ALMA MATER STUDIORUM
UNIVERSITÀ DI BOLOGNA

ARCHIVIO ISTITUZIONALE
DELLA RICERCA

Alma Mater Studiorum Università di Bologna
Archivio istituzionale della ricerca

Lime and cement mortar consolidation by ammonium phosphate

This is the final peer-reviewed author's accepted manuscript (postprint) of the following publication:

Published Version:
Sassoni E., Franzoni E. (2020). Lime and cement mortar consolidation by ammonium phosphate. CONSTRUCTION AND BUILDING MATERIALS, 245, 1-13 [10.1016/j.conbuildmat.2020.118409].

Availability:
This version is available at: https://hdl.handle.net/11585/760540 since: 2020-05-30

Published:
DOI: http://doi.org/10.1016/j.conbuildmat.2020.118409

Terms of use:

Some rights reserved. The terms and conditions for the reuse of this version of the manuscript are specified in the publishing policy. For all terms of use and more information see the publisher's website.

This item was downloaded from IRIS Università di Bologna (https://cris.unibo.it/).
When citing, please refer to the published version.

(Article begins on next page)

23 January 2025

LIME AND CEMENT MORTAR CONSOLIDATION BY AMMONIUM PHOSPHATE

Enrico Sassoni*, Elisa Franzoni

Department of Civil, Chemical, Environmental & Materials Engineering (DICAM)
University of Bologna, Italy
* Corresponding author: enrico.sassoni2@unibo.it

ABSTRACT
The present study investigates the strengthening ability and the compatibility of two different ammonium phosphate solutions used for consolidation of mortars based on slaked lime, natural hydraulic lime or cement, to resemble historic and modern mortars. After impregnation for 24 hours, new calcium phosphate phases were detected in all types of mortar. New calcium phosphates induced significant mechanical consolidation, with only slight alterations in the pore system and in water transport properties. In lime-based mortars (initially white) no color alteration was visible after treatment, while colored mortars experienced some color change when the more concentrated phosphate solution was used.

KEYWORDS
Historic mortars; Repair mortars; Slaked lime; Cocciopesto; Brick powder; Natural hydraulic lime; Cement mortars; Inorganic consolidants; Hydroxyapatite; Calcium phosphates

HIGHLIGHTS
- Ammonium phosphate solutions were investigated for mortar consolidation
- Mortars based on slaked lime, natural hydraulic lime or cement were considered
- After treatment for 24 hours, mechanical properties were increased in all mortars
- Only minor alterations in the pore system and water transport properties were found
- Some color change was visible only when highly concentrated solutions were used

1. INTRODUCTION

The use of ammonium phosphate solutions for consolidation of natural carbonate stones, such as limestone and marble, has received increasing attention in the last few years, because of the several advantages of this treatment compared to traditional consolidants [1-9]. Mechanical improvement is achieved by formation of calcium phosphates (CaP) at grain boundaries, as the reaction product between calcium ions coming from the stone [1] (and/or externally provided [2,3]) and phosphate ions supplied by impregnating the stone with an aqueous phosphate solution. In this way, stone grains are more effectively bonded and mechanical properties are increased [1,5,9]. Because the new CaP do not completely occlude pores and leave the stone hydrophilic, the phosphate treatment does not significantly alter the stone transport properties [1,9-11], unlike organic consolidants and TEOS-based consolidants (which cause temporary hydrophobicity) [12]. Moreover, the phosphate treatment also has the advantage of being effective after a few hours, since the new CaP are formed after reaction for 24-48 h [1,4,9], whereas lime- and TEOS-based consolidants require curing for several weeks [12,13]. Furthermore, CaP are very stable in standard environmental conditions, so formation of a CaP layer over stone surface is able provide the stone with significant protection against dissolution in rain [14-18].

Considering the potential of the phosphate treatment, several studies have been aimed at optimizing its consolidating and protective ability [18], investigating different application techniques [19], characterizing the new CaP phases formed after treatment [6,20] and assessing the treatment effects on a variety of lithotypes [21-24]. In spite of the abundant literature regarding natural stones, only a few studies have explored the use of ammonium phosphate for the conservation of "artificial stones", such as gypsum stuccoes [25], archaeological wall paintings [26] and recently also concrete [27].

In this paper, for the first time a systematic study is reported on the effectiveness and the compatibility of ammonium phosphate for consolidation of different types of mortar, designed to resemble mortars used in historic and modern architecture. Seven mortar types were considered, differing in terms of binder (slaked lime, natural hydraulic lime or cement), aggregates (siliceous or calcareous), possible addition of a pozzolanic fraction (brick dust, the so-called "*cocciopesto*") and water to binder ratio. First, formation of new CaP phases was monitored over time, to define the best treatment duration. Then, the consolidating effectiveness of the phosphate treatment (i.e., its ability to mechanically strengthen the mortars) was determined. Finally, the treatment compatibility was assessed, in terms of alterations in pore size distribution, water transport properties and aesthetical appearance.

2. MATERIALS AND METHODS

2.1. Mortar samples

Seven types of mortar were considered, as summarized in Table 1.

Table 1. Labelling and mix design of the different mortars (parts are expressed by volume)

Label	Slaked lime	NHL	CEM	Brick dust	Siliceous sand	Calcareous sand	Water	Water/binder ratio (v/v)
L+SIL_0.75	1	-	-	-	2	-	0.75	0.75
L+SIL_1	1	-	-	-	2	-	1	1
L+CAL_0.75	1	-	-	-	-	2	0.75	0.75
L+CAL_1	1	-	-	-	-	2	1	1
L+BRICK	1	-	-	1	2	-	1	1
NHL	-	1	-	-	3	-	1	1
CEM	-	-	1	-	3	-	2	2

"L" = lime, "NHL" = natural hydraulic lime, "CEM" = cement, "SIL" = siliceous sand, "CAL" = calcareous sand, "BRICK" = brick dust. The numbers "_0.75" or "_1" indicate the water to binder ratio.

For mortar preparation, slaked lime ("L"), natural hydraulic lime ("NHL", NHL 3.5 according to EN 459-1 [28]), Portland cement ("CEM", CEM I 32.5 R according to EN 197-1 [29]), brick dust ("BRICK), standard siliceous sand ("SIL", according to EN 196-1 [30]) and calcareous sand ("CAL") were used. Calcareous sand was used only in the case of lime-based mortars, to investigate the effect of using unreactive (siliceous) or reactive (calcareous) aggregates, for a given type of binder. Calcareous sand was sieved so as to reproduce the same particle size distribution as standard siliceous sand.

The binder to aggregate ratio and the water to binder ratio were designed to produce specimens with composition similar to historic mortars and with microstructural and mechanical properties resembling the conditions of weathered mortars. In the case of the lime-based specimens, two water to binder ratios were considered (0.75 v/v and 1 v/v), to investigate the effects of the consolidating treatments on mortars with the same mineralogical composition and different porosity and mechanical properties.

For all mortar types, standard prismatic specimens (4×4×16 cm^3) were prepared using a Hobart mixer. Specimens based on slaked lime and NHL were cured for 1 week in

steel molds, then demolded and cured in laboratory conditions (RH = 50±5%, T = 21 ± 2 °C) for 7 years before testing. Specimens based on cement were demolded after 24 hours and then cured in controlled conditions (RH > 95%, T = 21 ± 2 °C) for at least 28 days. Before testing, all the samples were dried at room temperature until constant weight.

As illustrated in Figure 1, for all mortar types small samples (about 2×2×1 cm^3) were obtained from one standard prism by wet sawing. These small samples were used to identify the best treatment duration, by treatment for increasing time and analysis by FT-IR and SEM, as described in detail in § 2.3.

In the case of the "CEM" mortar, thanks to the higher mechanical properties compared to the other mortar types, it was possible to slice standard prisms into samples with 4×4×2 cm^3 size, without the risk of fracturing the specimens. These smaller samples were used to determine the mortar mechanical strength by double punch testing (DPT), as described in detail in § 2.3. The advantage of the DPT procedure, compared to standard mechanical testing (performed for the other mortar types), is that a much higher number of samples could be tested from the same standard prism, which allows for a better statistical representativeness of the obtained results.

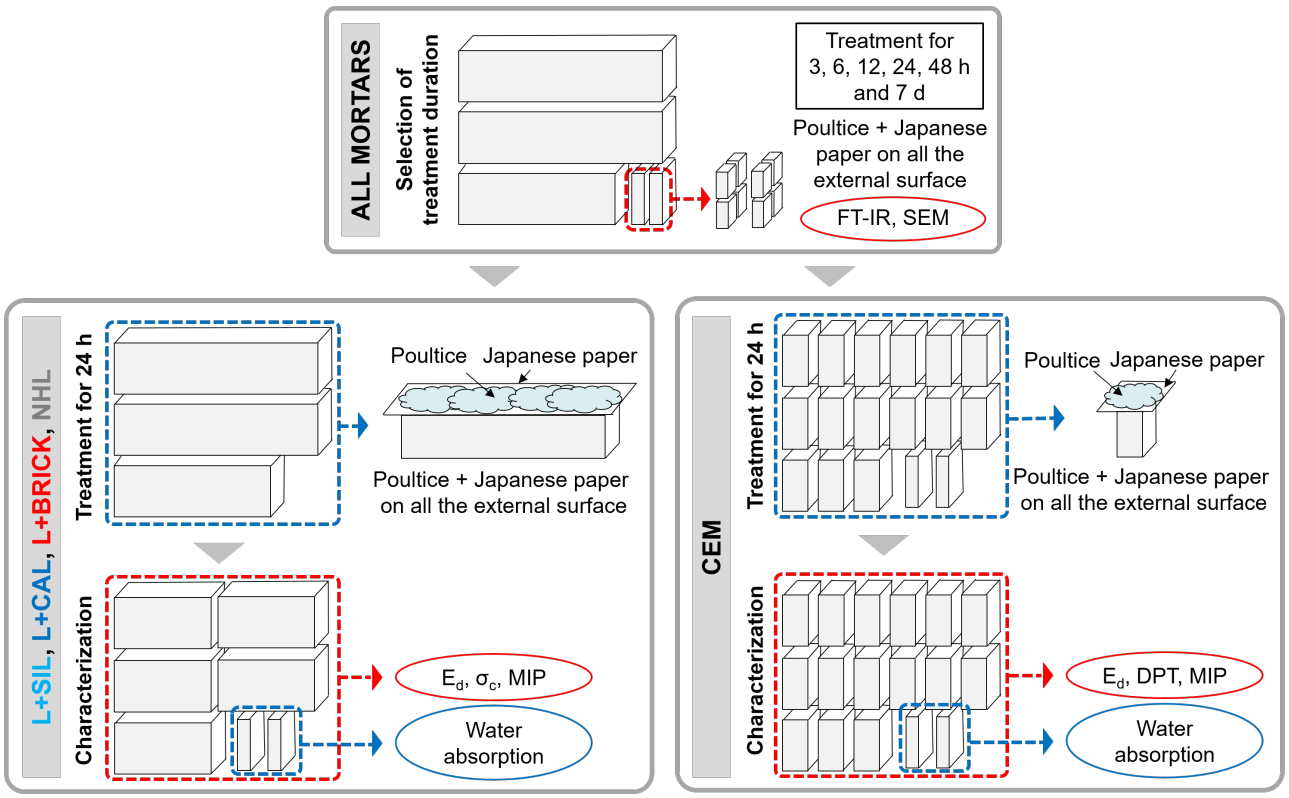

Figure 1. Scheme illustrating the rationale of the study, the sample production and testing.

2.2. Consolidating treatments

Two formulations of the phosphate treatment, recently developed for marble conservation [31], were tested. Their composition is reported in Table 2.

Table 2. Labelling and composition of the two formulations of the phosphate treatment.

Label	DAP	$CaCl_2 \cdot 2H_2O$	EtOH
0.1 M DAP	0.1 M	0.1 mM	30 vol%
2 M DAP	2 M	2 mM	10 vol%

"DAP" = diammonium hydrogen phosphate, EtOH = ethanol.

The two formulations differed in terms of concentration of the phosphate precursor (diammonium hydrogen phosphate, DAP, $(NH_4)_2HPO_4$), external calcium source (calcium chloride, $CaCl_2 \cdot 2H_2O$) and ethanol (EtOH). Calcium chloride was added as it accelerates CaP formation [4,14], while EtOH was added as it helps densification of the new CaP phases [16,18]. For both formulations, the maximum EtOH addition not leading to immediate precipitation was used. All reagents were purchased from Sigma-Aldrich (assay > 99%).

In all the phases of the study, the treatments were applied by poulticing. First, a poultice was prepared using cellulose pulp (MH300 Phase, Italy) and DAP solution, with a cellulose pulp:solution ratio of 1:4 by weight. All the external surfaces of the specimens were covered with a 1 cm-thick layer of poultice, inserting a sheet of Japanese paper between the sample and the poultice to avoid sticking (Figure 1). Then, specimens were wrapped with a plastic film to prevent evaporation and left to cure for the desired time. Finally, the plastic film and the poultice were removed, the samples rinsed with deionized water and left to dry at room temperature until constant weight.

The treatment duration varied depending on the phase of the study. In the first phase, aimed at identifying the best treatment duration itself (Figure 1), the small samples (2×2×1 cm^3) were left to react for 3, 6, 12, 24, 48 hours and 7 days. For the development of the new CaP phases, the mortar mineralogical composition was regarded as the most important parameter, hence results obtained on “L+SIL_1” and “L+CAL_1” specimens were assumed as also representative for the “L+SIL_0.75” and “L+CAL_0.75” specimens, respectively.

Once identified the best treatment duration (24 h, cf. § 3), in the second phase the bigger specimens were left to react for 24 h to determine the treatment consolidating ability and compatibility. Both formulations of the phosphate treatments were tested on all mortar types, except for the “L+SIL_1” and “L+BRICK” mortars, for which only the “2 M DAP” formulation was tested because some samples had fractured during demolding.

2.3. Sample characterization

To characterize the behavior of untreated and treated mortars, the characterization tests described in the following were performed. The type, size and number of replicates of samples used for each test are reported in Table 3.

Table 3. Type, size and number of replicate samples used for each characterization test

Characterization test	Mortar type	Sample	Size	Replicates
FT-IR	All	Powder	-	1
SEM-EDS	All	Fragment	~1 cm^3	1
Penetration depth	All	Prism	4×4×1 cm^3	1
Dynamic elastic modulus	lime, lime+brick, NHL	Prism	4×4×8 cm^3	5
Dynamic elastic modulus	CEM	Prism	4×4×2 cm^3	12
Compressive strength	lime, lime+brick, NHL	Prism	4×4×8 cm^3	5
Double punch test	CEM	Prism	4×4×2 cm^3	12
MIP	All	Fragment	~1 cm^3	2
Water absoprtion	All	Prism	4×4×1 cm^3	2
Color change	All	Prism	4×4×8 cm^3	2

Composition and morphology of the new phases. To define the best treatment duration, the small specimens treated for increasing time were analyzed by Fourier Transform Infrared Spectrometry (FT-IR, Perkin Elmer Spectrum One spectrometer), to detect and identify newly formed CaP phases. Considering that new CaP would be mostly present in the binder fraction of the mortar, binder and aggregates were manually separated and then the fraction <0.075 mm (assumed as mostly composed of binder [32])

was analyzed by FT-IR. In the case of the "CEM" samples, given their high mechanical properties, manual separation was not possible, so powder was scratched from the sample surface using a spatula. To determine the morphology and the elemental composition of the new CaP phases, fracture samples of the treated specimens were also analyzed by scanning electron microscopy (SEM, Philips XL20), coupled with energy dispersive spectrometry (EDS, EDAX probe). For SEM observation, samples were preliminarily coated with aluminum to make them conductive.

Penetration depth. For all mortar types, the penetration depth of the two consolidating solutions was determined by visually assessing the height of capillary rise of solutions into 4×4×1 cm^3 specimens as a function of time. The solutions were let penetrate the samples through one 4×1 cm^2 face, by putting samples over poultices soaked with the solutions (prepared as described above).

Dynamic elastic modulus. On samples treated for 24 hours, the consolidating ability was first assessed in terms of dynamic elastic modulus (E_d), measured before and after treatment, taking advantage of the non-destructive nature of this test. E_d was calculated according to the formula $E_d = \rho \times v^2$, where ρ is the density and v is the ultrasonic pulse velocity, measured using a Matest instrument with 55 kHz transducers. In the case of lime- and NHL-based mortars, E_d was measured by transmission method across the 4 cm-side of the 4×4×16 cm^3 specimens (at least 5 replicates for each condition); in the case of the "CEM" mortar, E_d was measured across the 2 cm-thickness of the 4×4×2 cm^3 prisms (at least 12 replicates for each condition) (Figure 1). After measuring E_d, the specimens were subjected to destructive mechanical testing, which differed depending on the mortar type, as described below.

Compressive strength. In the case of lime- and NHL-based mortars, the compressive strength (R_c) was determined by subjecting standard prisms to compressive test according to EN 196-1 [30], using an Amsler-Wolpert loading machine. At least 5 replicates were tested for each condition.

Double punch test. In the case of the "CEM" mortar, the compressive strength by double punch test ($R_{c,DPT}$) was determined by subjecting the 4×4×2 cm^3 specimens to double punch test (DPT) [33], following the procedure illustrated in Figure 2. The specimens were loaded onto the 4×4 cm^2 faces by means of two steel cylindrical platens (2 cm diameter) until failure. Compared to standard compressive test (leading to 2 R_c values for each standard prism), the DPT has the advantage of providing a much higher number of results (up to 6 $R_{c,DPT}$ values for each standard prism). The 2 cm-thickness of the specimens for DPT was selected based on a previous study [34], which highlighted that testing samples with thickness (2 cm) similar to the diameter of the steel platens (2 cm) leads to $R_{c,DPT}$ values in very good correlation with the standard R_c values. For each condition, at least 12 replicates were tested.

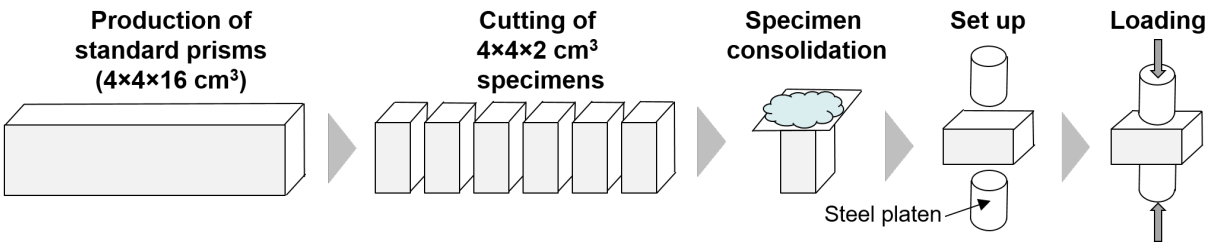

Figure 2. Scheme illustrating the procedure of the double punch test (DPT).

Pore size distribution. To determine the alterations in total open porosity and pore size distribution following consolidation, samples were obtained by chisel from the specimens used for destructive tests and then subjected to mercury intrusion porosimetry (MIP, Porosimeter 2000 Carlo Erba with Fisons Macropore Unit 120). MIP samples were

obtained close to the surface of the specimens, as alterations in the pore system were expected to be most pronounced near the surface. Two replicates were tested for each condition.

Water sorptivity. The alteration in water sorptivity was determined by subjecting 4×4×1 cm^3 specimens to water capillarity test according to EN 15801 [35], water being let penetrate the samples through one 4×1 cm^2 face. Two replicates were tested for each condition.

Color change. The aesthetic compatibility of the treatments was evaluated by visually comparing treated and untreated specimens. In fact, the composite nature of mortar samples, resulting in a composite visual appearance, made the use of a single colorimetric parameter (such as the CIELAB ΔE^* parameter [36]) scarcely representative in this specific case.

3. RESULTS AND DISCUSSION

The FT-IR spectra of the various mortar types, treated for increasing time, are reported in the Supplementary material (Figures S1-S5), while the spectra registered after treatment for 24 hours are summarized in Figure 3.

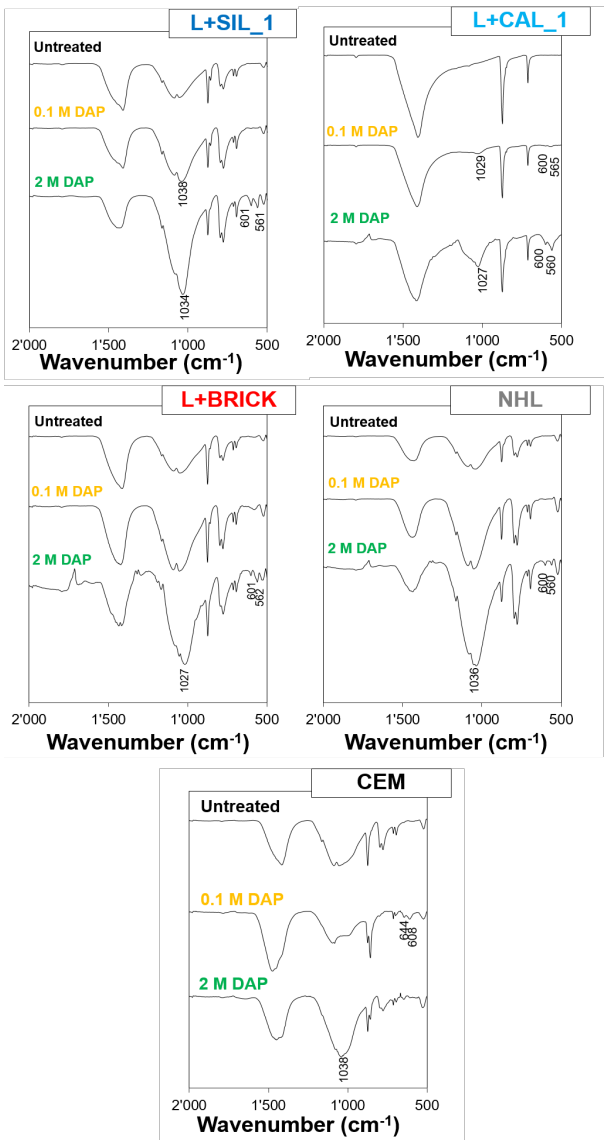

Figure 3. FT-IR spectra of the various mortar types after treatment for 24 hours. Bands owing to new CaP phases are indicated, while bands owing to the substrates are omitted.

At all times, the “L+CAL_1” mortar exhibited the most pronounced bands owing to new CaP formation. This is consistent with the fact that this mortar type, composed of calcium carbonate both in the binder and in the aggregates, can virtually totally react with the phosphate solution to form new CaP (although the binder, composed of finer crystals, is expected to be more reactive than the aggregates). In the “L+CAL_1” sample, the position of the new bands (1027-1029, 600, 560-565 cm^{-1}) suggests formation of hydroxyapatite (HAP, $Ca_{10}(PO_4)_6(OH)_2$, the most stable CaP at pH>4), having bands at 1031, 604, 563 cm^{-1} [37]. Similarly, also in the case of the “L+BRICK” mortar HAP seems to be the main new CaP phase, although the overlapping with the quartz bands (owing to the aggregate) make the identification less straightforward. In the case of the “L+SIL_1”, “NHL” and ”CEM” mortars, the new bands appearing after treatment seem more compatible with formation of octacalcium phosphate (OCP, $Ca_8(HPO_4)_2(PO_4)_4 \cdot 5H_2O$), having bands at 1038, 602, 560 cm^{-1} [37]. Although more soluble than HAP, OCP is significantly less soluble than calcite [9], hence its formation is expected to provide durable consolidating action, as assessed in previous studies [18]. The fact that all mortar types exhibited formation of new CaP after treatment, notwithstanding the lower amount of calcium ions that can dissolve from the substrate in the other mortars compared to the “L+CAL_1” one, suggests that the addition of a calcium source directly into the DAP solution is sufficient to guarantee formation of new CaP phases. In all cases, bands owing to new CaP were more pronounced after the “2 M DAP” treatment, suggesting that the higher the DAP concentration, the more abundant the formation of new CaP. This was expected to some extent, even though addition of ethanol to the DAP solution was expected to substantially boost formation of new CaP, even for low DAP concentrations [16,18].

Considering that, for all mortar types, no major increase in new phase formation was registered after treatment for 48 hours or 7 days (Figures S1-S5), treatment for 24 hours was selected as the reference treatment duration for the prosecution of the study. Such duration was selected also considering its feasibility in the onsite practice of architectural conservation, whereas longer durations might become challenging.

Notably, FT-IR analysis did not reveal any band owing to unreacted DAP or highly soluble CaP phases. This is important, because in case any soluble fraction remains in the substrate at the end of the treatment, durability issues may arise in the long term. Such durability issues may include migration of soluble fractions from the consolidated mortar to the substrate (e.g., masonry or concrete) or towards the surface due to the presence of damp, with consequent possible formation of efflorescence or sub-efflorescence. Moreover, phosphates may act as nutrients for microorganisms, thus potentially favoring biological growth in the treated substrate [9]. In the present case, the lack of any FT-IR band owing to soluble fractions (neither revealed by SEM, see below) allows to expect no issues related to efflorescence formation or biological growth.

Consistent with FT-IR results, SEM observation of samples treated for 24 hours (Figure 4) revealed evident formation of new CaP in the case of the “L+CAL_1” mortar, where the typical flower-like morphology of CaP [9] was visible after treatment with both “0.1 M DAP” and, to a higher extent, “2 M DAP”. In the other mortar types, especially those based on slaked lime, recognition of the new CaP phases was less straightforward, because the morphology of the untreated mortars (characterized by the presence of many tiny particles) did not allow a clear distinction between the substrate and the new phases. Nonetheless, the presence of a phosphorus peak in the EDS spectra confirmed formation of new CaP phases in all mortar types. Consistently with the trend already assessed by FT-IR, the phosphorus peak was always more pronounced in the samples treated with the “2 M DAP” formulation, compared to the “0.1 M DAP” one. It is noteworthy that, in the

“CEM” samples, treatments led to formation of new CaP films at grain boundaries exhibiting cracking, especially in the case of the more concentrated solution (Figure 4).

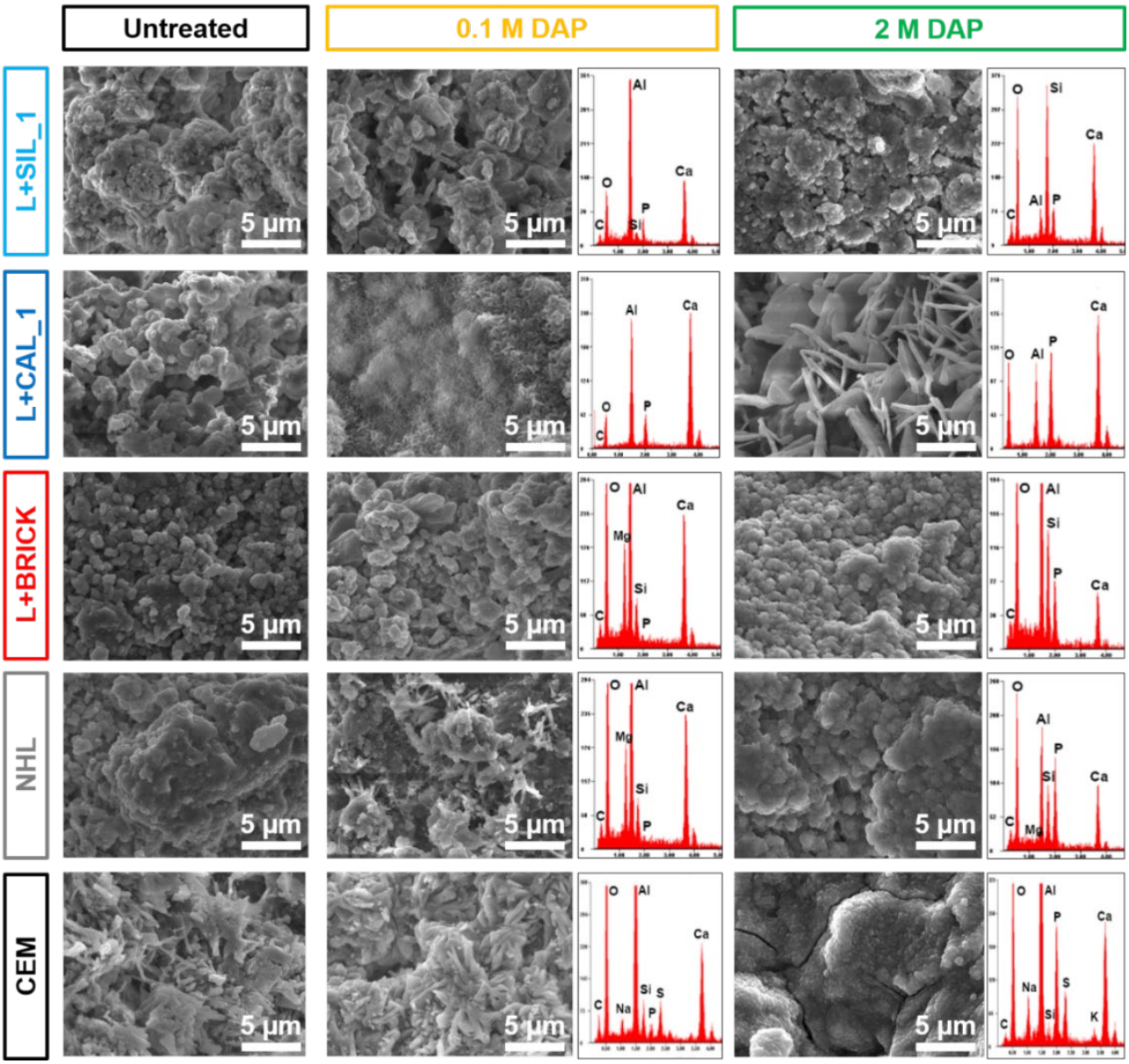

Figure 4. FT-IR spectra of the various mortar types after treatment for 24 hours.

SEM-EDS analysis also allowed to obtain some further important insight into formation of new phases. As reported in Figure 5, in several mortar types, when magnesium was present as an impurity, the phosphate treatment led to formation of some big isolated crystals, containing Mg and P (as indicated by EDS). Formation of magnesium phosphates (MgP) has been reported in the literature in studies where ammonium phosphate solutions were used to consolidate dolomite-rich natural stones [24] and also archaeological bones [38]. Because MgP grow as isolated crystals, they cannot provide any effective consolidating action, hence their formation is counterproductive. This should be taken into account and possibly prevented when substrates containing magnesium are treated.

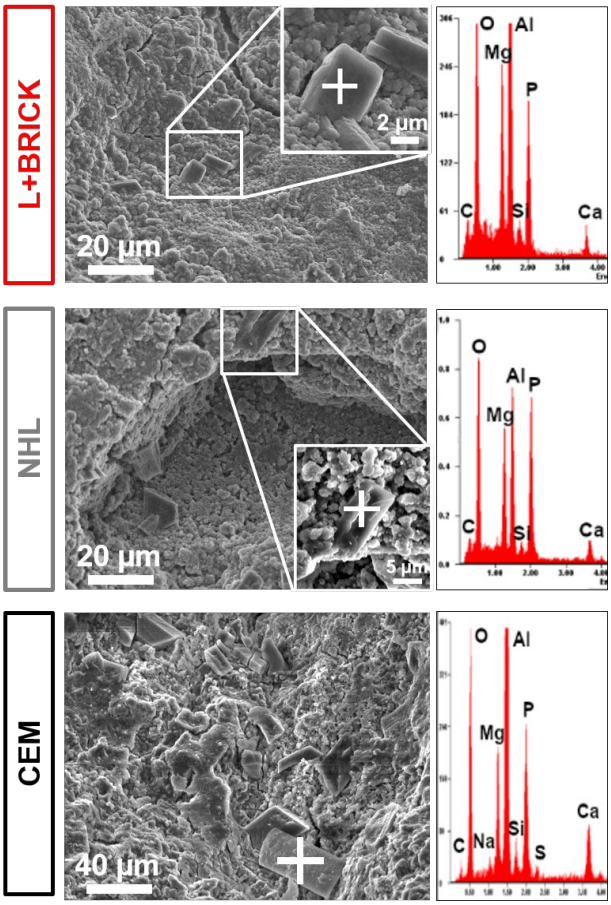

Figure 5. FT-IR spectra of the various mortar types after treatment for 24 hours.

To evaluate the consolidating ability of the two phosphate solutions, their ability to penetrate into the various mortar types was first investigated. As illustrated in Figure 6, the "0.1 M DAP" solution was able to penetrate more quickly than the "2 M DAP" solution into all mortar types. This is thought to be due to the lower viscosity of the less concentrated solution (although viscosity was not experimentally determined in this study). For a given solution and a given mortar, the penetration depth was higher in the specimens with higher water/binder ratio ("_1" compared to "_0.75"), as expected. With the exception of the "CEM" mortars, after 24 hours both solutions were able to saturate completely all the lime- and NHL-based specimens, thus indicating that in these mortars the penetration depth after 24 hours was at least 40 mm. Such penetration depth can be regarded as fully satisfactory, compared to the penetration depth reported in the literature for alternative products for lime mortar consolidation: for nanolimes, 5 mm [39] to 8 mm [40]; for ethyl silicate, 16-30 mm (depending on the mortar porosity) [39]; for barium hydroxide solutions, 5-30 mm (depending on the mortar porosity) [39]. In the case of the "CEM" mortars, the penetration depth of the DAP solutions was lower than in the other mortars, as a consequence of the lower porosity and smaller pore size of this mortar type (cf. MIP results in the following). In the "CEM" mortars, the penetration depth was about 25 mm for the "0.1 M DAP" solution and about 20 mm for the "2 M DAP" solution, as a consequence of the higher viscosity of the latter solution. These values are in line with the penetration depth reported in the literature for ethyl silicate applied to cement mortars, for which a penetration depth of at least 20 mm was registered [41]. However, when comparing values of penetration depth reported in different studies, it should be borne in mind that mortars with the same type of binder may actually be quite different in terms of porosity, which depends on the water to binder ratio and which, in turn, influences the consolidant penetration depth.

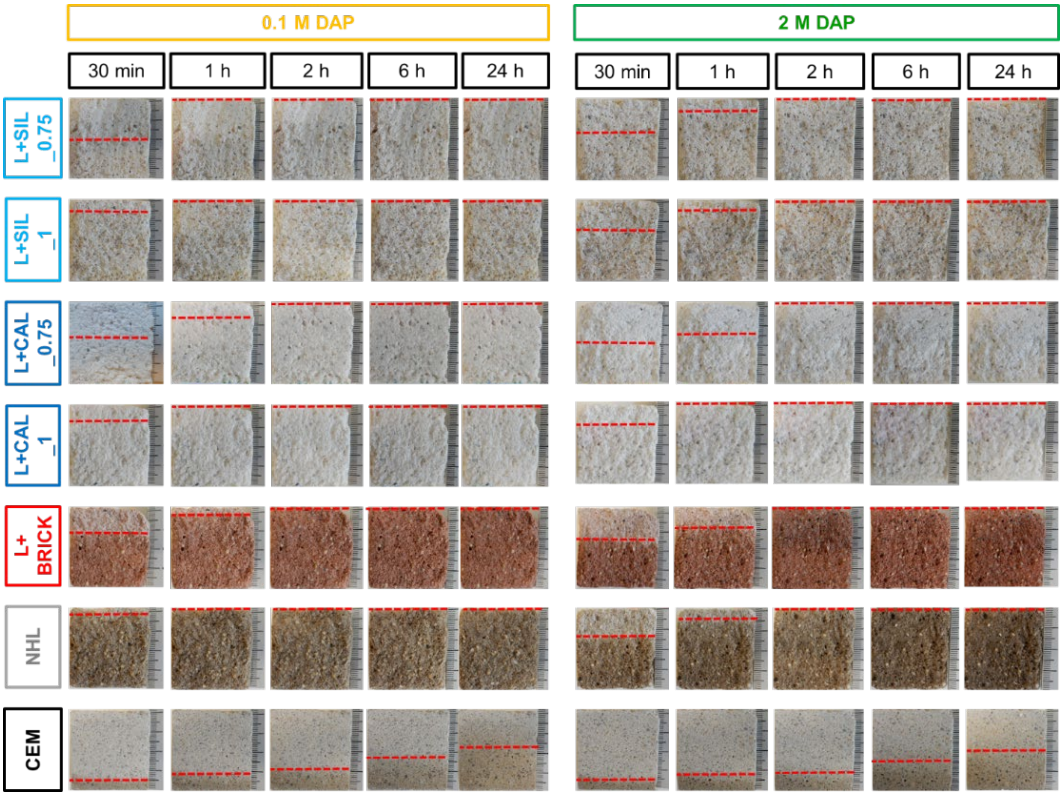

Figure 6. Penetration depth of the phosphate solutions into the various mortar types.

Thanks to the high penetration depth of the phosphate solutions and to the consequent formation of new CaP phases, the phosphate treatment was able to significantly improve mortar mechanical properties, as illustrated in Figure 7 and Figure 8 for lime- and NHL-based mortars and in Figure 9 for the cement mortar.

Before consolidation (gray bars in Figures 7 and 8), the lime-based specimens with higher water to binder ratio exhibited lower E_d and lower R_c, as expected. At given water to binder ratio, the addition of brick dust led to higher mechanical properties compared to mortars only containing slaked lime, as a consequence of C-S-H formation. The "NHL" specimens (produced using NHL 3.5 binder) exhibited low mechanical properties, which can be attributed to the high water to binder ratio (Table 1). In the case of the "CEM" specimens, notwithstanding the high water to binder ratio, the final compressive strength was close to the nominal one (samples were produced using CEM I 32.5).

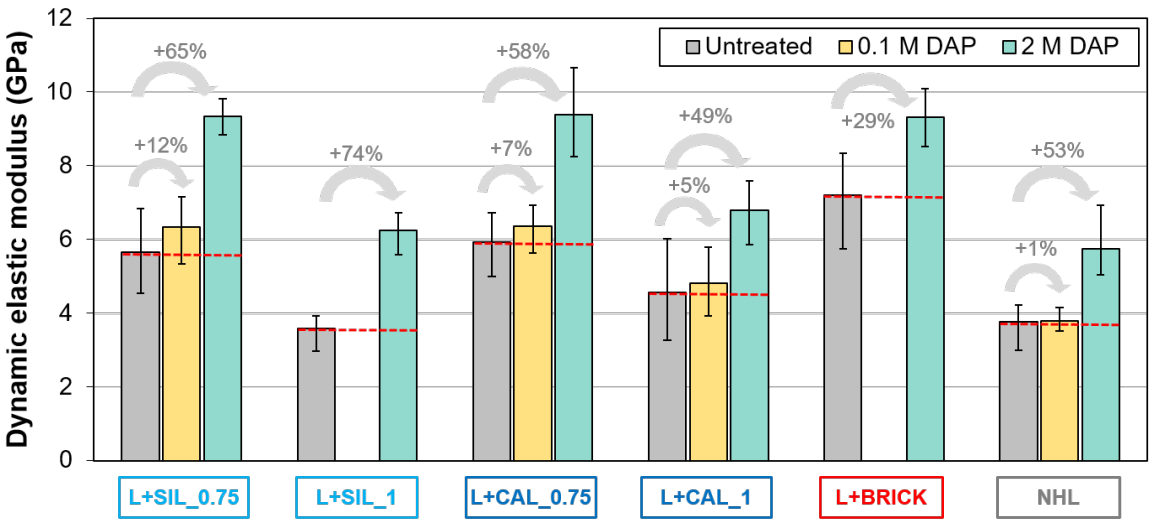

Figure 7. Dynamic elastic modulus (E_d) of untreated and treated lime- and NHL-based specimens.

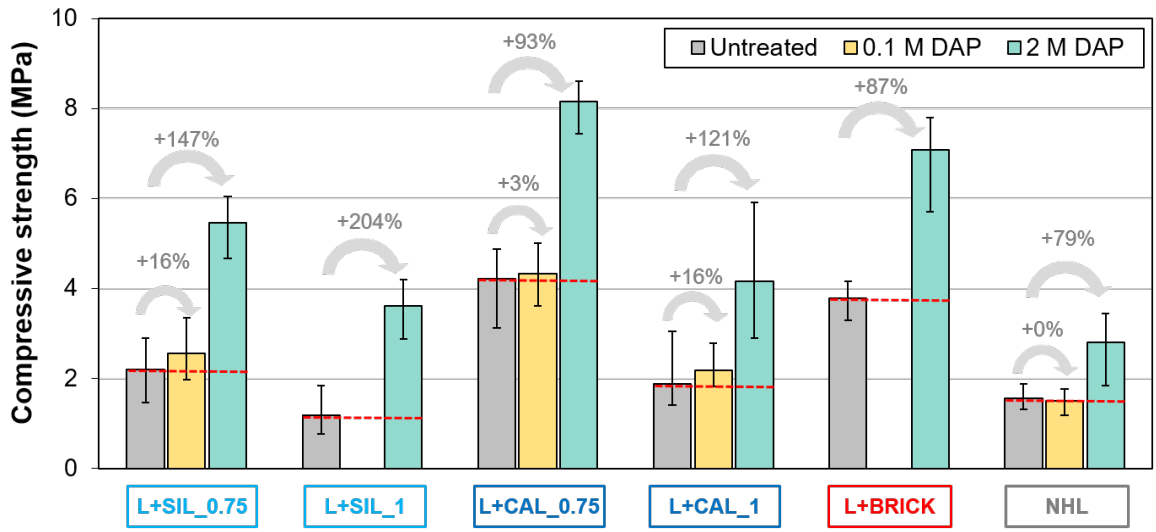

Figure 8. Compressive strength (R_c) of untreated and treated lime- and NHL-based specimens.

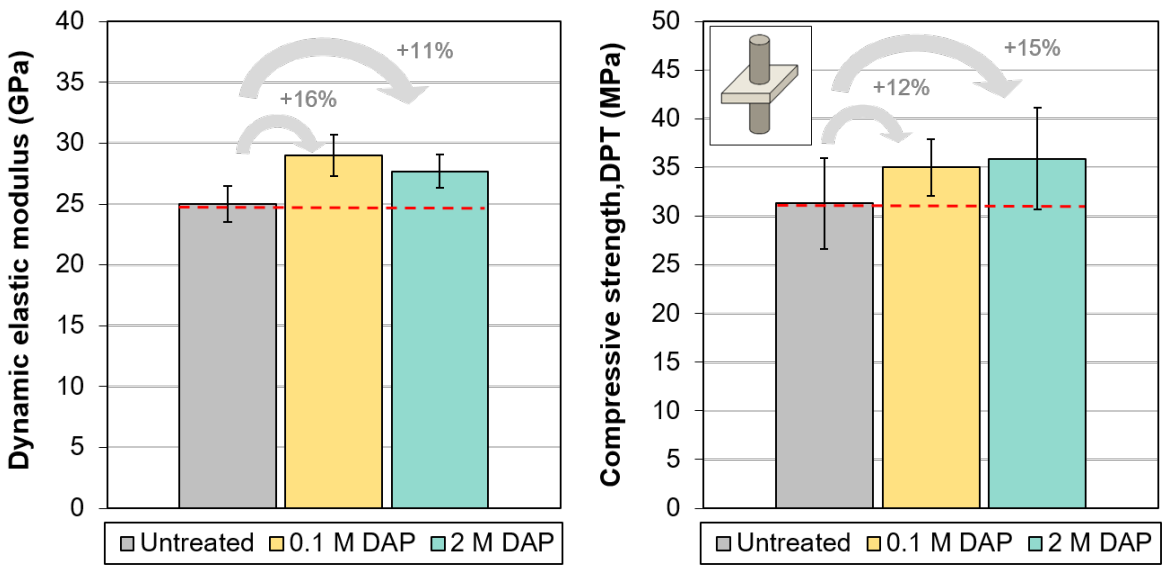

Figure 9. Dynamic elastic modulus (E_d) and compressive strength determined by DPT ($R_{c,DPT}$) of untreated and treated "CEM" specimens.

After consolidation, the lime- and NHL-based mortars experienced limited increases in E_d (+1 to +16%) and R_c (0 to +16%) after treatment with the "0.1 M DAP" solution, while much higher improvements were obtained with the "2 M DAP" solution (+29 to +65% increase in E_d, +87 to +204% increase in R_c). Such difference in consolidating ability between the two formulations is a consequence of the different amounts of new CaP phases formed in the two cases, as already assessed by FT-IR and SEM-EDS. The mechanical improvement was higher in the "L+SIL" and "L+CAL" mortars (where the binding fraction was made of calcium carbonate, highly reactive to form new CaP), compared to the "L+BRICK" and "NHL" mortars (where the binding fraction was mostly calcium silicate hydrates, less reactive than calcium carbonate, which in these specimens amounted to ~35 wt%). Nonetheless, some mechanical improvement was registered for all the mortar types, especially in the case of the more concentrated solution, even in cases where formation of new CaP was not very evident from FT-IR and SEM-EDS. This confirms that, thanks to the addition of a calcium source already in the DAP solution, significant consolidation can be achieved even on substrates that contain relatively low amounts of calcium-rich fractions. The beneficial effect of calcium ions supplied directly in the DAP solution, together with the predominant role of the binding fraction compared to

the aggregates, explains why no major differences were found between the “L+SIL” and “L+CAL” mortars.

Compared to alternative consolidants, the performance of ammonium phosphate can be regarded as fully comparable, if not superior. Nanolimes were reported to cause increases in ultrasonic pulse velocity of 1-10% [42] and compressive strength increases of 4-33% [39], hence similar to the “0.1 M DAP” solution, while the benefit deriving from the “2 M DAP” formulation was definitely higher. Ethyl silicate, causing compressive strength increases up to 89% [39] and flexural strength increases up to 116% [42], can be regarded as more effective than the “0.1 M DAP” solution, but less effective than the “2 M DAP” one. In the case of barium hydroxide, increases in compressive strength up to 67% were reported [39] (hence, intermediate between the consolidating effectiveness found in this study for the two DAP solutions), but a decrease in flexural strength after consolidation with barium hydroxide has actually been reported [43] (likely because of the high amounts of water used as solvent), therefore the use of barium hydroxide seems to need further investigation.

In the case of the “CEM” mortar (containing ~24 wt% calcium carbonate), substantially similar improvements in mechanical properties were achieved by either the “0.1 M DAP” or the “2 M DAP” solution (E_d increases of +16% and + 11%, respectively, and $R_{c,DPT}$ increases of +12 and +15%, respectively). The absence of significant differences between the two solutions in the case of the cement mortar, unlike the case of lime- and NHL-based mortars, is most likely a consequence of the fact that, notwithstanding the high water to binder ratio (Table 1), the specimens exhibited high mechanical properties and low porosity (Figure 9 and Figure 10, discussed in the following), so the starting material was not in a condition of severe loss of cohesion and consequent need of consolidation.

Among the few studies available in the literature about consolidation of cement-based mortars, ethyl silicate has been reported to cause “slight increases” in compressive strength [44], so the level of consolidation achieved by ammonium phosphate seems to be at least comparable.

For all mortar types, to evaluate whether the level of mechanical consolidation achieved by ammonium phosphate can be regarded as suitable or may result excessive, the reference thresholds proposed for stone consolidation can be assumed in the first stage. According to the literature, the risk of overstrengthening and consequent incompatibility issues may arise if the difference in mechanical properties between the treated and the untreated substrate is higher 25% [39] or 50% [43], even though increases up to 100% of the initial values have been regarded as satisfactory [45]. In the case of the “CEM” mortars analyzed in this study, both formulations of the DAP-based treatment can be regarded as mechanically compatible, since in no case was the minimum reference threshold exceeded. In the case of lime- and NHL-based mortars, not excessive mechanical improvement was obtained with the “0.1 M DAP” solution, while the “2 M DAP” solution caused increases in mechanical properties that in some cases are higher than the reference thresholds, so that some incompatibility risks owing to overstrengthening might arise. However, each case should be considered individually, taking into account the conditions of the sound mortar and those of the decayed mortar: an improvement of +50% in the mechanical properties of the decayed mortar might appear excessive, but the final properties of the consolidated mortar could equal those of the sound mortar, in the case the decayed condition was the result of severe deterioration starting from the sound condition. In any case, to tune the final mechanical strengthening different treatment parameters (e.g., DAP concentration, application method, treatment duration) may be adopted. This will be the subject of future research.

The pore size distributions of untreated and treated mortars are illustrated in Figure 10. As expected, lime-based mortars with higher water to binder ratios exhibited higher open porosity (OP) than mortars with the same composition but a lower ratio: OP was 28.3% for “L+SIL_1” and 24.7% for “L+SIL_0.75”, while OP was 26.2% for “L+CAL_1” and 24.8% for “L+CAL_0.75”. As expected, the “CEM” specimens were the least porous ones (OP = 17.0%). In general, duplicate samples exhibited fair reproducibility, although in some cases some difference was found between the two samples tested for each condition (especially, in the “L+SIL_1” and “NHL” mortars).

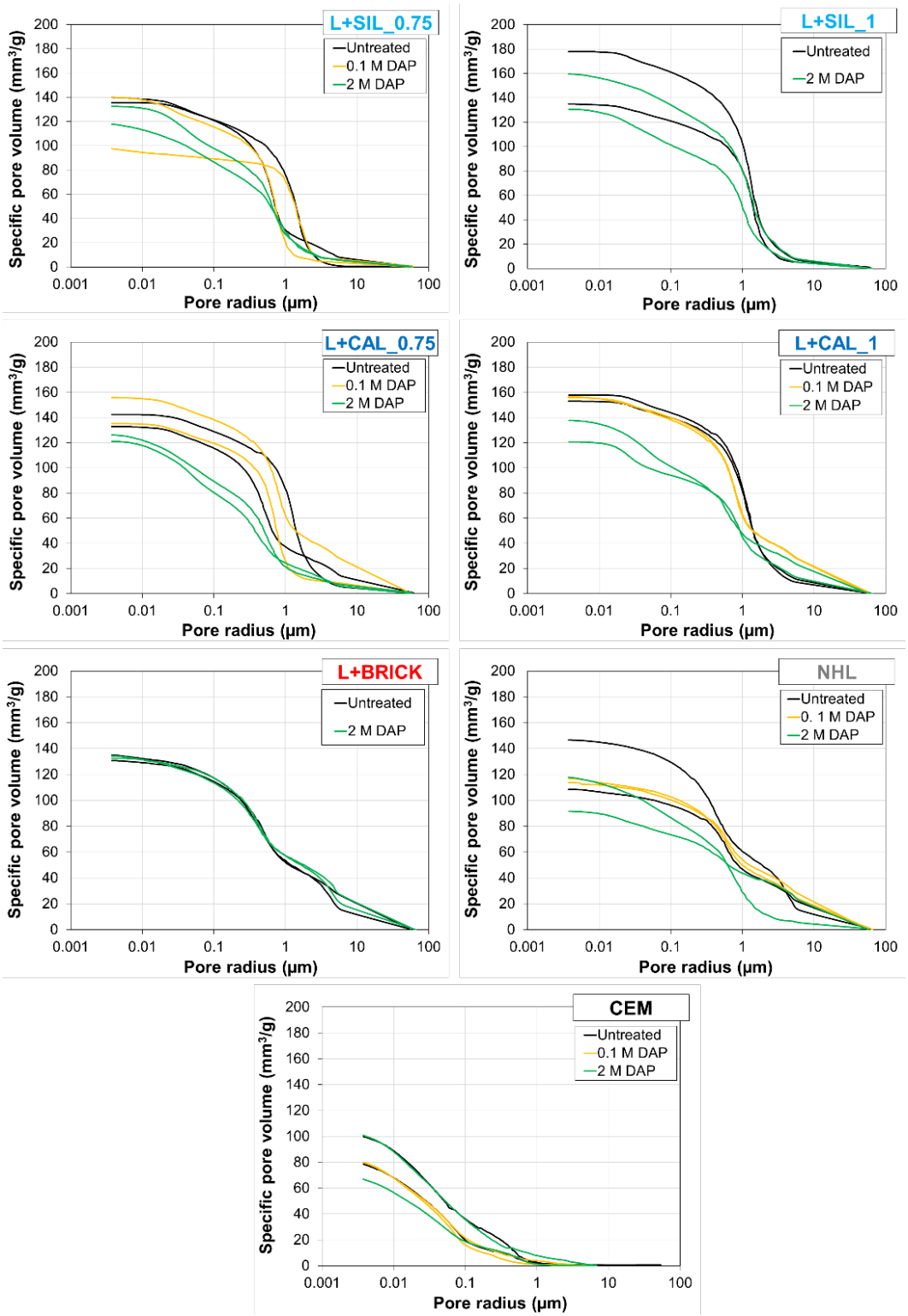

Figure 10. Pore size distribution of untreated and treated mortars.

Formation of new CaP phases resulted in some reduction in the total open porosity and some alteration in pore size distribution, which were more pronounced after treatment with the “2 M DAP” solution, as a consequence of the higher amount of new CaP phases formed in this case. With this formulation, some shift of the pore size distribution towards smaller pores took place, but the final total open porosity was only slightly reduced compared to the untreated condition, the reduction often falling within the variability of the untreated references. Passing from the untreated to the “2 M DAP”-treated condition, OP changed from 24.7 to 24.9% for “L+SIL_0.75”, from 28.3 to 26.0% for “L+SIL_1”, from 24.8 to 22.3% for “L+CAL_0.75”, from 26.2 to 24.8% for “L+CAL_1”, from 25.1 to 23.6% for “L+BRICK”, from 21.6 to 20.5% for “NHL”, from 17.0 to 15.8% for “CEM”. The fact that in no case did significant pore occlusion take place can be regarded as a positive feature, because strong alterations in the pore system might lead to significant changes in water transport properties, with consequent durability issues [11,12]. Moreover, because no significant increase in the fraction of smallest pores occurred, the mortar resistance to freeze-thaw and salt crystallization cycles is not expected to be negatively affected, but specific tests are needed to confirm this. The lack of complete pore occlusion is common to other alternative products used for lime and cement mortar consolidation, such as nanolimes [4] and ethyl silicate [41].

As a consequence of the limited alterations in the pore system, also water transport properties were left basically unchanged after treatment with DAP solutions. As illustrated in Figure 11, minor reductions in water sorptivity and water absorption at the end of the test were registered, slightly more pronounced in the case of the “2 M DAP” solution. However, in no case was water absorption significantly inhibited after treatment.

This is a positive feature, because the consolidated material needs to be able to exchange liquid water with the environment, to avoid durability issues [12]. As for alternative consolidants, this is not always the case: whereas nanolimes were reported to cause only slight reductions in water absorption [40], ethyl silicate is known to cause strong alterations in water absorption and sorptivity [41,42], because of the presence of hydrophobic ethoxy groups on the treated surface until hydrolysis-condensation reactions are completed [12].

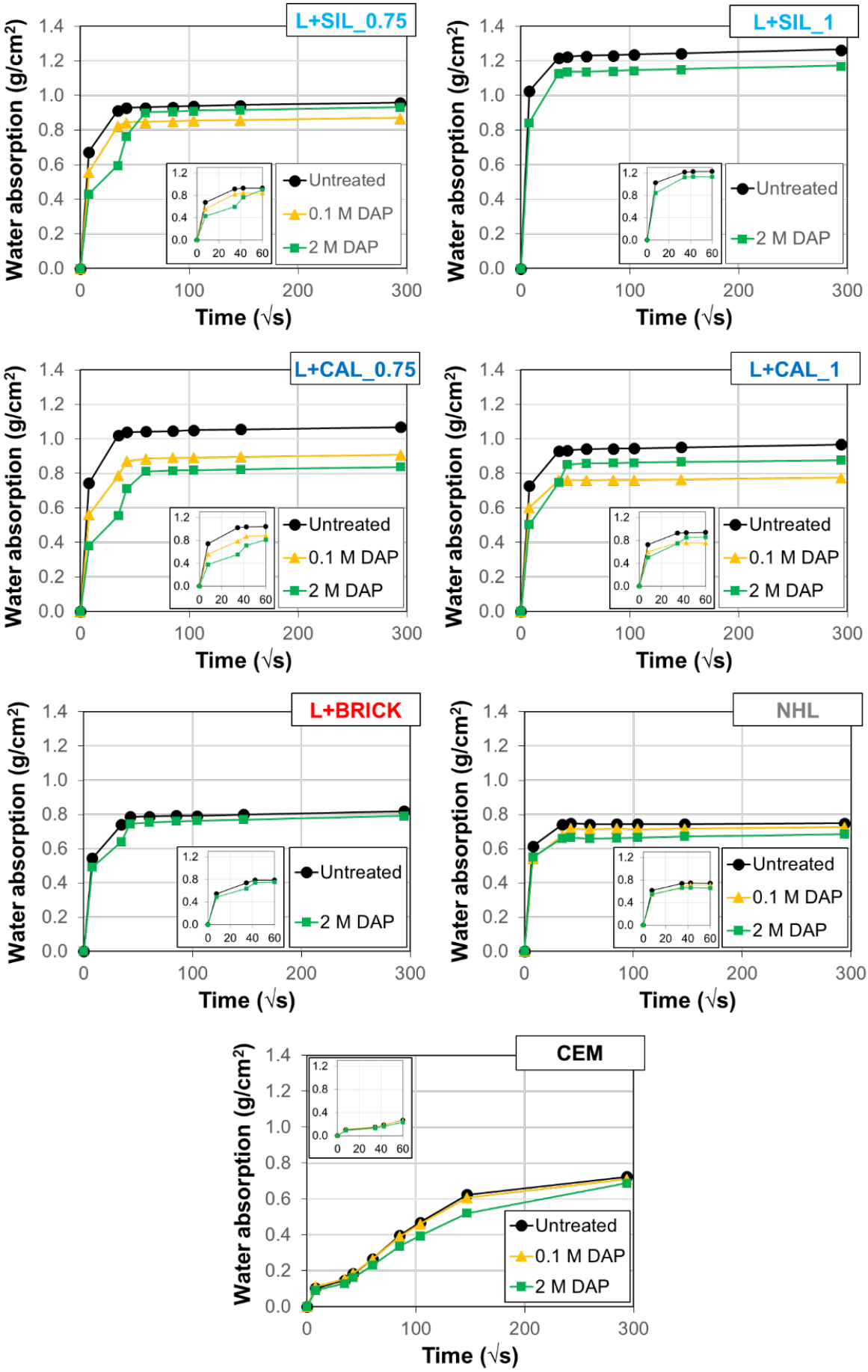

Figure 11. Water sorptivity of untreated and treated mortars (values are averages for 2 specimens).

In terms of aesthetical compatibility, no visible color change occurred in the lime-based mortars, initially white, after consolidation with either formulation of the phosphate treatment (Figure 12). In the case of the other mortars ("L+BRICK" originally pink, "NHL" originally brownish, "CEM" originally gray), the "0.1 M DAP" solution caused no visible color change, but some whitening occurred after treatment with the "2 M DAP" formulation (Figure 12). This suggests that, while no particular issue is expected when white substrates are treated, in the case of colored substrates preliminary tests are recommended to ensure that no undesired aesthetic alteration takes place.

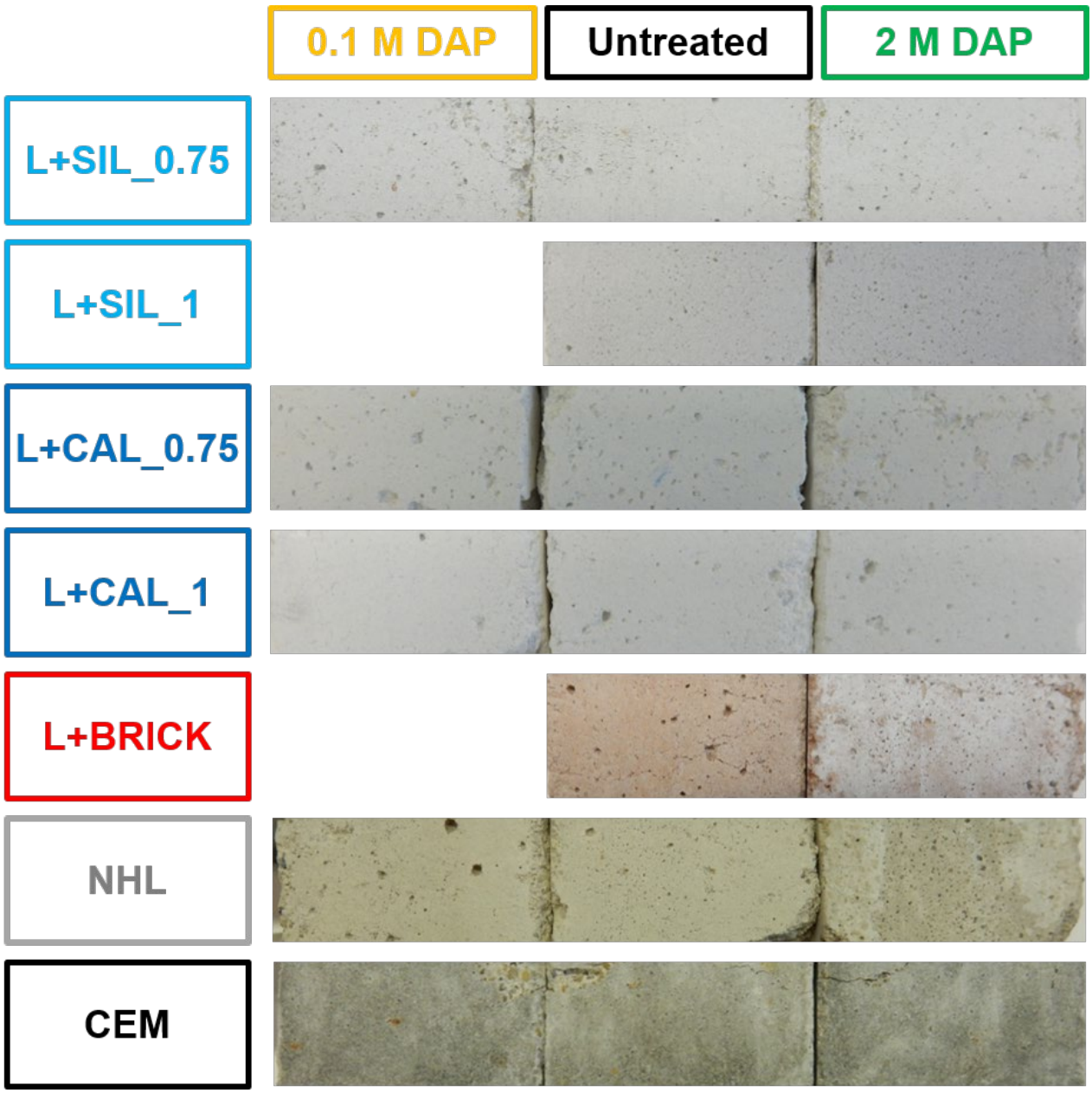

Figure 12. Visual appearance of untreated and treated mortars.

Color change after consolidation is a delicate aspect, which in the case of alternative consolidants may actually limit their suitability: while nanolimes were reported to cause invisible [40] or visible [42] color changes (depending on the commercial product tested) but mostly still acceptable, Paraloid B72 applied onto lime mortars was found to cause an evident color change (darkening and yellowing) [43], which limits its applicability.

4. CONCLUSIONS

Based on results obtained in the present study, aimed at evaluating the effectiveness and the compatibility of two different formulations of the phosphate treatment used for consolidation of seven mortar types, the following conclusions can be drawn:

- Treatment for 24 hours was sufficient to cause formation of new calcium phosphate phases in all the treated mortars (most likely, hydroxyapatite in the “L+CAL” and “L+BRICK” mortars, octacalcium phosphate in the “L+SIL”, “NHL” and “CEM” mortars). The new phases were sensibly more abundant in the case of the “2 M DAP” solution, compared to the “0.1 M DAP” one. Thanks to the addition of a calcium source directly into the phosphate solution, new calcium phosphate phases (and the resulting consolidating action) were found also in the case of mortars where the availability of calcium from the substrate was low (e.g. “L+BRICK”, “NHL” and “CEM” mortars).
- The penetration depth of both solutions was higher than 40 mm in lime- and NHL-based mortars, while in the “CEM” mortar the penetration depth reached 25 mm for the “0.1 M DAP” solution and 20 mm for the “2 M DAP” one (having higher viscosity).
- After consolidation, mechanical properties were increased for all types of mortar. In the case of the lime- and NHL-based specimens, the “0.1 M DAP” solution caused limited increases (ΔE_d = 1÷16% and ΔR_c = 0÷16%), while much higher increases were registered with the “2 M DAP” solution (ΔE_d = 29÷65% and ΔR_c = 87÷204%). In the cement mortar, the two solutions gave substantially similar improvements (ΔE_d = 11÷16% and $\Delta R_{c,DPT}$ = 12÷15%), most likely because the untreated specimens already had high mechanical properties, so increases in cohesion and mechanical consolidation was not actually needed.
- After consolidation, in no case was dramatic pore occlusion registered, thanks to the fact that the new calcium phosphate phases formed in thin layers at the grain boundaries, without occluding the pores. In the case of the “2 M DAP” solution, some shift of the pore size distribution towards smaller pores took place, but the final total open porosity was only slightly reduced compared to the untreated condition. As a consequence of the limited alterations in the pore system, only minor alterations in water transport properties were registered after consolidation. This allows to expect no particular durability issues, even though specific durability tests are needed to confirm this.
- In terms of aesthetic appearance, the “0.1 M DAP” formulation did not cause any visible alteration in any of the investigated mortars. The “2 M DAP” formulation, instead, did not cause any visible alteration in the lime-based mortars (originally white), but induced some whitening in the other mortar types, originally colored (“L+BRICK” initially pink, “NHL” initially brownish, “CEM” initially gray).

In summary, the present study confirmed the high potential of the phosphate treatment for consolidation of historic and modern mortars, also in comparison with alternative consolidants (nanolimes, ethyl silicate, barium hydroxide). In the case of lime-based mortars, the good performance of ammonium phosphate was anticipated, considering that the mineralogical composition of lime mortars is similar to that of carbonate stones, for which the treatment had originally been developed. In the case of cement mortars, having significantly different composition, the suitability of the phosphate treatment was assessed in this study for the first time and further optimization is expected in the future. The main positive feature of the phosphate treatment is that it allows to obtain significant mechanical improvement after treatment for just 24 hours, with only minor alterations in the pore system and in water transport properties. By further tuning the concentration of the phosphate solution, its application method and the treatment duration, the level of mechanical strengthening and color alteration is expected to be controlled,

thus overcoming some limitations encountered in the present study when high DAP concentrations were used. By combination of the findings of this study with recent results on the effects of ammonium phosphate solutions on traditional pigments [46], it is expected that in the future ammonium phosphate can be successfully used also for conservation of frescoes and wall paintings.

ACKNOWLEDGMENTS
M.Eng. Cesare Pizzigatti, M.Eng. Sofia Fantini and M.Eng. Federica Pignataro are gratefully acknowledged for collaboration to experimental tests.

REFERENCES

[1] Sassoni, E.; Naidu, S.; Scherer, G.W. The use of hydroxyapatite as a new inorganic consolidant for damaged carbonate stones. *J. Cult. Herit.* **2011**, *12*, 346–355, doi:10.1016/j.culher.2011.02.005.
[2] Matteini, M.; Rescic, S.; Fratini, F.; Botticelli, G. Ammonium phosphates as consolidating agents for carbonatic stone materials used in architecture and cultural heritage: Preliminary research. *Int. J. Archit. Herit.* **2011**, *5*, 717–736, doi:10.1080/15583058.2010.495445.
[3] Yang, F.; Zhang, B.; Liu, Y.; Wei, G.; Zhang, H.; Chen, W.; Xu, Z. Biomimic conservation of weathered calcareous stones by apatite. *New J. Chem.* **2011**, *35*, 887–892, doi:10.1039/c0nj00783h.
[4] Naidu, S.; Scherer, G.W. Nucleation, growth and evolution of calcium phosphate films on calcite. *J. Colloid Interface Sci.* **2014**, *435*, 128–137, doi:10.1016/j.jcis.2014.08.018.
[5] Naidu, S.; Liu, C.; Scherer, G.W. Hydroxyapatite-based consolidant and the acceleration of hydrolysis of silicate-based consolidants. *J. Cult. Herit.* **2015**, *16*, 94–101, doi:10.1016/j.culher.2014.01.001.
[6] Possenti, E.; Colombo, C.; Bersani, D.; Bertasa, M.; Botteon, A.; Conti, C.; Lottici, P.P.; Realini, M. New insight on the interaction of diammonium hydrogen phosphate conservation treatment with carbonatic substrates: A multi-analytical approach. *Microchem. J.* **2016**, *127*, 79–86, doi:10.1016/j.microc.2016.02.008.
[7] Molina, E.; Rueda-Quero, L.; Benavente, D.; Burgos-Cara, A.; Ruiz-Agudo, E.; Cultrone, G. Gypsum crust as a source of calcium for the consolidation of carbonate stones using a calcium phosphate-based consolidant. *Construct. Build. Mater.* **2017**, *143*, 298–311, doi:10.1016/j.conbuildmat.2017.03.155.
[8] Ma, X.; Balonis, M.; Pasco, H.; Toumazou, M.; Counts, D.; Kakoulli, I. Evaluation of hydroxyapatite effects for the consolidation of a Hellenistic-Roman rock-cut chamber tomb at Athienou-Malloura in Cyprus. *Construct. Build. Mater.* **2017**, *150*, 333–344, doi:10.1016/j.conbuildmat.2017.06.012.
[9] Sassoni, E.; Hydroxyapatite and Other Calcium Phosphates for the Conservation of Cultural Heritage: A Review. *Materials*. **2018**, *11*, 557, doi:10.3390/ma11040557.
[10] Sassoni, E.; Graziani, G.; Franzoni, E. An innovative phosphate-based consolidant for limestone. Part 1: Effectiveness and compatibility in comparison with ethyl silicate. *Construct. Build. Mater.* **2016**, *102*, 918–930, doi:10.1016/j.conbuildmat.2015.04.026.
[11] Sassoni, E.; Graziani, G.; Franzoni, E. An innovative phosphate-based consolidant for limestone. Part 2: Durability in comparison with ethyl silicate. *Construct. Build. Mater.* **2016**, *102*, 931–942, doi:10.1016/j.conbuildmat.2015.10.202.
[12] Scherer, G.W.; Wheeler, G.S. Silicate consolidants for stone. *Key Eng. Mater.* **2009**, *391*, 1–25, doi:10.4028/0-87849-365-4.1.
[13] Rodriguez-Navarro, C; Ruiz-Agudo, E. Nanolimes: from synthesis to application. *Pure Appl. Chem*. **2018**, *90*, 523–550, doi: 10.1515/pac-2017-0506

[14] Naidu, S.; Sassoni, E.; Scherer, G.W. New treatment for corrosion-resistant coatings for marble and consolidation of limestone. In *Jardins de Pierres—Conservation of Stone in Parks, Gardens and Cemeteries*; Stefanaggi, M., Vergès-Belmin, V., Eds.; XL Print, Paris, France, 2011; pp. 289–294.
[15] Naidu, S.; Blair, J.; Scherer, G.W. Acid-resistant coatings on marble. *J. Am. Ceram. Soc.* **2016**, *99*, 3421–3428, doi:10.1111/jace.14355.
[16] Graziani, G.; Sassoni, E.; Franzoni, E.; Scherer, G.W. Hydroxyapatite coatings for marble protection: Optimization of calcite covering and acid resistance. *Appl. Surf. Sci.* **2016**, *368*, 241–257, doi:10.1016/j.apsusc.2016.01.202.
[17] Graziani, G.; Sassoni, E.; Scherer, G.W.; Franzoni, E. Resistance to simulated rain of hydroxyapatite- and calcium oxalate-based coatings for protection of marble against corrosion. *Corros. Sci.* **2017**, *127*, 168–174, doi:10.1016/j.corsci.2017.08.020.
[18] Sassoni, E.; Graziani, G.; Franzoni, E.; Scherer, G.W. Calcium phosphate coatings for marble conservation: Influence of ethanol and isopropanol addition to the precipitation medium on the coating microstructure and performance. *Corros. Sci.* **2018**, *136*, 255–267, doi:10.1016/j.corsci.2018.03.019.
[19] Franzoni, E.; Sassoni, E.; Graziani, G. Brushing, poultice or immersion? The role of the application technique on the performance of a novel hydroxyapatite-based consolidating treatment for limestone. *J. Cult. Herit.* **2015**, *16*, 173–184, doi:10.1016/j.culher.2014.05.009.
[20] Possenti, E.; Colombo, C.; Conti, C.; Gigli, L.; Merlini, M.; Rikkert Plaisier, J.; Realini, M.; Sali, D.; Gatta, G.D. Diammonium hydrogenphosphate for the consolidation of building materials. Investigation of newly-formed calcium phosphates. *Constr Build Mater*. **2019**, *195*, 557–563, doi:10.1016/j.conbuildmat.2018.11.077
[21] Yang, F.W.; Liu, Y.; Zhu, Y.C.; Long, S.J.; Zuo, G.F.; Wang, C.Q.; Guo, F.; Zhang, B.J.; Jiang, S.W. Conservation of weathered historic sandstone with biomimetic apatite. *Chin. Sci. Bull.* **2012**, *57*, 2171–2176, doi:10.1007/s11434-012-5039-9.
[22] Sassoni, E.; Franzoni, E.; Pigino, B.; Scherer, G.W.; Naidu, S. Consolidation of calcareous and siliceous sandstones by hydroxyapatite: Comparison with a TEOS-based consolidant. *J. Cult. Herit.* **2013**, *14*, e103–e108, doi:10.1016/j.culher.2012.11.029.
[23] Graziani, G.; Sassoni, E.; Franzoni, E.; Consolidation of porous carbonate stones by an innovative phosphate treatment: mechanical strengthening and physical-microstructural compatibility in comparison with TEOS-based treatments. *Heritage Science*. **2015**, *3*, 1-6, doi: 10.1186/s40494-014-0031-0
[24] Possenti, E.; Conti, C.; Gatta, G.D.; Realini, M.; Colombo, C.; Diammonium hydrogen phosphate treatment on dolostone: The role of Mg in the crystallization process. *Coatings*. **2019**, *9*, 169
[25] Sassoni, E.; Graziani, G.; Franzoni, E.; Scherer, G.W. Conversion of calcium sulfate dihydrate into calcium phosphates as a route for conservation of gypsum stuccoes and sulfated marble. *Construct. Build. Mater.* **2018**, *170*, 290–301, doi:10.1016/j.conbuildmat.2018.03.075.
[26] Balonis-Sant, M.; Ma, X.; Kakoulli, I. Preliminary results on biomimetic methods based on soluble ammonium phosphate precursors for the consolidation of archaeological wall paintings. In *Archaeological Chemistry VIII*, ACS Symposium Series; American Chemical Society: Washington, DC, USA, 2013; Volume 1147, pp. 419–447, doi:10.1021/bk-2013-1147.ch022.
[27] Li, Q.; Liu, Z.; Chen, W.; Yuan, B.; Liu, X.; Chen, W. A novel bio-inspired bone-mimic self-healing cement paste based on hydroxyapatite formation. *Cement Concrete Comp*. **2019**, *104*, 103357, doi:10.1016/j.cemconcomp.2019.103357

[28] European standard EN 459-1, Building lime - Part 1: Definitions, specifications and conformity criteria, 2015
[29] European standard EN 197-1, Cement - Part 1: Composition, specifications and conformity criteria for common cements, 2011
[30] European standard EN 196-1, Methods of testing cement - Part 1: Determination of strength, 2005
[31] Sassoni, E.; Masi, G.; Bignozzi, M.C.; Franzoni, E., Electrodeposition of hydroxyapatite coatings for marble protection: Preliminary results. *Coatings*. **2019**, *9*, 207, doi:10.3390/coatings9030207
[32] Sandrolini, F.; Franzoni, E. Characterization procedure for ancient mortars' restoration: the plasters of the Cavallerizza courtyard in the Ducal Palace in Mantua (Italy). *Mater. Character*. **2010**, *61*, 97-104, DOI: 10.1016/j.matchar.2009.10.012
[33] Henzel, J.; Karl, S. Determination of strength of mortar in the joints of masonry by compression tests on small specimens, *Darmstadt Concrete*. **1987**, *2*, 123-136
[34] Sassoni, E.; Franzoni, E.; Mazzotti, C. Influence of sample thickness and capping on characterization of bedding mortars from historic masonries by double punch test (DPT). *Key Eng Mater*. **2015**, *624*, 322-329, doi:10.4028/www.scientific.net/KEM.624.330
[35] European Standard EN 15801, Conservation of cultural property - Test methods - Determination of water absorption by capillarity, 2010
[36] Sharma, G. Color fundamentals for digital imaging. In *Digital Color Imagining Handbook*; CRC Press: Boca Raton, FL, USA, 2003.
[37] Karampas, I.A.; Kontoyannis, C.G. Characterization of calcium phosphates mixtures. *Vib Spectrosc*. **2013**, *64*,126– 133, doi:10.1016/j.vibspec.2012.11.003
[38] North, A.; Balonis, M.; Kakoulli, I. Biomimetic hydroxyapatite as a new consolidating agent for archaeological bone. *Stud. Conserv.* **2016**, *61*, 146–161, doi:10.1179/2047058415Y.0000000020.
[39] Delgado Rodrigues, J.; Ferreira Pinto, A.P.; Nogueira, R.; Gomes, A. Consolidation of lime mortars with ethyl silicate, nanolime and barium hydroxide. Effectiveness assessment with microdrilling data, *J. Cult. Herit*. **2018**, *29*, 43–53, doi:10.1016/j.culher.2017.07.006
[40] Borsoi, G.; Lubelli, B.; van Hees, R.; Veiga, R.; Silva, A.S. Evaluation of the effectiveness and compatibility of nanolime consolidants with improved properties. *Construct. Building Mater.* **2017**, *142*, 385-394, doi:10.1016/j.conbuildmat.2017.03.097
[41] Franzoni, E.; Varum, H.; Natali, M.E.; Bignozzi, M.C.; Melo, J.; Rocha, L.; Pereira, E. Improvement of historic reinforced concrete/mortars by impregnation and electrochemical methods. *Cement Concrete Comp.* **2014**, *49*, 50–58, doi:10.1016/j.cemconcomp.2013.12.013
[42] Arizzi, A.; Gomez-Villalba, L.S.; Lopez-Arce, P.; Cultrone, G.; Fort, R. Lime mortar consolidation with nanostructured calcium hydroxide dispersions: the efficacy of different consolidating products for heritage conservation. *Eur. J. Miner.* **2015**, *27*, 311-323, doi:10.1127/ejm/2015/0027-2437
[43] Toniolo, L.; Paradisi, A.; Goidanich, S.; Pennati, G. Mechanical behaviour of lime based mortars after surface consolidation. *Construct. Building Mater.* **2011**, *25*, 1553–1559, doi:10.1016/j.conbuildmat.2010.08.010
[44] Cai, Y.; Hou, P.; Duan, C.; Zhang, R.; Zhou, Z.; Cheng, X.; Shah, S. The use of tetraethyl orthosilicate silane (TEOS) for surface-treatment of hardened cement-based materials: A comparison study with normal treatment agents, *Construct. Building Mater.* **2016**, *117*, 144-151, doi:10.1016/j.conbuildmat.2016.05.028

[45] Delgado Rodrigues, J.; Grossi, A. Indicators and ratings for the compatibility assessment of conservation actions. *J. Cult. Herit.* **2007**, *8*, 32–43, doi:10.1016/j.culher.2006.04.007.
[46] Ma, X.; Pasco, H.; Balonis, M.; Kakoulli, I. Investigation of the optical, physical, and chemical interactions between diammonium hydrogen phosphate (DAP) and pigments, *Sustainability*. **2019**, *11*, 3803

SUPPLEMENTARY MATERIAL

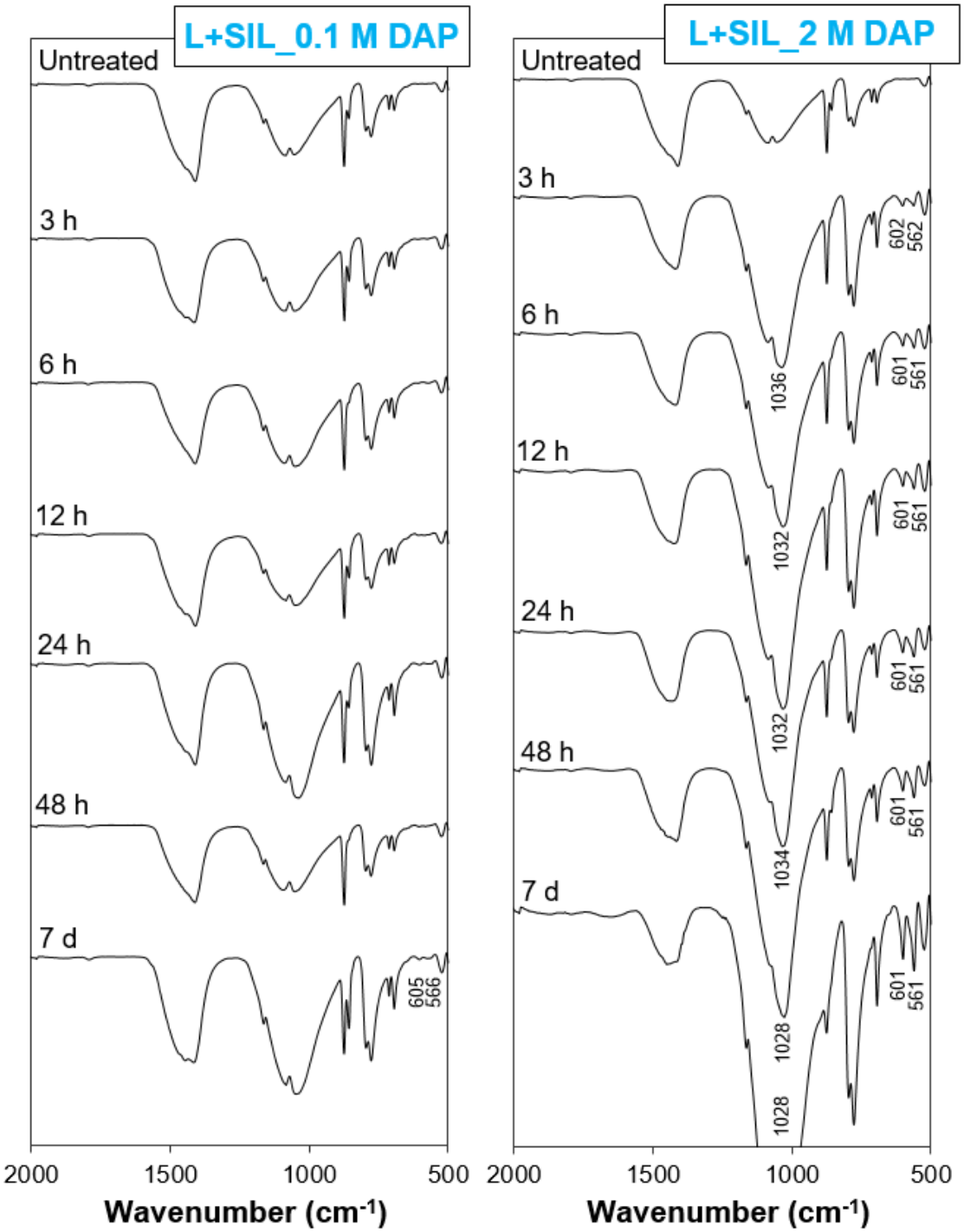

Figure S1. FT-IR spectra of "L+SIL" samples treated for increasing time.

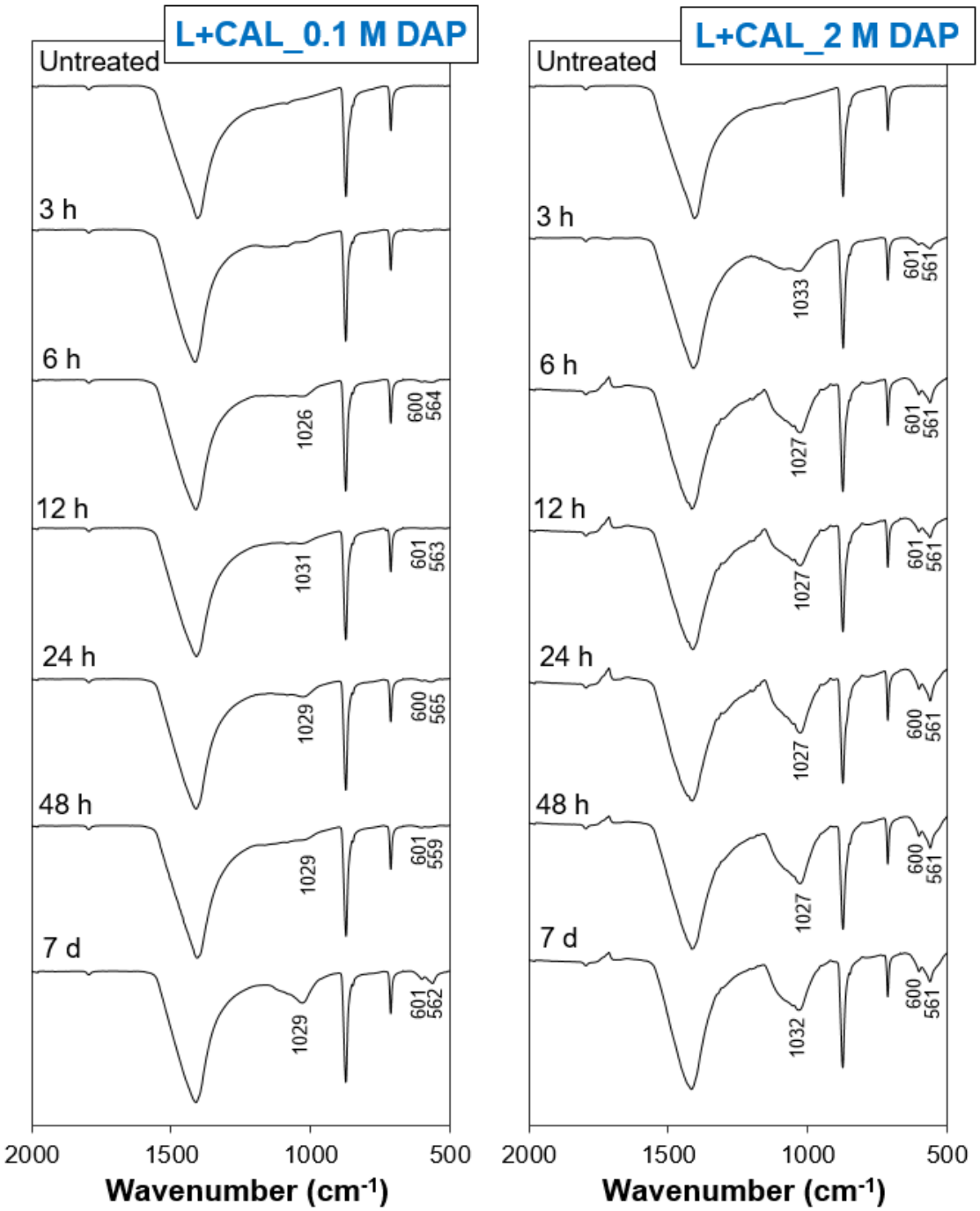

Figure S2. FT-IR spectra of “L+CAL” samples treated for increasing time.

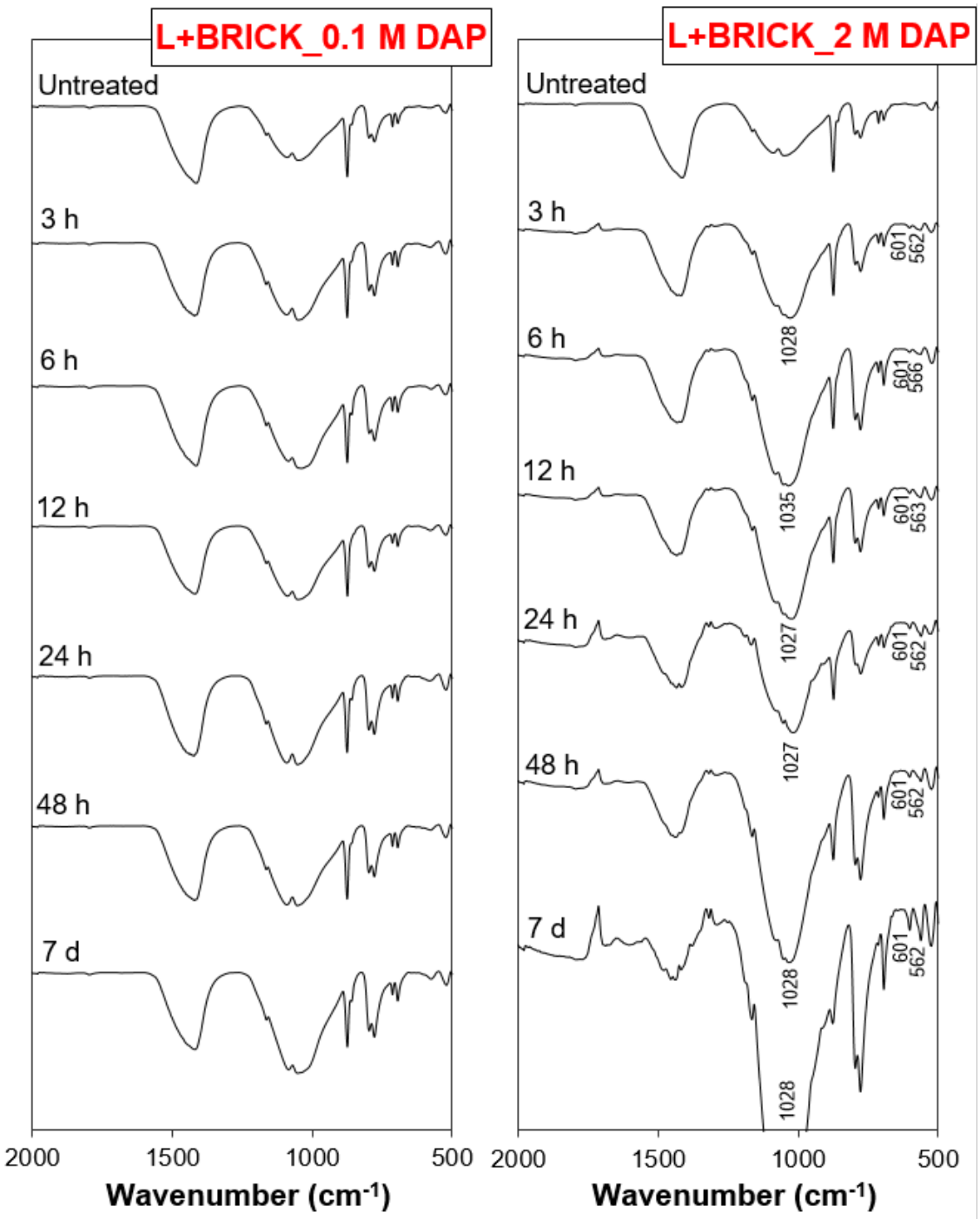

Figure S3. FT-IR spectra of “L+BRICK” samples treated for increasing time.

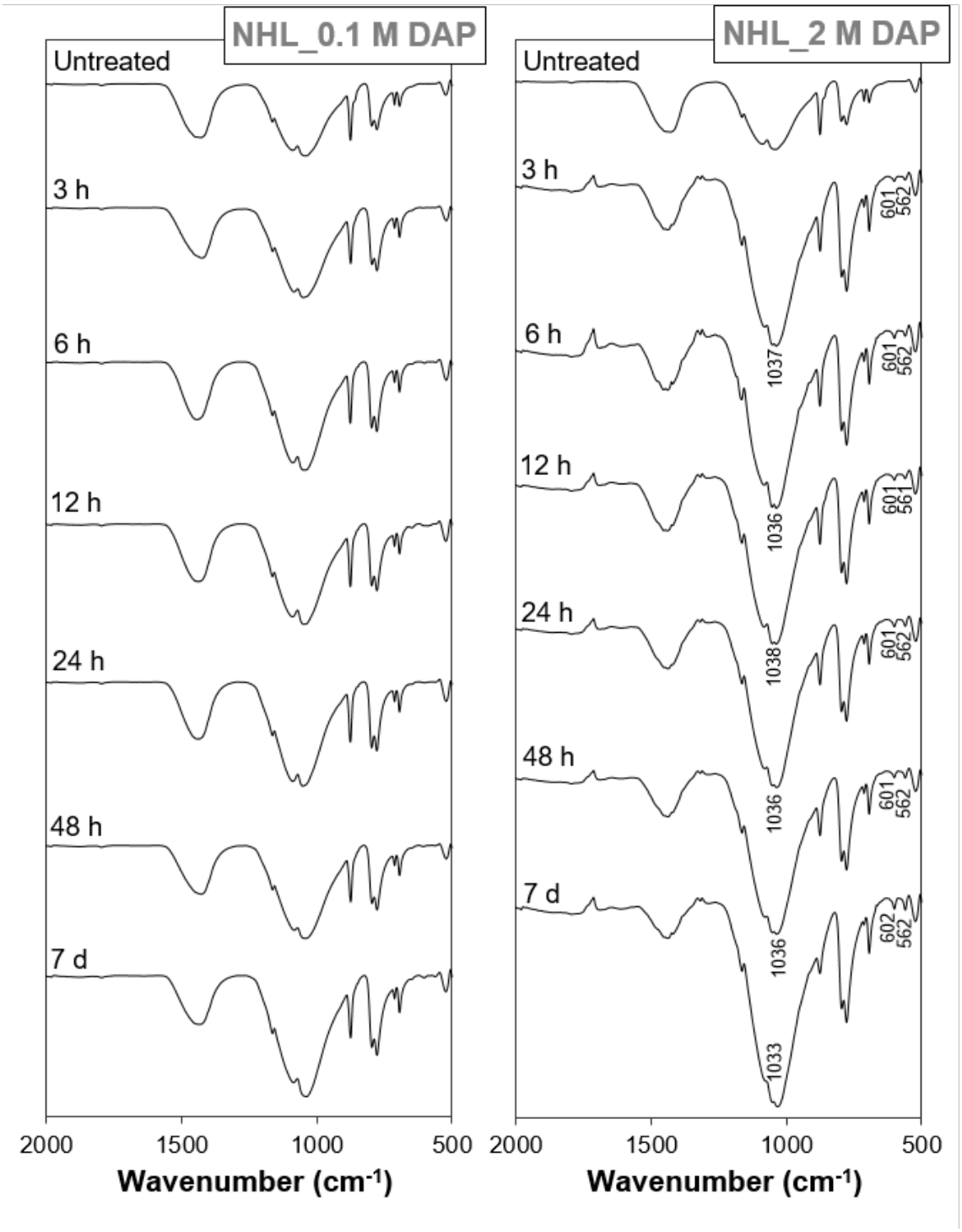

Figure S4. FT-IR spectra of “NHL” samples treated for increasing time.

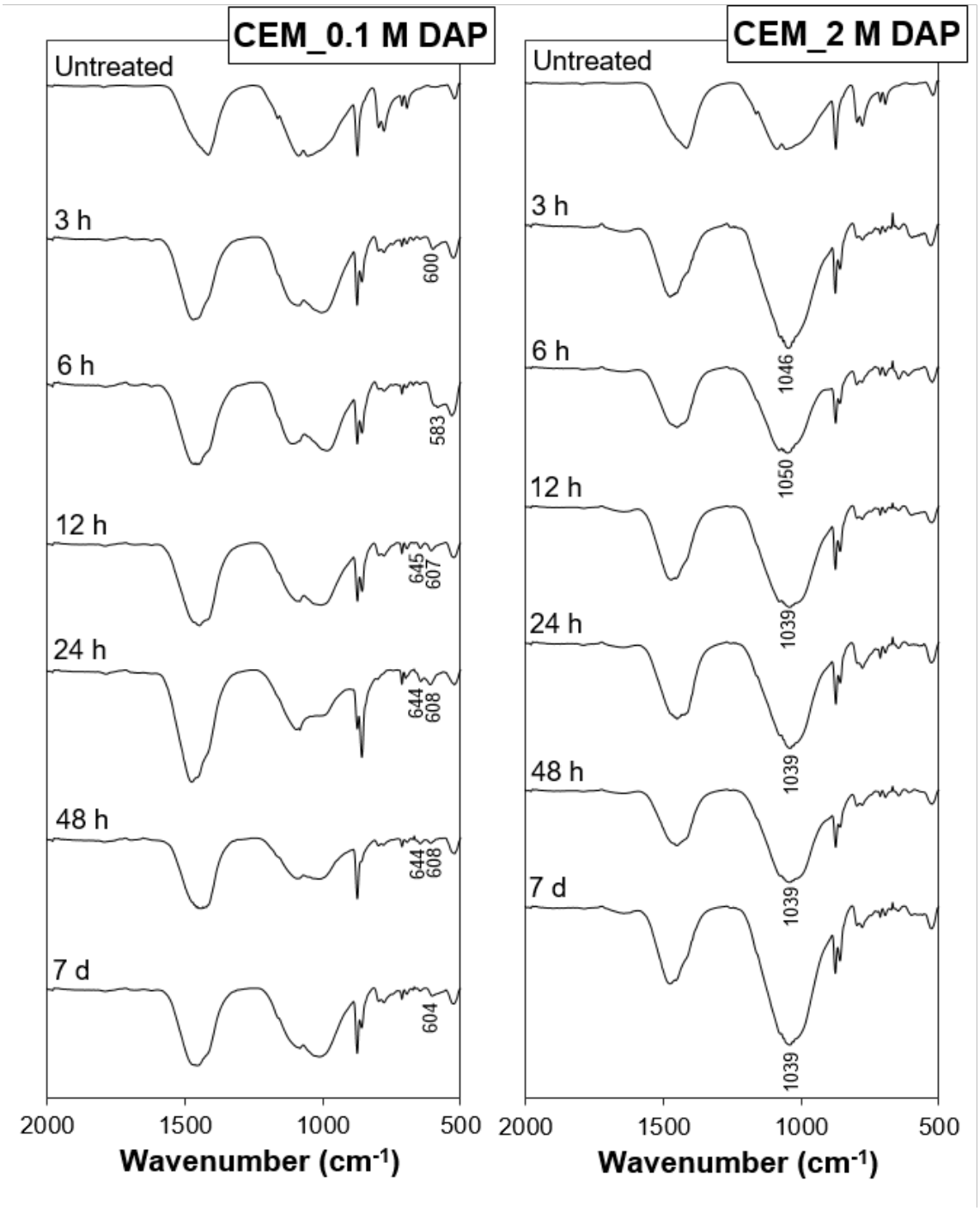

Figure S5. FT-IR spectra of “CEM” samples treated for increasing time.