

# Di-ammonium hydrogen phosphate for the consolidation of lime-based historic mortars – preliminary research

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*Abstract: The present paper investigates the use of di-ammonium hydrogen phosphate (DAP) as a possible consolidation treatment for lime-based mortars. Different DAP concentrations were proposed, additional post-treatment limewater application was used on some specimens. The results of application were evaluated in terms of mechanical property modification (dynamic elastic modulus, weight loss due to the peeling test), penetration depth, consolidant's distribution (P/Ca ratio), colour change and water transport properties. Newly-precipitated phosphate-based phases were detected after the treatment and the relation towards treatment modality (i.e. DAP solution molarity and further limewater application) was evaluated. In case of mechanical improvement, the outcomes indicate that phosphate-based treatment is highly promising for mortar consolidation. Some non-negligible colour change was detected as well as a result of DAP application.*

**Key words: mortar, conservation, di-ammonium hydrogen phosphate, consolidation, HAP**

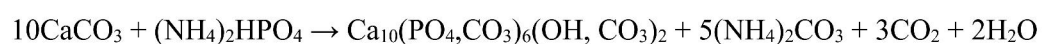
## 1. Introduction

As with the passing of time historic materials, especially mortars, may undergo severe decay processes, preservation of their original features with simultaneous microstructure restoration is considered as particularly important task. For decades multiple methods and treatments have been proposed for this purpose, yet each of it displaying certain lacks in effectiveness. For this reason the need of searching and developing new consolidation treatments is constantly considered as an essential task in architecture conservation.

The use of di-ammonium hydrogen phosphate (DAP) as a chemical product allows achieving a consolidation effect of cultural heritage materials through the formation of hydroxyapatite (HAP) or other calcium phosphates (Ca-P); it was proposed in 2011 as a possible conservation treatment for marble and limestone [1]–[4]. Furtherly, the research upon its use was spread to the other substrates, such as sandstone [5], [6], gypsum based stuccoes [7], [8], mortars [9], [10], concrete [11], archaeological bones [12], [13] and paper [14], including some minor attempts of HAP nano-particles usage [14].

In the field of lime-based materials (either historical or contemporary), the lack of effective consolidating treatments able to restore the original microstructural features was the main motivation for finding some other conservation treatments from which phosphate-based application has arisen. The main premise was to seek for the material in the inorganic products' field, due to the previously proven overall lack of compatibility and low durability of organic products, such as, e.g. acrylic resins, silicone resins or epoxy resins [15]–[17]. For that reason HAP consolidation treatment was proposed as a mineral having unit cell parameters very close to those of calcite and having much lower solubility and dissolution rate than calcite thus posing highly promising results as a possible conservation treatment overcoming the previous critical issues [1].

All of the proposed methods allowing for HAP formation involve the reaction of calcium-based substrate with a phosphate salt introduced as an aqueous solution, able to provide the  $\text{PO}_4^{3-}$  ions required for HAP precipitation [18]. Ammonium phosphate salts were assessed to be the most suited medium due to their high solubility in water (68.9 g/100 ml at 20°C for di-ammonium hydrogen phosphate) and absence of undesired residue [9], among which DAP  $((\text{NH}_4)_2\text{HPO}_4)$  was the first salt to be researched for HAP deposition [3], [8] following the below reaction:



1 The above reaction, which was stated to proceed at ambient temperature [1] may lead to the  
2 precipitation of several metastable Ca-P phases as well, whose formation is strictly related to the  
3 reaction conditions, including pH, contact time and molarity of employed solution [1], [19]–[21] and  
4 which are expected to eventually convert into HAP, considered as the most stable Ca-P phase at pH >  
5 4 [22] and for that reason the most desirable to precipitate. However, it shall be kept in mind that other  
6 Ca-P are not considered as undesirable, as, even though being more soluble than HAP, some of them  
7 still remain significantly less soluble than calcite [18]. Additionally octacalcium phosphate (OCP)  
8 coatings were recognised to provide greater protection against acid attack in comparison to HAP+OCP  
9 system [23].  
10

11 Due to the fact that DAP solution molarity has been considered as a possible factor influencing the  
12 amount of formed phosphates [1], a treatment based on a high concentration of this compound has  
13 been proposed (> 1.0 M) [1], [2], [9], [10], [24]–[28]. Some recent publications indicated as well that  
14 the ratio between the phosphate ions in the solution depends on its pH [22], [29], therefore some  
15 experimentations upon the applications of DAP solutions at controlled pH level have been undertaken,  
16 mainly on limestone [3], [30]. The time of reaction allowing for an achievement of suitable  
17 consolidation effect has been set to be usually 3 to 8 hours [31], [32], however majority of  
18 recommendations stated that the DAP application time should take at least 24 hours for a limestone  
19 substrate ([1], [23], [24], [33], [34]), claiming as well the feasibility of a 24–48 h treatment duration in  
20 the onsite practice of cultural heritage conservation [18]. As far as the application method is  
21 concerned, some attempts have been undertaken to externally provide calcium ions in order to support  
22 the HAP formation, while the main Ca<sup>2+</sup> sources that has been investigated were Ca(OH)<sub>2</sub> [35], CaCl<sub>2</sub>  
23 [2], [10], [36], Ca(NO<sub>3</sub>)<sub>2</sub> [2], calcium formate [33] and calcium gluconate [33]. In case of pre-  
24 treatment with calcium sources, the main techniques were based on limewater (i.e. saturated Ca(OH)<sub>2</sub>  
25 solution) [35] and Ca(OH)<sub>2</sub> nano-particles [4], [5] applications, whereas both methodologies have  
26 contributed to the achievement of good results however with no significant advantage [18]. Some  
27 investigations were based as well upon the post-treatment limewater application [1], [24]–[27], [34],  
28 [37] additionally aiming for the removal of unreacted DAP residue, thus avoiding the undesirable salt  
29 bleaching [34], while the results indicated the successful escalation of HAP precipitation and no  
30 presence of superficial DAP remaining, even while using very high solution concentrations (3.0 M)  
31 [27].  
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33 Several studies evaluated as well the depth of the consolidation front [1], [10], [24], [34], [38]. The  
34 results indicated that for 3.0 M DAP treatment with subsequent limewater poultice application  
35 performed on artificially weathered Carrara marble, calcium phosphate formation was detected at least  
36 4 mm underneath the surface [24], whilst on Globigerina limestone – minimum 7.5 mm (10 mm as to  
37 FT-IR examination) [34]. For 1.0 M DAP treatment of Indiana limestone calcium phosphates were  
38 registered on the depth of 20 mm [1], for 2.0 M DAP + 2 mM CaCl<sub>2</sub> treatment of lime-based mortars –  
39 more than 40 mm [10] while 5% DAP solution application on the Lecce stone and Tuffeau de  
40 Maastricht resulted in HAP formation at least 10 mm underneath the surface [3]. A minimum depth of  
41 20 mm was reached both for 3.0 M DAP + limewater application [24] and 0.1 M DAP + 0.1 mM  
42 CaCl<sub>2</sub> (in 10% isopropanol) treatments for marble specimens [38] and lime-based mortars [10] and at  
43 least 25 mm for Globigerina limestone treatment (3.0 M DAP + limewater) [34].  
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45 Despite the fact that the literature upon DAP treatments is very rich and includes as well several  
46 treatments on site [31], [36], [39]–[42], there is a significant lack of research focused on phosphate-  
47 based applications on mortars' surfaces, for which only minor studies have been so far undertaken  
48 including laboratory examination [9], [10] and on site application [31]. Preliminary results indicated  
49 the effectiveness of such application and detected HAP formation on surfaces, yet multiple open  
50 questions (such as the appearance of excessive whitening, optimization of application method etc.)  
51 have been raised to be investigated in further studies.  
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1 To correctly assess the actual usefulness of DAP treatment method in the field of mortars'  
2 conservation it is essential to provide results pertaining to basic requirements imposed to the historic  
3 materials' consolidants, i.e. surface cohesion increase, improvement of mechanical properties, proper  
4 penetration depth, good chemical compatibility, water capillarity and non-exceeding colour change.  
5 While investigating the above listed properties, the paper takes into consideration the effectiveness of  
6 the treatment, linked to the homogenous penetration through the substrate with its simultaneous  
7 mechanical improvement [43]–[45] and its compatibility, that is to say the evaluation of possible  
8 substrate alterations due to the treatment, such as, inter alia, colour change [45], [46] and water  
9 transport properties influence [22], [26]. For the reasons stated above, this research is considered as  
10 essential input into DAP mortar consolidation studies.  
11

## 12 **2. Materials and methods**

### 13 **2.1. Materials**

#### 14 *Mortar*

15 Mortar used in the examination was prepared by mechanical mixing of lime putty with aggregate  
16 (Ticino silicate-sand) in 1:3 volumetric ratio. The mixtures, having the consistency of a dense paste,  
17 were placed in lubricated superficially wooden forms (5x5x2 cm) and left to cure in a climatic  
18 chamber with 90% RH and 25°C for one week. Subsequently, the specimens were de-moulded and left  
19 for 10 months in the conditions of 60% RH and 25°C in order to ensure the best carbonation  
20 environment. The open porosity of the mortar specimens measured by mercury intrusion porosimeter  
21 was ~29%, with the main presence of ~6.88 µm radius' pores.  
22

#### 23 *DAP consolidation treatment*

24 Previous studies indicated that it is advised to use a high concentration level of DAP for consolidation  
25 purposes [33], as only limited amount of DAP (less than 1%) dissociates into  $\text{PO}_4^{3-}$  which, unlike other  
26 anions formed due to DAP dissociation –  $\text{HPO}_4^{2-}$  and  $\text{H}_2\text{PO}_4^-$ , is able to react with calcium ions  
27 contributing to the formation of HAP. Moreover, it had been pointed out that the increase of DAP  
28 concentration results in highly noticeable growth of mechanical properties [1]. As different DAP  
29 molarities influence the crystallization of new phases (in terms of their amount and composition),  
30 taking into account the above stated considerations, different DAP molarities were proposed as  
31 follows: 2.0 M, 3.0 M and 3.7 M (saturation level at ambient temperature) as solution in de-ionized  
32 water.  
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34 To assess the effects induced to the crystallization of the different consolidation modalities, the set of  
35 specimens was divided into three groups regarding the used DAP molarity (three specimens per set),  
36 and subdivided in respect to the subsequent application method. All of the DAP treatments were  
37 applied on the front surface by cellulose poultice (1000 micron fibres) for 24 hours, which was stated  
38 to provide a good penetration-depth effect [34]. Directly after the treatment the specimen were  
39 wrapped in plastic film for 24 hours preventing fast evaporation.  
40

41 To avoid the possible precipitation of metastable calcium phosphate phases or efflorescences  
42 originating from the presence of unreacted DAP remaining in the substrate, the post-treatment  
43 application of limewater poultice was proposed as a second step of the procedure. This procedure  
44 follows a methodology proposed in previous researches [33], [34] and aims at providing an additional  
45 amount of free calcium ions for the DAP reaction.  
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For that reason, after specimens' oven drying, limewater poultice was subsequently applied for 24 hours to half of the mortar specimens in order to compare the consolidation effect with and without its application. Limewater was prepared by mixing 1.7 g of  $\text{Ca}(\text{OH})_2$  with 1 L of de-ionized water at ambient temperature, providing complete saturation. The weight ratio of limewater to dry cellulose pulp was set at 1:5.5. After the application the specimens were wrapped with plastic film for 24 hours. The last step of the treatment procedure was the immediate application of de-ionized water poultice for 24 hours to remove any superficial DAP residue (without specimens' oven drying). After the whole procedure the specimens were left to dry in laboratory conditions ( $T = 20 \pm 2^\circ\text{C}$ ,  $\text{RH} = 50 \pm 5\%$ ) until achieving a constant weight. Table 1 shows the precise specimens' organization.

Table 1. Organization of treatment and specimens in the examination.

Specimen name	DAP molarity	Limewater application
2.0	2.0	NO
2.0L	2.0	YES
3.0	3.0	NO
3.0L	3.0	YES
3.7	3.7	NO
3.7L	3.7	YES

## 2.2. Methods

### 2.2.1. Weight measurement

The specimens' weight was measured before and after the consolidating treatment (i.e. after obtaining a constant mass level) using a balance of 0.0001 g accuracy. A variation of weight can be considered as an indirect indicator of the newly-formed phases' presence within the substrate's matrix. To verify if weight increase is correlated with the crystallization of new P-phases directly responsible for consolidation effect, its measurement was supported with further evaluation of mechanical strength change.

### 2.2.2. Ultrasonic pulse velocity

Dynamic elastic modulus was calculated on the basis of the ultrasonic pulse velocity (UPV) following the formula  $E_d = \rho \cdot \text{UPV}^2$  ( $\rho$  being the apparent density of the mortar). UPV with vertical orientation of the transducers (i.e. along the 2-cm thickness), considered as a non-destructive measurement, was undertaken before and after the treatment (3 replicates for each condition), firstly determining the mechanical state, and then indicating the eventual effect of consolidation supposedly improving the internal structure of specimens. The test was performed with the usage of "Controls" instrument equipped with 50 kHz transducers supported by rubber couplant allowing for an effective contact between the transducers and the specimen. UPV measurement was proved to be an effective indicator

of surface's degradation and consolidation state, particularly used in the studies upon DAP treatment in cultural heritage [1], [6], [10], [47]–[52].

### 2.2.3. Peeling test

Scotch tape peeling test was performed by the use of adhesive tape Scotch 1280 with a resistance to tensile load of 50.8 N/cm and adhesion capability of 3.2 N/cm – as specified by ASTM D-3759 [53] and ASTM D-3330 [54]. Scotch tape test allows for a semi-quantitative evaluation of consolidation treatment. The surface of each specimen subjected to the examination was thoroughly cleaned by gentle air-pressure of the potential loose and dirt particles that may affect the outcomes of the test. Then, the specimen weight was measured and the previously weighed strip of scotch tape of 4 cm long attached to the thin plastic rubber (to ease the application) was pressed onto the surface, firstly by fingertip pressure (to remove all of the visible air bubbles and provide a good contact between the adhesive side of the tape and the surface) and then by rolling pin moved 5 times on the surface covered up with protective plastic rubber of c.a. 7 mm thickness. After this step the tape was peeled off from the surface in a single smooth motion and again the mass of the scotch strip was measured. Each specimen was subjected to this procedure at the same place on the surface 6 times. At the end the weight of the specimen was measured again. The strategy of repeated peeling in the same place on the surface aims to eliminate the effect of the natural decrease of detached material, which might give an incorrect impression of consolidation result [55], [56].

### 2.2.4. Scanning electron microscopy coupled with energy dispersion spectrometry

The consolidation effect on microstructure was highlighted by investigating the penetration depth using SEM/EDS analysis (JEOL 5910 LV) scanning electron microscope with an energy dispersive X-ray spectrometer in BSE compositional image - accelerating voltage 20 kV). Analyses were performed on polished cross-sections of specimens pieces with the approximate observation area dimensions of 1 cm x 1 cm, providing maps of P-element distribution by means of EDS spectrometry, in reference to the consolidation penetration depth.

Further in-depth examination of EDS elemental analysis results allowed to evaluate the P-presence in relation with the molarity of DAP treatment and the subsequent limewater treatment. The P-presence was assessed by acquiring EDS spectra in areas from different samples keeping unchanged area sizes, working distance and spot size, as well as working with the same energy conditions supplied to the filament.

### 2.2.5. Colorimetry

To control chromatic changes caused by the treatment, the colour measurements were undertaken by the use of spectrophotometer (MINOLTA CM700d), which were interpreted in accordance with CIEL\*a\*b\* system, determining the change of colour ( $\Delta E$ ) assuming the proportional dependence between the distance of the points, which define individual colours and their actual perceptual difference, using the coordinates indicating their key attributes: lightness, saturation (Chroma) and hue [51]. The change of colour is determined as the Euclidean distance between two points (L, a, b and L', a', b') defined by the above specified attributes, as follows:  $\Delta E = (\Delta L^2 + \Delta a^2 + \Delta b^2)^{0.5}$ . The change of chromaticity ( $\Delta C$ ), defined as the distance of the same points characterized only by \*a and \*b values thus operating only in one plane was calculated accordingly with:  $\Delta C = C_1 - C_0$ , where  $C_i = (a_i^2 + b_i^2)^{0.5}$  [51]. For each specimen 5 measurements were undertaken at exactly the same points before and after the treatment.

## 2.2.6. Water absorption by capillarity

For assessing the effect of the treatment on water transport properties, water absorption test was performed (in accordance with UNI 10859 [57]). After obtaining a constant weight, the specimens were placed in contact with water through a layer of filter papers of about 0.5-0.8 cm. The amount of water was continuously re-filled during the test to assure its constant level. The measurement of mass of each specimen was carried out at regular time intervals (2.5, 5, 10, 15, 20, 30, 60, 120, 240, 360 min) and was reported in grams. After 6 hours the test was finished as the specimens reached the full saturation (a detailed description of the capillarity features is discussed in the “results and discussion” section). The absolute capillary absorption index (IC), referring to the maximum theoretical absorption, was calculated in accordance with the equation (1) [58]:

$$IC = \frac{\int_{t_0}^{t_f} f(Q) dt}{Q_{t_f} \cdot t_f} \quad (1)$$

Where:

$\int_{t_0}^{t_f} f(Q) dt$  – the amount of water absorbed during the testing, in  $\text{mg}/\text{cm}^2 \text{ s}^{1/2}$ ;

$Q_{t_f}$  – the total amount of absorbed water per surface unit, in  $\text{mg}/\text{cm}^2$ ;

$t_0$  – starting time, in  $\text{s}^{1/2}$ ;

$t_f$  – ending time, in  $\text{s}^{1/2}$ ;

In general, the IC index defines the capability of water absorption in time through the comparison of water absorbed during the test with the maximum theoretical absorption for the specified material.

## 3. Results and discussion

The experimental results (before and after the treatment) are reported, discussed and subsequently compared in order to highlight the actual impact of the different consolidation modalities on the mortar properties.

### 3.1. Post-treatment weight change

The weight difference measured on all the specimens after the consolidating treatment and its standard deviation is shown in Table 2. All the specimens displayed similar specific weight increases related to the dry mass. The weight increase was higher for the specimens treated with a higher DAP molarity. In average, the weight increase of each specimen after the treatment ranges between 1.37-2.49%. The weight increase directly indicates the presence of active residue – solid phases, among which some may be attributed to consolidation effect. No evident effect of limewater treatment onto weight gain was noted. Previous studies displayed rather dispersed results of the dry weight change after the treatment ranging in 0.1-8.6%, highly depending on treatment's procedure, open porosity, specimen's shape and DAP molarity used [6], [25], [27], [34], [35]. No measurement of such type was carried out on mortar specimens, hence no comparison of this property can be undertaken.

Table 2. Average dry weight gain in % (active residue) for each application mode after the treatment.

Specimen	$\Delta m$ (%) – active residue	Standard deviation
2.0	1.50	0.08
2.0L	1.37	0.05
3.0	2.13	0.05
3.0L	1.96	0.06
3.7	2.49	0.06
3.7L	2.49	0.02

### 3.2. Dynamic modulus of elasticity change

Based on the results of UPV in vertical arrangement a remarkable consolidation effect was achieved for all of the applications (Table 3), as the average increase of  $E_d$  was ~100% (from 2.5 GPa to 5.1 GPa). The relative  $E_d$  values displayed no dependency on the DAP concentration and/or post-lime water treatment.

Table 3. Dynamic modulus of elasticity ( $E_d$ ) value for each treatment modality – UPV measurement in vertical arrangement.

Specimen	$E_d$ (GPa)		$\Delta E_d$ (%)	Standard deviation
	Untreated	Treated		
2.0	2.3	4.8	108.7	0.6
2.0L	2.5	5.1	104.0	1.4
3.0	2.4	5.1	112.5	1.6
3.0L	2.5	5.0	100.0	2.3
3.7	2.5	5.1	104.0	0.2
3.7L	2.6	5.2	100.0	1.2

In case of UPV measured with the horizontal arrangement of the transducers (i.e. along the 5-cm thickness) all of the specimens before the treatment achieved the  $E_d$  values near 1 GPa and increased by the treatment by c.a. 8-25 % (Table 4). The difference between horizontal and vertical UPV outcomes may originate from the fact that specimens were prepared in non-isotropic conditions.

Moreover, transducers' diameter (3 cm) was larger than samples' height (2 cm), which may have had an impact on the measurement and its results.

Table 4. Average dynamic modulus of elasticity ( $E_d$ ) values for each treatment modality – UPV measurement in horizontal arrangement.

Specimen	$E_d$ (GPa)		$\Delta E_d$ (%)	Standard deviation
	Untreated	Treated		
2.0	0.99	1.12	13.1	0.7
2.0L	0.90	1.02	13.3	0.9
3.0	1.02	1.11	8.8	0.2
3.0L	0.84	1.05	25.0	1.3
3.7	1.01	1.16	14.8	1.1
3.7L	1.06	1.22	15.1	0.3

In case of lime-based mortars consolidation UPV testing has only been used and researched once [10], while obtained results indicated up to +74%  $E_d$  growth after treatment. However taking into consideration wide diversity of mortars' structure it is rather difficult to assess the actual extent of  $E_d$  change. Basic approach usually adopted in case of consolidating treatments considers them as sufficiently effective if they were able to restore mechanical properties of the material yet without surpassing its strength [59]. Nevertheless in case of such requirement, it shall be taken into consideration that it assumes the treatment on the deteriorated surfaces (and not on the input ones) that are obviously characterized with decreased strength while comparing to their original condition. For that reason, at this moment it is impossible to precisely evaluate the results of that testing, as – at this stage – it provides only the information about the influence of the treatment on the mechanical properties and its possible relationship with Ca-P phases crystallization.

### 3.3. Surface cohesion change

The possible variation of cohesion properties after the consolidating treatment was explored by the scotch tape peeling test performed on the non-treated and treated surfaces. The collected results are shown in Figure 1 and demonstrate a superficial mechanical improvement due to the consolidation. It has been previously highlighted that the peeling test used on the surfaces with sharp grains and coarse texture, such as mortars, may impair the outcomes of the examination due to the fact that loosened particles present on the rough surface, in that case do not represent the cohesion characteristics of the material [55]. For that reason the actual cohesive model in case of mortar specimens is represented by the repeatable peelings undertaken in the same place, while the consolidation effect is expressed through a cumulative mass loss calculation. Thus, the graph of Figure 1 presents the average weight of material detached due to the subsequent peels considering each application mode in comparison with the non-treated surface condition. The first remark is an unambiguous indication on the effective consolidation result achieved by each specimen - material's detachment in case of non-treated specimens reached an average weight of 0.53 mg/cm<sup>2</sup>, while the range of achieved outcomes in case of consolidated surfaces falls within 0.12-0.34 mg/cm<sup>2</sup>, hence at least 35% lower. There is no dependency on the application mode, especially regarding post limewater treatment.



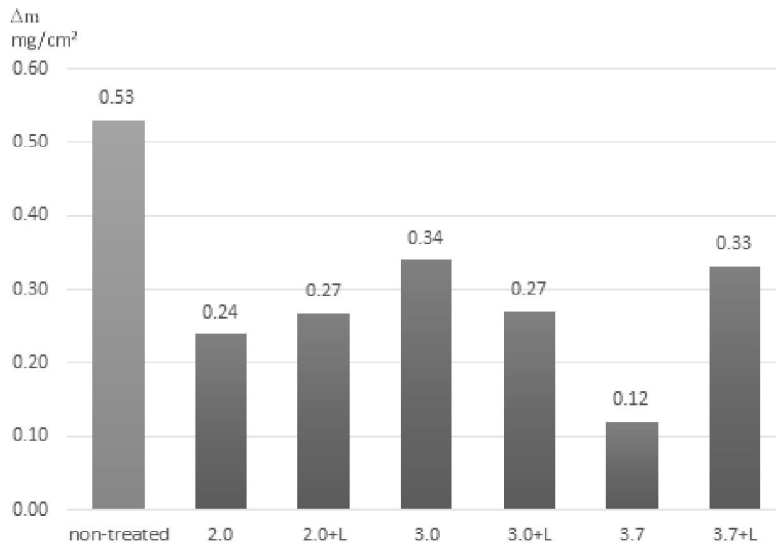


Figure 1. Cumulative mass loss due to the peeling test (after 6 subsequent peels) indicated for each specimen reflecting the amount of material detached in mg/cm<sup>2</sup>.

### 3.4. Consolidant's distribution and minimum penetration depth

The binder of the specimens has multiple internal discontinuities (pores and cracks) which constitute a preferential corridors for the penetration of the treatment (Figure 2-0). The application of DAP determined the formation of new microcrystalline phases composed of Ca and P at the edges of calcite grains, belonging to the portions with micrometric dimensions of the binder (Figure 2-1 and 2-2). The treatment did not produce superficial crust or a sharp layer disconnections. This observation is reckoned as positive outcome as the requirements upon such features are considered as an essential issue of consolidant application [43], [45], [60]. Phosphorus was detected in all of the treated specimens in the overall investigated depth – its presence is distinguished mainly along the distribution paths, with no observed gradient from the surface to the bottom (Figure 3). In the untreated specimens phosphorus was not detected. This observation confirms that P present in treated specimens is the direct result of DAP treatment. The fact that P has been detected by EDS down to the bottom of the treated specimens suggests that each DAP solution penetrated for at least 1 cm distance from the treated surface. The substantial depth of treatment penetration is thought to result from fast absorption of the solution by the large pores of highly porous mortar, followed by drainage into the smaller pores [61]. It may be as well correlated to the used application method (i.e. via poultice). The usual recommendations for penetration depth of the consolidation treatments claim that the greater the depth reached by consolidant, the better for the substrate [43]–[45], [62]; ideally, the consolidation front should reach the depth of the unweathered substrate fragments [25]. However, taking into account the average historic plaster thickness of 1-2 cm, the deterioration level may correspond to the total depth of the material. Therefore the achieved consolidation depth is considered as a satisfactory result.

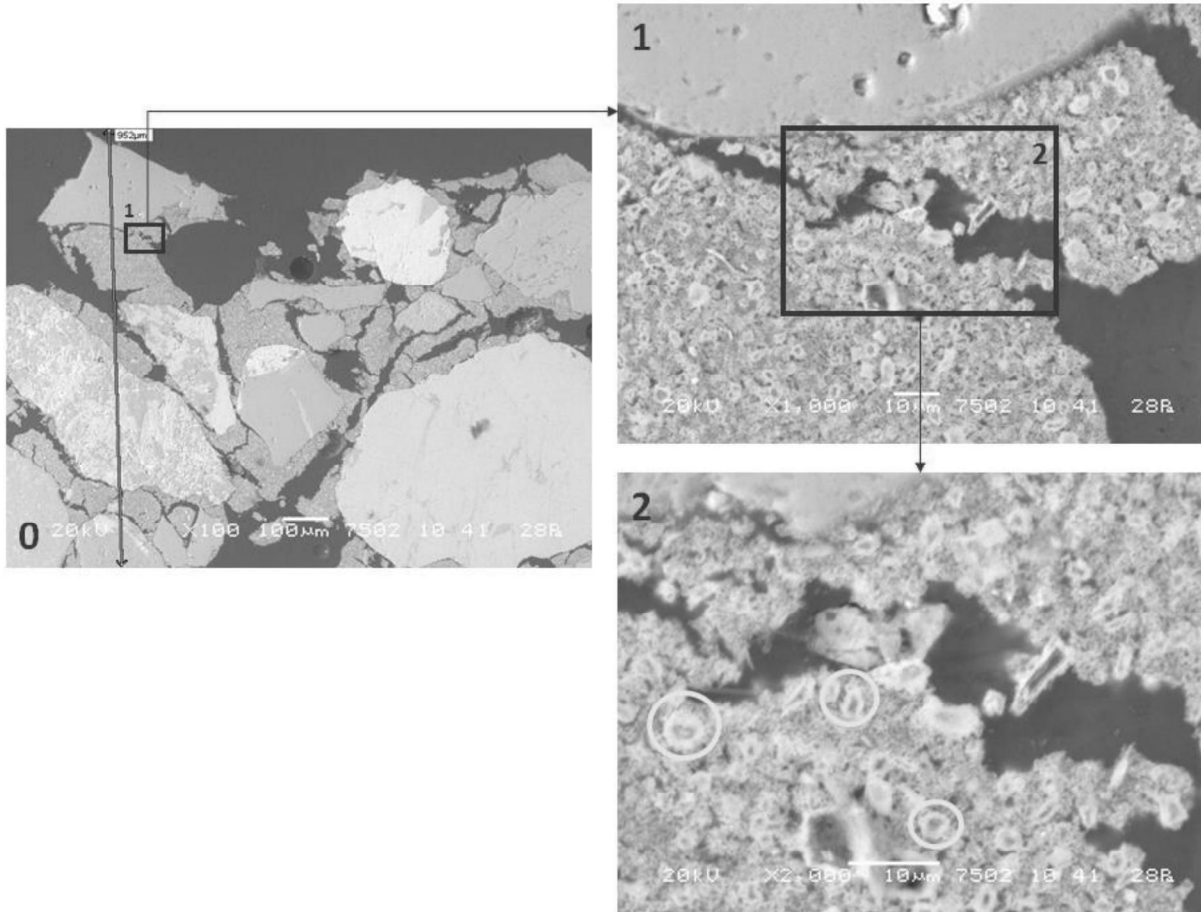
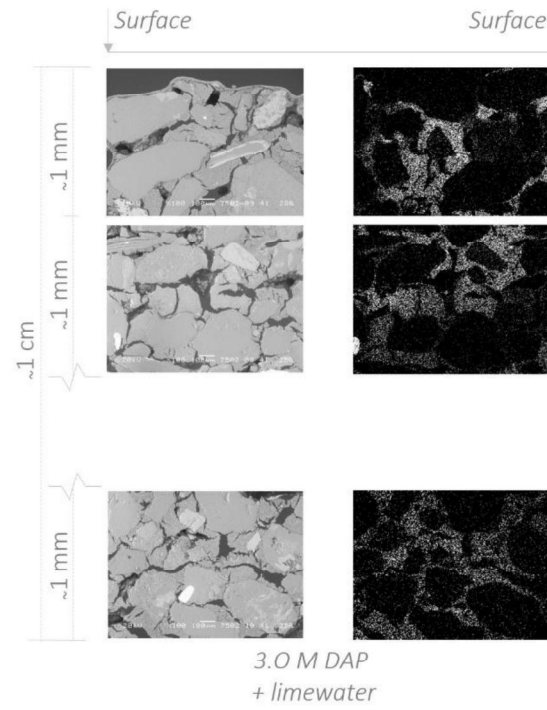
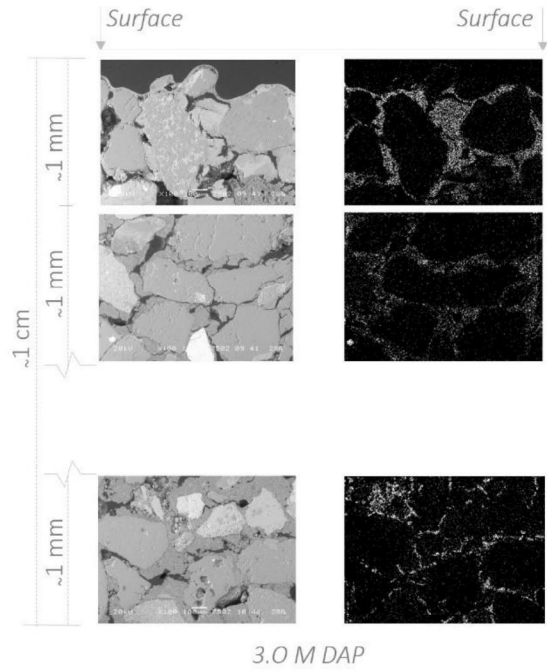


Figure 2. Ca-P phase identification in the SEM/BSE images seen in the magnification of 100x (0), 1000x (1) and 2000x (2). Circles indicate precipitated annular Ca-P.

The average semi-quantitative P level observed in EDS spectra (measured in the areas of  $10 \mu\text{m}^2$ ) revealed some variations between specimens treated with different DAP solutions. In case of 3.7 M DAP solution, homogeneity of P distribution is disrupted at most – neighbouring binder fragments frequently have very different P level. Comparing, specimens treated with lower DAP molarities (2.0 M and 3.0 M) exhibit more visible homogeneity in P distribution. In case of specimens subsequently treated with limewater, more even distribution of the treatment in the binder matrix is detected regardless of DAP molarity used, presumably due to the further reaction of previously unreacted DAP with limewater.

For all of the treatment modalities, an important factor influencing P level is the presence of aggregate in the mortar: it can be observed, that larger grains or clasts of aggregate created an “umbrella” effect during the treatment, preventing applied DAP solution from unfettered spread beneath them - binder fragments placed below larger aggregate clasts are characterized with drastically decreased P level comparing to the neighbouring areas (Figure 4).

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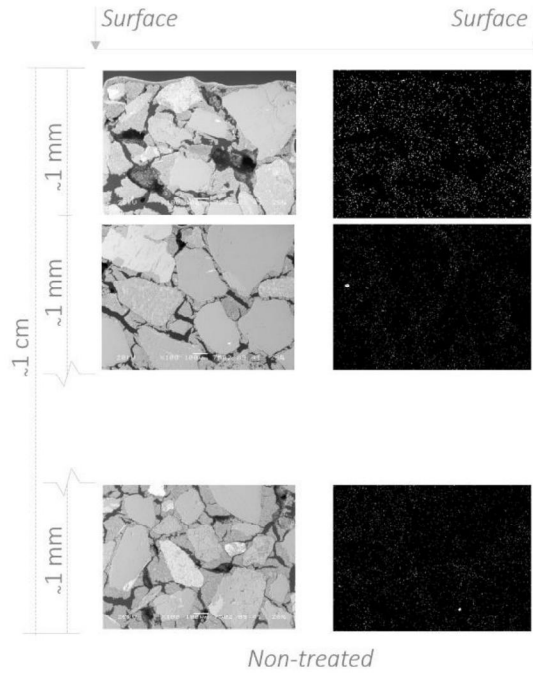
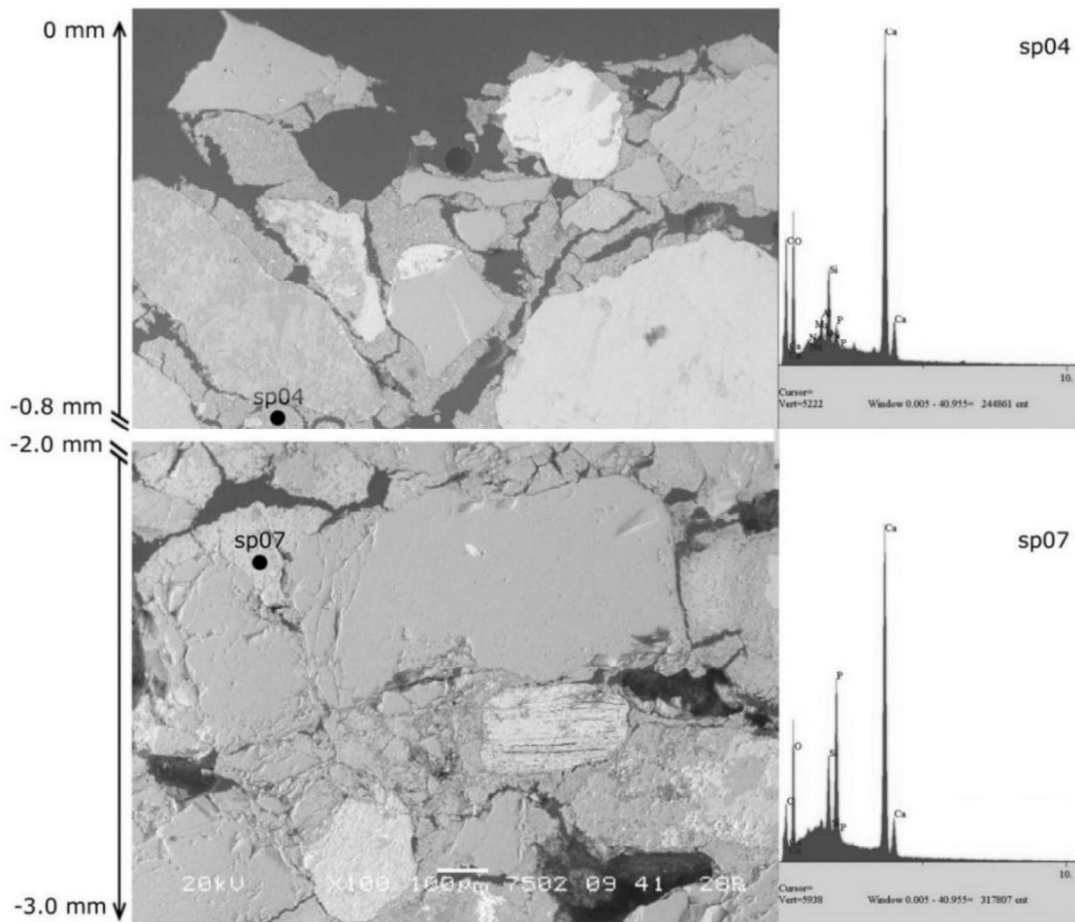


Figure 3. SEM/BSE images (left) and EDS P-mapping (right) of specimen cross-sections at different depth for randomly selected 3.0 M DAP treatments and untreated specimen.



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Figure 4. SEM/BSE images and EDS spectra: influence of aggregate presence on P distribution: the low P level of binder in the area sp04 placed directly underneath the large aggregate clast (green colour) testify the “umbrella” effect caused by its “overhead” position. The P peak in sp07 area is very high despite its deeper location.

### 3.5. Colour change

The colour change assessment was considered as a particularly important step of this examination, allowing to distinguish the eventual differences between the applied DAP solution (and subsequent selective limewater application) as well as the eventual chromatic alteration caused by the treatment. The quantitative values of the outcomes are displayed in Table 5. The proper evaluation of colour alteration in cultural heritage conservation field poses a lot of difficulties, mainly deriving from the ambiguous guidelines allowing for its relevant acceptance limitations. Despite the fact that the standard CIEL\*a\*b\* system clearly specifies the colour differences in reference to the  $\Delta E$  value indicating that in the range of  $3.5 > \Delta E > 2$  the colour deviation is visible for inexperienced observers while for  $\Delta E > 3.5$  the clear divergence of colour is noted [46], significant number of publications refer to  $\Delta E = 5$  as an upper limitation in cultural heritage conservation field [18], [24], [34], [51], [63]–[67]. The explanation of this premise originates from CIEL\*a\*b\* denotation of such value being a threshold of recognition for two separate colours [46]. Some attempt leading to the proper categorisation of  $\Delta E$  values for materials and operations used in cultural heritage conservation field was proposed by Rodrigues [68] suggesting - in case of consolidants - the usage of  $\Delta E$  rating in terms of the incompatibility risk between pre- and post-consolidation visual surface appearance. The proposed scale divided  $\Delta E$  value referring to “low risk” in case of  $0 \div 3$  limitation, “medium risk” for  $3 \div 5$  range placement and “high risk” for  $> 5$  results. Considering the fact that in case of historic mortars superficial decoration presence is particularly ubiquitous, it is essential to evaluate the outcomes of this examination respecting the proposed “low risk” limitation minimizing the occurrence of mismatch with the original surface’s appearance, hence acknowledging  $\Delta E = 3$  as a threshold of acceptance.

As far as the outcomes of this test are concerned, the spread of  $\Delta E$  values is ranged in  $2.0 \div 4.3$ , while relatively high deviations of  $\Delta E$  may be explained by the inhomogeneous characteristics of the mortar surface. The  $\Delta E = 3$  limitation is fulfilled by four treatment modalities (average values), excluding 2.0 M DAP + limewater application ( $\Delta E = 3.68$ ) and 3.0 M DAP application ( $\Delta E = 4.34$ ) which results were placed beyond this threshold. Considering this outcome, it is evident that the treatment is not linearly dependent on the increase of DAP molarity nor post-limewater application, and secondly that approximately 30% of treated surfaces pose a high risk of visual effects. Subsequent analysis of  $\Delta L$  value attributed to the lightness of the surface (ranging in  $0 \div 100$ , where 0 corresponds to black and 100 is the maximum possible to obtain intensity without causing eye damage) allows to indicate the slight darkening of every surface subjected to treatment (without noted dependency towards DAP solution molarity applied). Further chroma ( $\Delta C$ ) calculation defined as the distance of the same points characterized only by  $a^*$  and  $b^*$  values, specifying the change of colourfulness balance revealed the distinguishable post-treatment saturation diminishing, following the general premise that the  $\Delta C < 0$  corresponds to colour desaturation, while  $\Delta C > 0$  reflects its increase. Taking into account the above considerations it is possible to specify the superficial colour alteration as a slight darkening and intensity diminution, in c.a. 30% of specimens posing a medium risk for visual incompatibility occurrence. Previous studies on DAP treatment influence on colour darkening/lightening displayed rather dispersed results,  $\Delta L$  ranging from  $-2.0$  to  $+2.1$  with no visible relation towards treatment procedure [23], [24], [37]. For that reason, the unequivocal conclusion regarding this matter cannot be stated and further studies regarding only this issue are strongly advised.

Table 5. Average results of colour measurements for each treatment modality, calculated from 5 measurements on each surface.

Specimen	Average values										
	Before DAP treatment				After DAP treatment				$\Delta E$	$\Delta L$	$\Delta C$
	L	a	b	C	L	a	b	C			
2.0	81.31	0.48	5.83	5.85	78.90	0.47	4.91	4.93	2.78	-2.41	-0.92
2.0L	80.28	0.58	5.78	5.81	77.04	0.58	5.16	5.20	3.68	-3.25	-0.61
3.0	81.42	0.50	5.40	5.42	77.17	0.51	4.50	4.53	4.34	-4.24	-0.89
3.0L	77.47	0.73	8.02	8.05	75.65	0.85	6.64	6.69	2.38	-1.82	-1.36
3.7	78.87	0.74	7.99	8.02	77.35	0.83	6.48	6.54	2.83	-1.52	-1.49
3.7L	78.15	0.69	7.99	8.02	76.68	0.80	6.65	6.70	2.06	-1.48	-1.32

### 3.6. Water absorption change

In the water absorption by capillarity test, both treated and non-treated specimens obtained an asymptotic value between 20 minutes and 1 hour of testing time, indicating the material's capability of water absorption for that time that equalled c.a. 11 grams of absorbed water (Figure 5). As regards the linear increase of water uptake before achieving asymptotic values, there are no significant differences between both types of specimens, i.e. treated and non-treated. It is essential to point out that in case of treated specimens, the values of water absorption within the first 15 minutes do not vary, hence it may be assumed that the applied treatment methodology (i.e. concentration of DAP applied and subsequent limewater application) does not influence the final outcome. Water absorption rate and IC index for each specimen is presented in the table below (Table 6). The direct observation of the displayed data indicate that the overall water absorption rate is approximately 5% lower for treated specimens, without any significant differences towards the application mode.

The outcomes of the water absorption test indicate no significant change in the pore structure after the treatment. The fact that there is no measurable difference in sorptivity after consolidation is regarded as a positive feature.

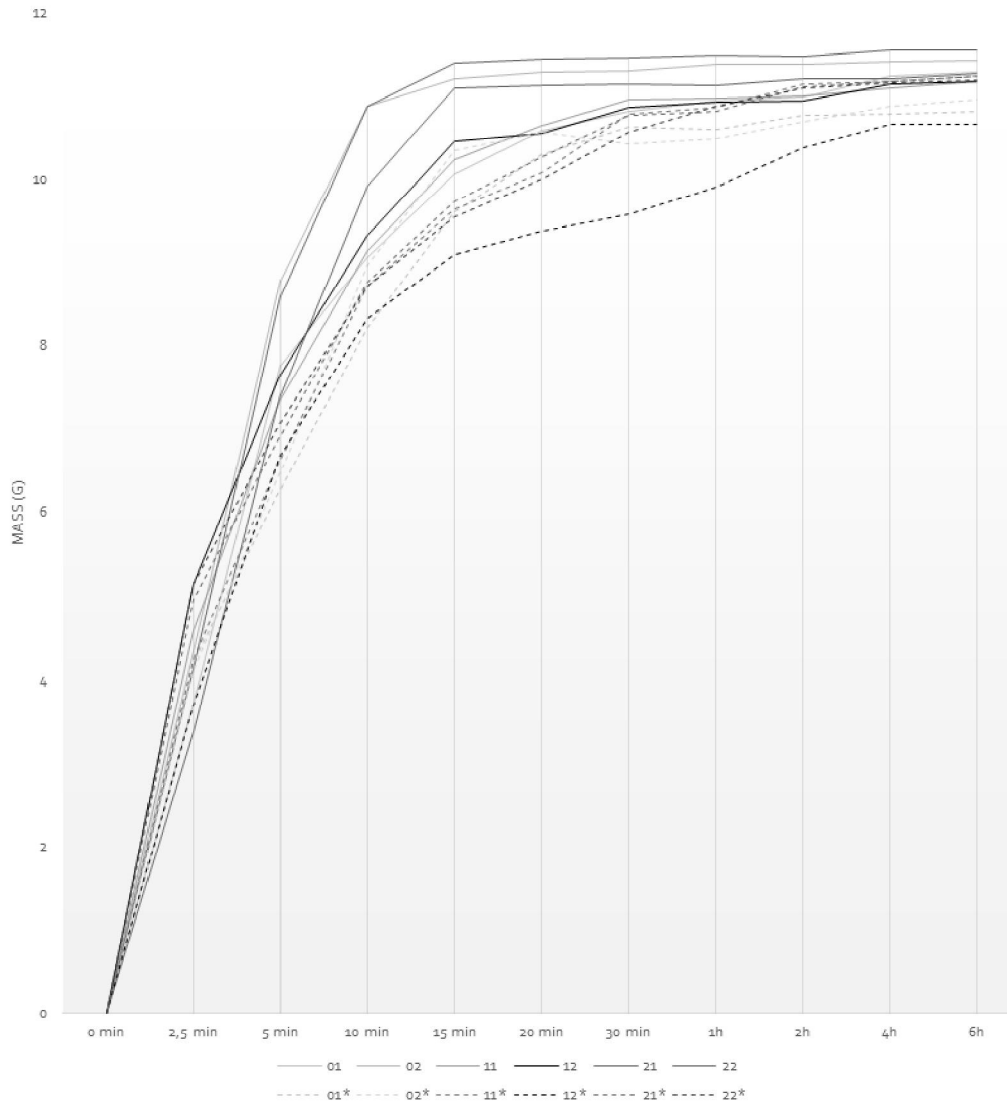


Figure 5. Water absorption change expressed by mass change in time. 01\* - 2.0 M DAP + limewater; 02\* - 2.0 M DAP; 11\* - 3.0 M DAP + limewater; 12\* - 3.0 M DAP; 21\* - 3.7 M DAP + limewater; 22\* - 3.7 M DAP. The 01, 02, 11, 12, 21, 22 indications correspond to non-treated specimens.

Table 6. Amount of water absorbed by capillarity per surface unit (Q) and absolute capillary index (IC) for each specimen before and after the treatment.

Specimen		Absorption	
		Q (mg/cm <sup>2</sup> )	IC
Non-treated	2.0	457.07	2.76
	2.0L	451.49	2.75
	3.0	447.38	2.76
	3.0L	447.46	2.76
	3.7	462.28	2.76
	3.7L	450.68	2.76

Treated	2.0	438.65	2.75
	2.0L	432.68	2.76
	3.0	426.75	2.75
	3.0L	449.92	2.75
	3.7	447.88	2.76
	3.7L	449.70	2.76

#### 4. Conclusions

The research presented in this paper provides a preliminary evaluation of the DAP consolidation of lime-based mortars perceived for cultural heritage conservation including the preliminary testing of treatment's effectiveness and compatibility in relation to the subjected application method.

Based on the results the conclusions are as follows:

- The presence of newly-precipitated phases was confirmed by post-treatment dry weight increase and SEM/EDS analysis detecting P within binder. DAP molarity did not influenced P presence, which was detected along the whole depth of treated specimens (i.e. 1 cm) without any gradual decrease, possibly because of the great mortar porosity and the use of poultice as application method. Subsequent limewater application uniformed P distribution in the binder, presumably due to the secondary reaction of limewater with unreacted DAP present in the matrix. P level was not affected nor by DAP molarity neither by limewater application, yet its value strongly depends on the position of binder fragments towards large aggregate clasts that create an "umbrella" effect – beneath them P level is usually drastically decreased.
- The effectiveness of the treatment, i.e. the consolidation effect was confirmed by UPV and peeling test outcomes. Substantial increase of mechanical properties was displayed in the doubling  $E_d$  modulus value (in vertical arrangement of transducers) and improvement of cohesion qualities was indicated by at least 35% lower material loss due to the peeling test. No relation towards treatment modality (i.e. DAP solution molarity and post-limewater application) was observed. The increase of UPV values in general indicated the consolidation effect and confirmed its correlation to Ca-P phases' crystallization. Due to the achievement of high post-treatment  $E_d$  values it is advised to undertake further in-depth analysis regarding mortar overstrengthening.
- All of the acquired treatments caused some non-negligible colour change – c.a. 30% of outcomes are considered as beyond the adapted threshold of acceptance (i.e.  $\Delta E > 3$ ).
- Further evaluation of water capillary absorption exhibited substantial similarities towards untreated references, demonstrating post-treatment hydrophilicity, considered as a preferable state after the consolidation that did not changed drastically initial features. Slight decrease of post-treatment water absorption rate (not related to treatment modality) is considered as well as a positive feature due to the lesser water amount uptake by consolidated mortar.

The results highlight no substantial disparities in effectiveness and compatibility for different DAP concentrations. With the limewater post-treatment, only moderately higher uniformity in P distribution was obtained. Given the above outcomes, in case of the application methodology based on 24 hours'



1 DAP poultice attachment with subsequent 24 hours' deionized water poultice use, the treatment  
2 modality may be limited to the method using the lowest quantity of chemical, i.e. 2.0 M DAP, which  
3 is expected to bring out satisfactory results. The use of lower DAP molarity can be as well considered  
4 as a positive aspect in order to minimize the risk of a possible microbe attack, as it offers less  
5 ammonium salts accumulation inside the mortar that may originate from the presence of unreacted  
6 DAP. To furtherly avoid this possible problem, scrupulous post-treatment surface washing with de-  
7 ionized water is essential, alternatively proceeded by limewater application boosting secondary  
8 reaction of calcium ions with remained DAP residue.  
9

10 Given the results indicated in this paper, a consolidation of mortars with the use of DAP can be  
11 considered as a highly promising method in terms of effectiveness and compatibility, while the main  
12 factor of treatment's optimization shall be focalized on the minimalization of the negative colour  
13 alteration, possible uniformization of Ca-P phases distribution and overstrengthening effect  
14 assessment. In order to fully characterize the potential of this consolidation method, it is essential to  
15 evaluate its further behaviour on the mortar surfaces previously subjected to accelerated ageing tests  
16 thus assessing its impact on the highly degraded surfaces, posing an actual urge for an intervention.  
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