEM (Tescan Mira3). Before observation, the sample surface was made conductive by sputter coating with aluminium.
The aesthetic compatibility of the treatments was assessed by determining the CIELAB color parameters L*, a* and b*, using a NH310 colorimeter. The color difference ΔE* between untreated and treated specimens was then calculated using the formula $\Delta E^* = (a^{*2} + b^{*2} + c^{*2})^{1/2}$. For each condition, three specimens were tested, the measurement being repeated in three different spots for each specimen.
The physical compatibility of the treatments was assessed by determining the water sorptivity and the amount of water absorbed by capillarity after 2 hours (sufficient to reach saturation). The specimens were placed on top of a 1-cm thick layer of filter papers saturated with deionized water, with the mortar layer in contact with the filter paper. In this way, water absorption occurred first through the mortar layer and then through the brick layer. Three specimens were tested for each condition.

3. Results and discussion

The FT-IR spectra of untreated and treated specimens are illustrated in Figure 1. In the untreated reference, bands owing to calcite (i.e., the carbonated binder) and quartz (i.e., the aggregate) are present. After the DAP treatment, new bands at 1036, 604 and 567 cm^{-1} are present. These bands can be attributed to formation of hydroxyapatite (HAP, $Ca_{10}(PO_4)_6(OH)_2$), although formation of octacalcium phosphate (OCP, $Ca_8(HPO_4)_2(PO_4)_4 \cdot 5H_2O$) cannot be completely excluded [14]. Being less soluble than calcite, both minerals are expected to give rise to long lasting consolidating action, the benefit being higher in case of HAP (which is the least soluble CaP phase at pH>4).

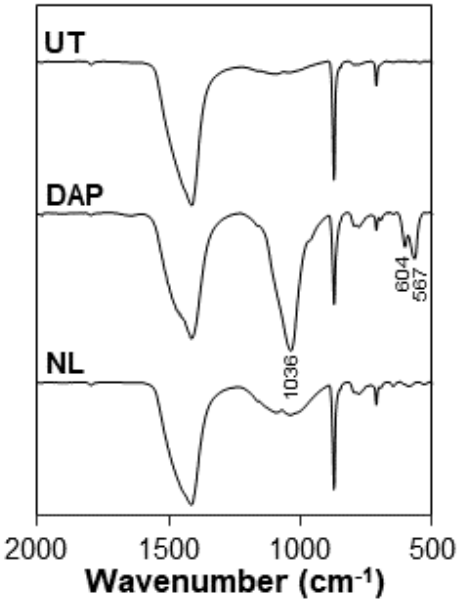

Figure 1. FT-IR spectra of untreated and treated specimens.

After treatment with nanolimes, no band owing to new phases can be detected. This was expected, because bands owing to calcium carbonate originated by carbonation of nanolimes overlap with the bands owing to the substrate. Bands owing to quartz are slightly more pronounced compared to the untreated reference, but this is due to the influence of the siliceous aggregates, present in all the mortars.

The morphology of the untreated render and of the treated specimens is illustrated in Figure 2. New CaP phases, having a typical flower-like morphology, can be seen on the surface of the DAP-treated specimens. In the case of the NL-treated specimen, the distinction of the new phases is less straightforward, because of the similarity between the new calcite phases and the substrate. However, a distinct layer can be observed on the surface of the NL-treated sample, which may be attributed to formation of a new layer of calcite crystals over the sample surface.

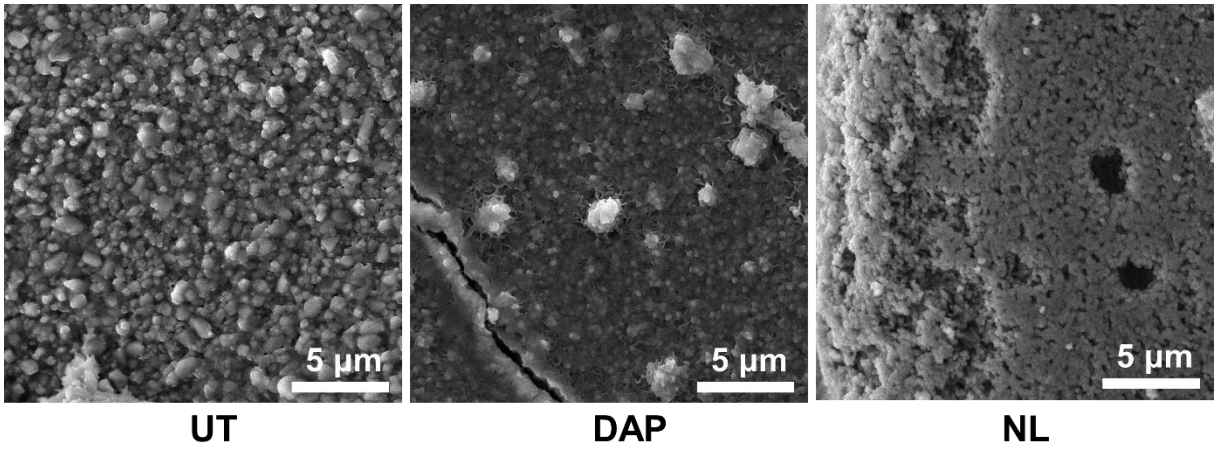

Figure 2. SEM images of untreated and treated specimens.

The effects of the new phases on the mortar ultrasonic pulse velocity are reported in Table 1. Before consolidation, all the specimens exhibited comparable UPV, ranging from 1.65 to 1.76 km/s. When repeated 6 weeks later (after that DAP and NL specimens had been consolidated and properly cured), even the untreated specimens exhibited some improvement ($\Delta UPV = +18\%$). Apart from some intrinsic variability in the experimental results, such improvement is likely to be ascribed to a progress in the carbonation of lime mortar, even after curing for 4 months. (The rate of carbonation had been investigated by X-ray diffraction before consolidating the specimens and no trace of portlandite had been detected, likely because it was below the instrument sensitivity.) Considering the UPV increase of the untreated reference, in the case of the consolidated specimens only improvements higher than those exhibited by the untreated reference were regarded as significant. These additional improvements amount to $\Delta UPV_{,net} = +17\%$ in the case of DAP and $\Delta UPV_{,net} = +5\%$ (Table 1). These increases in mortar cohesion determined by ultrasounds are in line with previous results reported for ammonium phosphate treatments [7] and nanolimes [4]. Between the two treatments, DAP seems able to provide a greater improvement in the bonding between the grains, compared to nanolimes.

Table 1. Ultrasonic pulse velocity (UPV) of untreated and treated specimens (the "net" UPV increase is calculated by subtracting the improvement of the untreated reference to isolate the benefit deriving from consolidation. Values are averages for 3 specimens.

	UPV (km/s)		ΔUPV (%)	ΔUPV (%)
Specimen	Before	After	Total	Net
UT	1.76 ± 0.21	2.05 ± 0.18	+18%	-
DAP	1.66 ± 0.18	2.23 ± 0.27	+35%	+17%
NL	1.65 ± 0.15	2.03 ± 0.22	+23%	+5%

A similar trend as assessed by ultrasounds was confirmed by the scotch tape test. As illustrated in Figures 3 and 4, the amount of material removed after each test was consistently lower for the consolidated specimens, compared to the untreated reference. In particular, after 10 tests, the DAP-treated specimens exhibited the lowest cumulative material removal (22.9 mg/cm^2), followed by specimens treated by NL (27.7 mg/cm^2), while the untreated reference underwent a cumulative material removal of 40.5 mg/cm^2.

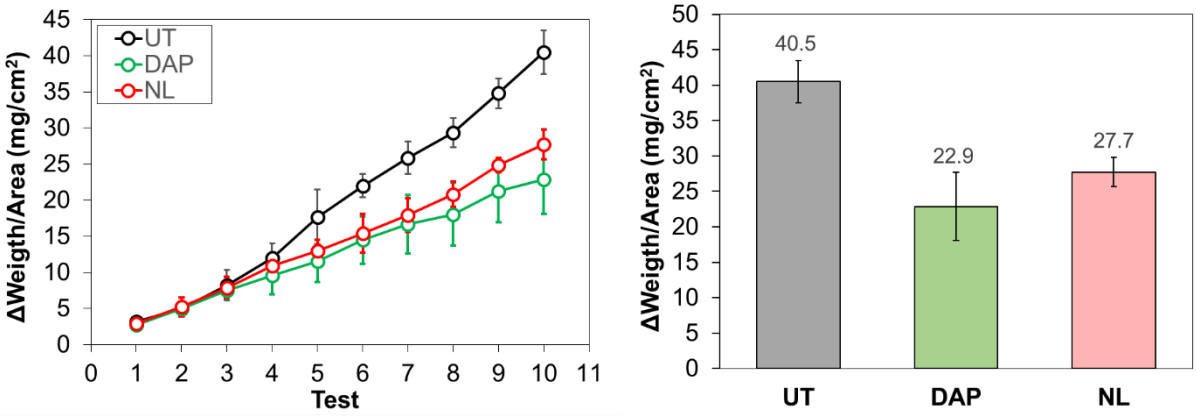

Figure 3. Results of the STT: progressive (left) and total (right) material removal after 10 tests.

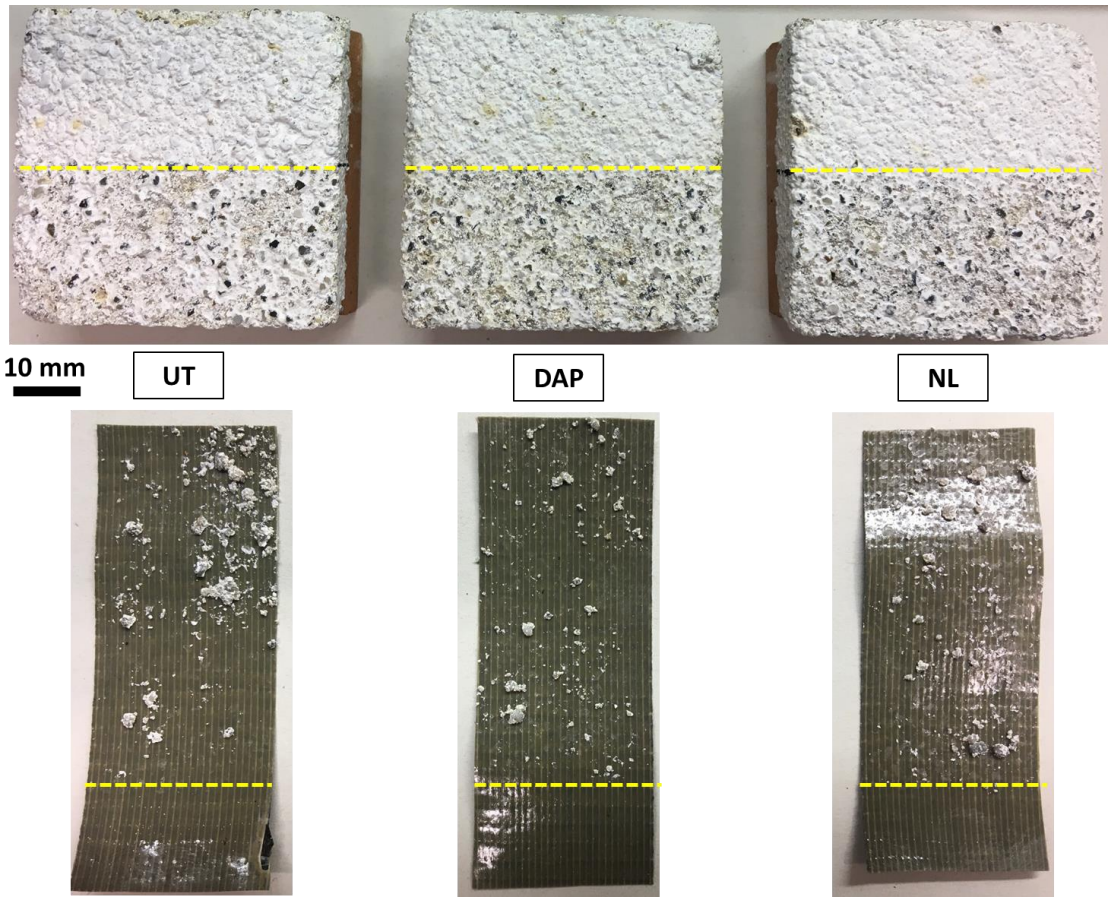

Figure 4. Sample appearance after 10 STT (top) and material removed in the 10th test (bottom).

In terms of aesthetic compatibility, both consolidants caused a color change below the visibility limit of the human eye (ΔE* = 2.3 [15]), thus well below the threshold commonly accepted in the field of conservation (ΔE* = 5, [2]). The color change caused by nanolimes is lower than that caused by DAP, which mostly induces an increase in the L* parameter (thus some whitening).

Table 2. Color parameters (L* = black÷white, a* = green÷red, b* = blue÷yellow) of untreated and treated specimens and color difference (ΔE*) between the two. Values are averages for 3 specimens, each tested in 3 different spots.

Specimen	L*	a*	b*	ΔE*
UT	88.29 ± 0.57	-0.24 ± 0.08	2.93 ± 0.07	-
DAP	90.51 ± 0.28	-0.56 ± 0.08	2.93 ± 0.26	2.24
NL	88.03 ± 1.03	-0.31 ± 0.14	3.17 ± 0.25	0.36

In terms of physical compatibility, both consolidants only caused minor alterations in the rate in water absorption and water absorbed after 2 hours (corresponding to specimen saturation), as illustrated in Figure 5. This can regarded as a positive feature of both consolidants, as the exchange of liquid water between the treated renders and the environment is not significantly inhibited.

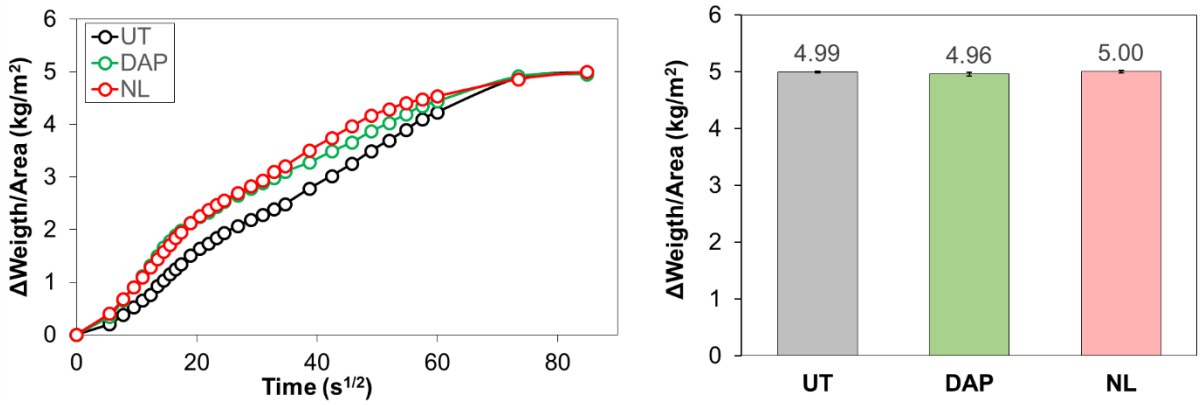

Figure 5. Results of the sorptivity test: sorptivity (left) and water absorption after 2 hours (right).

Conclusions

In the present study, a comparison was carried out on the use of ammonium phosphate solutions and nanolimes for the consolidation of lime-based renders. Both treatments demonstrated to be highly compatible from the aesthetical point of view, causing color changes below the human eye detection limit. However, the ammonium phosphate treatment caused a higher increase in ultrasonic pulse velocity and a higher reduction in material loss caused by scotch tape test, thus demonstrating higher mechanical effectiveness compared to nanolimes. This was possible thanks to formation of new calcium phosphates, able to improve the bonding among aggregates. Compared to nanolimes, the ammonium phosphate treatment also has the advantage of being effective in a much shorter time (24 h compared to 4 weeks). By combining results of the present study with recent findings on the effects of ammonium phosphate solutions onto historic pigments [16], future research will be dedicated to evaluate the suitability of ammonium phosphate for consolidation of frescoes and wall paintings, as well as the durability of the treated renders, which strongly depends on the specific environmental conditions [17].

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