# AN INNOVATIVE PHOSPHATE-BASED CONSOLIDANT FOR LIMESTONE. PART 1: EFFECTIVENESS AND COMPATIBILITY IN COMPARISON WITH ETHYL SILICATE

Enrico Sassoni<sup>\*</sup>, Gabriela Graziani, Elisa Franzoni

Department of Civil, Chemical, Environmental and Materials Engineering (DICAM), University of Bologna, Via Terracini 28, 40131, Bologna (Italy)

\* Corresponding Author

Tel: +39 051 2090363, Fax: +39 051 2090322, e-mail: enrico.sassoni2@unibo.it

### ABSTRACT

For consolidation of weathered carbonate materials (such as marble, limestone and lime-based mortars) no fully satisfactory treatment currently exists. In this paper, an innovative phosphate treatment was investigated as a possible consolidant for limestone and compared with a commercial ethyl silicate (ES). The two treatments were evaluated in terms of effectiveness (i.e., ability to restore cohesion and mechanical properties, by measuring penetration depth, dynamic elastic modulus, tensile strength, resistance to abrasion) and compatibility (i.e. lack of any negative consequence on the original substrate, by assessing mechanical match, colour change, new phases composition, pore size distribution, water and water vapour transport properties, drying rate and thermal behaviour). The phosphate treatment proved to be very promising, being able to overcome some ES limitations.

# **KEYWORDS**

Hydroxyapatite; Tetraethylortosilicate; TEOS; Ammonium phosphate; Inorganic consolidants; Penetration depth

# 1. INTRODUCTION

Porous materials used in historic and modern buildings, such as natural stones, bricks and mortars, are exposed to weathering processes (e.g., salt crystallization [1,2], freeze-thaw cycles [3], dissolution of soluble fractions [4]) that seriously threaten their durability. Due to weathering, these materials undergo progressive alterations in microstructural and physical properties (namely increases in open porosity, water absorption and sorptivity), that generally result in a decrease in mechanical properties [5,6]. As a consequence, especially in the case of historic buildings belonging to Cultural Heritage, it has become common practice to apply consolidants (i.e., products that penetrate deep enough into the weathered material to bind loose grains, improve their cohesion and adhesion to the sound substrate [7-11]) and/or repair mortars (i.e., mortars used for filling cracks or replicating lacking parts [12]).

Consolidants are usually distinguished in organic products (mainly acrylic and epoxy resins) and inorganic products (mainly alkoxysilanes, lime-based and barium hydroxide-based) [7-9,13]. Organic consolidants have been found to be in general scarcely compatible with the inorganic substrates and affected by low durability [14,15], hence research has recently mainly focused on inorganic consolidants. Among these latter, ethyl silicate (ES) has proved to be a rather satisfactory consolidating product for silicate materials, such as quartzitic sandstones and bricks [16,17], thanks to its ability of chemically bonding to the substrate and thanks to its stability. On the contrary, in the case of carbonate materials, such as marble, limestone, calcareous sandstone and lime-based mortars, no fully satisfactory consolidating treatments are currently available. Indeed, ES is less effective on carbonate materials, because in this case only physical-mechanical bonding to the substrate takes place [16], while lime-based consolidants, although compatible with carbonate substrates, are generally affected by low efficacy, low penetration depth and slow carbonation [18]. As a result, ES is currently the most widely used consolidant also for carbonate stones, in spite of its limited efficacy on this kind of substrate, mainly due to the lack of more suitable and effective alternatives [19].

A potentially good alternative to ES for carbonate stone consolidation is an innovative phosphate-based treatment that has recently been proposed [18]. The core idea is that stone can be consolidated thanks to the formation of hydroxyapatite (HAP,  $Ca_{10}(PO_4)_6(OH)_2$ ) inside pores and micro-cracks between grains. HAP can be formed from the reaction between  $Ca^{2+}$  ions coming from dissolution of calcite grains and  $PO_4^{3-}$  ions coming from an aqueous solution of diammonium hydrogen phosphate (DAP), that is the product with which stone is impregnated [18]. With respect to existing commercial consolidants, the HAP-treatment is highly innovative for several reasons: (i)

the product with which stone is impregnated (the aqueous DAP solution, free from any organic solvent) has viscosity similar to that of water and contains no particles (not even at the nano-scale), hence it is able to overcome limitations in penetration depth and effectiveness often exhibited by existing consolidants, e.g. nano-limes [20]; (ii) the binding mineral that forms from the reaction between DAP and the calcitic substrate (HAP) is expected to bond chemically to the stone [21], thus overcoming limitations exhibited by existing consolidants that bond to carbonate stones only physically-mechanically, such as ethyl silicate [16]; (iii) HAP is expected to be highly compatible with calcite, thanks to the similarity in crystal structure and lattice parameters between the two minerals, and also highly durable, thanks to its very low solubility and very slow dissolution rate [18,21]; (iv) the treatment causes no dramatic pore occlusion [18]. For these reasons, in the last few years several studies have been aimed at developing the HAP-treatment for consolidation of porous stones with different mineralogical composition and porosity [22-26] and for protection of marble against dissolution in acid environment [21,27,28], in both cases giving promising results.

In particular, previous papers by the authors and other groups were mainly aimed at optimizing the treatment conditions, so as to favour HAP formation and enhance the treatment efficacy. Several different methods to boost HAP formation have been proposed (e.g., use of different phosphate salts, cationic additions, pH control, limewater poultice application, etc.) and research is currently still progress [18,21-28]. The cited studies mainly focussed on specific aspects, such as composition of the new calcium phosphate phases, mechanical improvement and alterations in water transport properties. However, no comprehensive laboratory study on the treatment effectiveness, compatibility and durability has been reported yet, to the authors' best knowledge.

Therefore, in the present study the first attempt to evaluate the performance of the HAPtreatment from a 360-degree perspective is presented, comprising *all* the main requirements that stone consolidants must fulfil (namely, effectiveness, compatibility and durability). For the HAPtreatment, the parameters and application procedure recently proposed by the authors in [23] were adopted. Even if HAP-treatment conditions may be optimized in the future and hence be changed with respect to those adopted in the present study, still a comprehensive evaluation of the treatment performance at the present state of research, at least in laboratory conditions, is of fundamental importance. The obtained results are expected also to provide essential inputs for further treatment optimization and improvement. For example, unsatisfactory findings on the HAP-treatment durability might even result in the need of substantially modifying the treatment parameters.

The study is articulated in two parts: Part 1 (the present paper), dealing with the HAPtreatment effectiveness and compatibility, and Part 2 [29], dealing with durability. Moreover, to evaluate whether the HAP-treatment can actually be considered as a promising alternative to ES for

consolidation of porous limestone, all the tests were carried out also on ES-treated samples and results obtained for the two consolidants were systematically compared.

Although relatively easy in principle, achieving the research objectives describe above is more challenging than it seems. Firstly, this is because each of the previously mentioned requirements is a complex and articulated concept, as summarized in the following [16,30-32]:

- 1. <u>*Effectiveness*</u>. The consolidant must be able to penetrate homogenously deep into the stone, so as to reach the unweathered substrate, and to induce mechanical improvement of the treated stone, so that stone resistance to weathering processes is enhanced [7,8,30].
- 2. *Compatibility*. The newly introduced materials must not have negative consequences on the original substrate, in a broad sense [33]. Firstly, the treatment must cause neither short-term or long-term alterations of stone aesthetical aspect, such as darkening, colour change or wet appearance [30,32]. Moreover, the consolidant must not give rise to formation of by-products harmful for the stone [8,30] or evaporation of toxic components dangerous for human health [16]. In terms of microstructural and physical properties of the stone, some reduction in open porosity and water sorptivity is to be expected or may even be desirable [19,30]. However, consolidants that clog pores and/or dramatically alter stone transport properties should be avoided, because, in case liquid water and water vapour are blocked behind the treated layer, exfoliation of stone might occur, when the trapped water is subject to freezing or soluble salt crystallization [7,8,16,34]. For these reasons, the water vapour permeability of stone must be preserved, to allow it to "breathe", and the drying rate of treated stone should be altered as little as possible, to reduce the risk of treatment failure [19,30]. Furthermore, the consolidating treatment should induce a gradual variation in stone properties with depth, so that no superficial hard crust is formed after treatment but a gradual transition is assured [7,8]. Finally, the thermal expansion coefficient of the consolidant must be similar to that of the treated stone, so as to avoid possible damage induced by a mismatch in thermal behaviour [7,30].
- 3. <u>*Durability*</u>. The consolidant effectiveness should not be lost as a consequence of exposure to environmental weathering processes and the consolidant itself must not give rise to harmful products as a consequence of ageing [8].

According to conservation principles, a further requirement of stone consolidants is reversibility, i.e. it should be possible to undo a consolidation treatment at some future date [7,16]. However, this is not feasible in practice for stone consolidants, apart from thermoplastic organic resins by dissolution in solvents. Even in this latter case, it is however unlikely that the consolidant is completely removed from stone pores and the treated stone would likely be damaged by

consolidant removal [30]. Consequently, stone consolidants are usually required to be at least retreatable, i.e. it should be possible to re-treat the stone with either the same or a different consolidant in the future [16].

A further reason that makes it a very challenging task to evaluate the effectiveness, compatibility and durability of a consolidant is that it is not univocally defined what parameters should be tested and what test results should be considered as successful. Some useful indications have been provided by RILEM Tentative Recommendations [35] and by Italian "Istituto Centrale per il Restauro" (Central Institute for Restoration) [30]. However, depending on the reference source, different indications about the parameters to be tested and about the level of modification that should be achieved may be found. For instance, in the case of mechanical effectiveness, up to a dozen of different mechanical parameters have been suggested by different sources [8,30,36] and different indications about the outcome that should be achieved have been reported [19,30].

Therefore, in the present study the reasons behind the selection of each microstructural, physical and mechanical parameter to be tested have been reported and discussed. In this way, the characterization protocol followed in this study, although surely not exhaustive and surely improvable by addition of complementary tests (e.g., MDR, SEM, etc.), could be of use also for other researchers for a more conscious selection of test parameters and methods.

In detail, Part 1 of the study is mainly focused on HAP-treatment effectiveness and compatibility (some indirect considerations on retreatability and impact on human health and environment have been reported as well, based on experimental results and literature data). Part 2 [29] is focused on the HAP-treatment durability, intended both in the strict sense (i.e., permanence in time of the consolidating action) and in a wider sense, comprising possible compatibility issues that may arise when treated stone is subjected to environmental weathering processes (e.g., incompatibility occurring between the consolidated layer and the unconsolidated substrate).

# 2. MATERIALS AND METHODS

#### **2.1.** Stone

The stone used for the tests was Globigerina limestone, the lithotype typically used in historical architecture in Malta and subject to intense weathering processes, such as alveolization, flaking and powdering [37]. In Figure 1, an example of Globigerina limestone use in Baroque architecture in La Valletta (Malta) is illustrated, alongside some details of severely weathered architectural elements. Consolidation of Globigerina limestone is a very urgent task, which has led through the years to the

investigation of many possible treatments, including ES, ammonium oxalate and ammonium phosphate [23,38,39].

For the present study, a slab of Globigerina limestone ("Franka" variety [23]) quarried in the area of Qrendi and provided by Xelini Skip Hire and High-Up Service (Malta) was used. The stone has a carbonate content of ~93 wt.% (owing to calcite crystals and fossils, bonded by calcareous cement) and it also contains traces of quartz and possibly clays [6,40]. The microstructure of the stone is characterized by very high open porosity (~40%), mainly owing to pores with radius ~2  $\mu$ m, which leads to very high sorptivity (~15 mg/(cm<sup>2</sup> · s<sup>0.5</sup>)) [6,40]. Cubic samples (5 cm side) and prismatic samples (7×7×2.5 cm<sup>3</sup>) were sawn from the slab, parallel to the bedding planes, while cylindrical samples (5 cm height, 2 cm diameter) were core-drilled perpendicular to the bedding planes.

To evaluate the effects of the two consolidating treatments, all the samples (including reference untreated samples, labelled as "UNTR") were preliminarily artificially weathered, as recommended by Italian Recommendation NORMAL 20/85 [30]. According to a methodology previously developed by the authors, artificial weathering was performed by heating samples at 400 °C for 1 hour [6,18,40]. Compared to other alternative artificial weathering methods (salt crystallization cycles, freeze-thaw cycles, acid attack, mechanical pre-stress, etc.), heating was found to have both advantages and disadvantages. Among pros, heating is an easily controllable method for inducing homogenous porosity alterations in the entire volume and reproducible mechanical deterioration, which allows to use heated samples as fairly representative of the characteristics of damaged stone [6]. At the same time, samples artificially weathered by heating have the limitation of not exhibiting an interface between a damaged surface layer and an undamaged substrate, as would be the case in the field, but result entirely weathered. Heating also has the advantage of providing samples free from salt contamination [41]. Even if salt contamination is more representative of the real condition in the field and surely needs to be considered before any result obtained in laboratory is tentatively transported into the on-site practice, still it makes the evaluation of a consolidant performance definitely more complicated. For this reason, it was not considered in the present study, but it will be taken into account in a future step of research on HAP.

#### 2.2. Consolidating treatments

Both treatments were applied by brushing 10 times, waiting about 2 minutes between each brush stroke. Brushing was preferred over other application methods because this is generally the most frequently adopted technique in the field [23,36]. As for the number of brushing applications,

commercial products technical data sheet usually recommend application until apparent refusal. However, for very porous stones, such as Globigerina limestone, this may require a very high number of applications (as much as 35 applications are needed to saturate a 5 cm side cube of Globigerina limestone). As this is unlikely to be carried out in the field, for technical and economic reasons, a lower number of brushing applications is usually performed in the practice [42]. Previous studies carried out by the authors, to assess the influence of different application methods on consolidants effects, have pointed out brushing 10 times as the most suitable application method for both the DAP solution [23] and the specific ES product [43] (at least among the methods tested in the cited studies). Indeed, this method is able to combine actual feasibility in the field with good penetration depth and non-dramatic pore occlusion.

Cylindrical samples were treated on the whole external surface, while cubic and prismatic samples were treated on one single face, perpendicular to the bedding planes. In this way, cylindrical samples (being almost entirely saturated with the consolidants) allowed to study the properties of the consolidated layer alone, while cubes and prisms allowed to study properties transition from the treated layer to the untreated substrate.

## 2.2.1. Phosphate treatment

According to the method proposed in [23], a two-step treatment was performed.

The first step consisted in making calcite in the stone react with an aqueous solution of diammonium hydrogen phosphate (DAP), according to the chemical reaction [18]:

$$10CaCO_3 + 5(NH_4)_2HPO_4 \rightarrow Ca_{10}(PO_4,CO_3)_6(OH,CO_3)_2 + 5(NH_4)_2CO_3 + 3CO_2 + 2H_2O_3$$

where  $PO_4^{3-}$  and  $OH^-$  can be partially replaced by  $CO_3^{2-}$ . DAP (Sigma-Aldrich, reagent grade) and deionized water were used to prepare a 3.0 M DAP aqueous solution. This concentration (close to saturation at room temperature) was selected because the higher the DAP concentration, the more calcium phosphate phases are formed after reaction with calcite. Indeed, only a small percentage of phosphate ions coming from DAP dissolution are available as  $PO_4^{3-}$  to form HAP (the largest part being  $HPO_4^{2-}$  and secondarily  $H_2PO_4^{--}$ ) [21], so that high amounts of DAP are necessary to form small quantities of HAP. The DAP solution was applied by brushing and, at the end of the treatment, the samples were wrapped in a plastic film to prevent evaporation. After 48 hours, the samples were unwrapped, rinsed with de-ionized water and dried in an oven at 40 °C until constant weight (about 2-3 days).

Treatment with DAP solution alone however has two drawbacks: (i) not only HAP, but also other metastable calcium phosphate phases are formed [18]; (ii) small unreacted phosphate fractions remain in the stone [44]. To overcome these drawbacks, different strategies have been proposed and

currently are still under investigation, such as providing additional calcium sources, controlling the DAP solution pH and applying a limewater poultice as a second step [21,23]. In the present study, this latter method was followed.

The second step of the treatment hence consisted in applying a limewater poultice onto the treated surface of the samples (a sheet of filter paper being inserted between the sample and the poultice to avoid sticking). The limewater poultice was prepared using dry cellulose pulp (MH300 Phase, Italy) and the so-called limewater, i.e. a saturated solution of calcium hydroxide (Sigma-Aldrich, reagent grade) and de-ionized water. The weight ratio of limewater to dry cellulose pulp was 6:1. After poultice application, samples were wrapped in a plastic film for 24 hours (to avoid limewater evaporation). Afterwards, the samples were unwrapped and the poultice was left to dry in contact with the samples until constant weight (about 4-5 days in laboratory conditions, T=20±2 °C, RH=50±5%). The poultice was then removed, the samples were rinsed with de-ionized water and finally dried again in an oven at 40 °C until constant weight (about 2-3 days). When the poultice was present, samples were dried in laboratory conditions, as this acceleration might alter the migration of unreacted phosphate fractions from stone into the poultice.

Although being an additional step that complicates to a certain extent the HAP-treatment, application of limewater poultice has a two-fold beneficial effect: (i) by providing additional calcium ions and by shifting pH towards higher values (limewater having pH about 12), the limewater poultice promotes conversion of metastable phases into HAP and reaction of previously unreacted phosphate fractions to form additional HAP; (ii) during poultice drying, still unreacted phosphate fractions migrate from the stone into the poultice (in a similar way as soluble salts are transported out of the stone when desalinating poultices are applied) and finally crystallize in the poultice instead of in the stone [23].

It is noteworthy that all the reactions and mechanisms controlling HAP formation during each part of the two-step treatment are rather complex and still under investigation, to possibly further improve the treatment conditions in the future.

# 2.2.2. Silicate treatment

A commercial product was used, composed of 75 wt% ethyl silicate (40% monomers, 35% dimmers/trimers, also containing 1% dibutyltin dilaurate as catalyst) and 25 wt% white spirit (ESTEL 1000 by CTS s.r.l., Italy). The ES-based consolidant was applied by brushing and samples were left to cure for 1 month (as recommended in the product technical data sheet) in laboratory conditions (T=20±2 °C, RH=50±5%) before testing.

### **2.3.** Evaluation of the treatments

#### 2.3.1. *Effectiveness*

<u>Weight increase</u>. As recommended in [30], the increase in sample weight was measured after brushing and then again after 1 month. The weight increase was determined on the same cylindrical samples later used for mechanical tests.

<u>Penetration depth</u>. Many different methods have been proposed in the literature for determining the penetration depth of a consolidant, including cross sections observation by SEM; product specific coloration methods; FT-IR analysis performed at different depths; measurement of abrasion loss, porosity, water absorption and water vapour permeability at different depths, micro-drilling resistance (MDR) [13,36,45]. In the present study, the penetration depth of the two treatments was firstly assessed by visual observation of prismatic samples (15 mm thickness) fractured right after the end of brushing application. Moreover, after 1 month, the consolidant penetration depth was evaluated by measuring the variation with depth of (i) resistance to abrasion [9,36][9], (ii) open porosity and pore size distribution [30],(iii) newly formed phases [36], determined as described in the following.

<u>Mechanical properties</u>. Re-establishing cohesion between loose grains and hence improving mechanical properties are the fundamental tasks of any consolidant [7,8,31,36]. However, what parameters should be tested to evaluate the outcome of a consolidating treatment is not univocal. Among others, the following properties have been suggested as significant: compressive strength, tensile strength, bending strength, modulus of elasticity, ultrasonic pulse velocity, abrasion loss, surface hardness, "strength in depth" (basically corresponding to MDR), resistance to peeling [8,30,36,46]. However, the ability of some of the above-reported properties to actually highlight the grain-bonding and consolidating capacity of a consolidant is rather questionable. For instance, evaluating the increase in stone compressive strength might be scarcely significant, as this property is not as influenced by alterations in stone cohesion as other mechanical properties (e.g., tensile strength). Therefore, in the present study the following parameters were selected:

• Dynamic elastic modulus ( $E_d$ ), calculated from the ultrasonic pulse velocity (UPV) according to the formula  $E_d = \rho \times UPV^2$ , where  $\rho$  is the geometric density of the stone.  $E_d$  and UPV are often used to assess the effect of weathering and/or consolidation of natural stones, as these parameters can be non-destructively measured and provide accurate information about the presence of micro-cracks in the stone [47]. Consequently, UPV and  $E_d$  have been used in a large number of studies about degradation and consolidation of marble [22,48-50] and limestone [18,20,36,40,51,52]. In the present study,  $E_d$  was determined on 6 cylindrical samples (cf. § 2.1), by measuring the UPV along the height of the cylinder (using a Matest instrument with 55

kHz transducers) and repeating the measurement before and after consolidation. For achieving a good contact between the transducers and the samples, a rubber couplant was used. The measurement reproducibility was ensured by applying a constant 100 N load over the sample during the test.

- Tensile strength ( $\sigma_t$ ). This property is highly influenced by stone decohesion (in a similar way as resistance to peeling). Moreover, degradation processes such as salt crystallization and freezing-thawing cycles cause damage in the stone when the crystallization pressure exceeds stone tensile strength [1,16]. For this reason, the ability of a consolidant to increase stone *tensile* strength is way more important than increasing its *compressive* strength and indeed tensile strength has been selected as a key parameter for evaluating the effectiveness of consolidants in many researches [6,18,19,52]. In this study, tensile strength was determined on the same 6 cylindrical samples used for  $E_d$  measurement, by Brazilian splitting test using an Amsler-Wolpert loading machine (maximum load 10 kN) at a constant displacement rate of 4 mm/min.
- Resistance to abrasion. Consolidants are required to enhance stone resistance to pulverization [7], hence resistance to abrasion is a very relevant parameter to estimate stone cohesion and tendency to resist processes leading to pulverization [53]. This is particularly true in the case of Globigerina limestone, that in its natural environment is severely affected by wind erosion, leading to material loss down to a depth several centimetres from the original surface. Abrasion resistance was determined on duplicate prismatic samples for both untreated and treated conditions. Abrasion resistance was measured in terms of weight loss after an accelerated abrasion test, developed by modifying the PEI (Porcelain Enamel Institute) abrasion test and based on the use of steel spheres and corundum powder kept in rotatory motion over sample surface [54]. The weight loss after the abrasion test was measured on the treated surface of the slabs and then in depth, after cutting 5 mm-thick slices from the treated surface. In this way, it was possible to derive indirect information on the treatment penetration depth and on the possible formation of a hard crust in the impregnated layer [8], although not in a continuous way as for instance by MDR.

# 2.3.2. *Compatibility*

<u>Colour change</u>. To ascertain that the treatments do not lead to substantial modifications in stone aesthetic aspect [30][29], the colour change ( $\Delta E$ ) was determined using a Mercury 2000 Datacolor. The colour parameters  $L^*a^*b^*$  ( $L^*$  = black÷white;  $a^*$  = red÷green;  $b^*$  yellow÷blue) were measured on the treated face of consolidated slabs and on untreated references. The colour change was

determined according to the formula  $\Delta E = (\Delta L^{*2} + \Delta a^{*2} + \Delta b^{*2})^{1/2}$ . For each treatment condition, the average for 3 measurements was considered.

<u>Newly formed phases and secondary by-products</u>. The nature of phases formed after the treatment, as well as the possible formation of by-products that could damage the stone [30], was determined by Fourier transform infrared spectroscopy (FT-IR), using a Perkin Elmer Spectrum One and the KBr pellets method. FT-IR analysis was performed on powdered samples obtained from the cylinders used for mechanical tests. FT-IR analysis was repeated at different depths (0-5 mm and 5-10 mm) from the treated surface, so that an indication of treatment penetration depth could also be obtained. In the case of HAP-samples, the possible presence of metastable calcium phosphate phases was investigated by performing liquid ion chromatography using a Dionex ICS 1000). HAP-samples were ground, then soluble phases were extracted by using boiling de-ionized water and filtering.

<u>*Microstructure*</u>. The variations in open porosity and pore size distribution after the treatment were evaluated by mercury intrusion porosimetry (MIP), using a Fisons Macropore Unit 120 and a Porosimeter 2000 Carlo Erba. MIP analysis was performed on samples obtained by chisel from cylinders used for mechanical tests and from cubes. As recommended by Italian Recommendation NORMAL 20/85 [30], for each consolidant MIP was performed on samples coming from different depths from the treated surface (0-5 and 5-10 mm for the cylinders, 0-5, 5-10 and 10-15 mm for the cubes), so that a further indication of treatment penetration depth and microstructure modification with depth was derived [8]. For each treatment condition and each depth, a single sample was analyzed by MIP. One sample was considered as sufficient, as preliminary tests aimed at evaluating the variability of MIP results on samples obtained from different points of the same slab of Globigerina limestone (like in this study) exhibited limited variability (*C.o.V.* = 5% [40]).

Contact angle and time for absorption. The modification in stone hydrophilic behaviour, after 1 month curing, was evaluated in terms of contact angle ( $\alpha$ ) and time for absorption ( $t_a$ ). These parameters were measured by a Contact Angle Measuring device DSA30 – Krüss GmbH. The test was carried out by releasing a 4 µl drop of de-ionized water on the treated face of dry prismatic samples and recording its absorption into the stone. For each treatment condition, the average for 3 measurements was considered.

<u>Water sorptivity and water absorption</u>. To ascertain the effect of the treatments on water transport properties [30], water sorptivity and absorption coefficient (AC) of untreated and treated samples were determined on duplicate cubic samples according to EN 15801 [55]. Water was allowed to penetrate the samples through the treated face and rise parallel to the bedding planes, which corresponds to the situation that would be experienced in the field, where stones are usually

placed with the bedding planes horizontal (to exploit stone maximum compressive strength) and hence roughly parallel to wind-driven rain. The amount of water absorbed by capillarity into the samples after 24 hours ( $WA_{24h}$ ) and 7 days ( $WA_{7d}$ ) were also measured.

<u>Water vapour permeability</u>. The alteration in water vapour permeability after treatment was evaluated by measuring the water vapour diffusion resistance coefficient ( $\mu$ ) according to EN 15803 [56]. The test was carried out using a saturated aqueous solution of KNO<sub>3</sub> and allowing water vapour flow through the treated face of prismatic slabs.

<u>Drying rate</u>. The alteration in the rate of water evaporation form untreated and treated samples was measured according to the method reported in [35]. The weight decrease of initially water-saturated prismatic slabs was measured over time in laboratory conditions (T=20±2 °C, RH=50±5%). Water was let evaporate through only a single squared face of the prism (the other faces being sealed with a vapour-proof tape), so as to achieve one-dimensional evaporation.

*Thermal behaviour*. The thermal behaviour of untreated and treated stone was assessed by measuring the maximum strain ( $\varepsilon_{max}$ ), residual strain ( $\varepsilon_{res}$ ) and thermal expansion coefficient ( $\alpha_t$ ) of samples subjected to thermal cycles, by using a dilatometer L75/30/C/W Ceramic Instruments with computerized management system. Prismatic samples with 5 × 5 × 25 mm<sup>3</sup> dimensions, obtained in the direction perpendicular to stone bedding planes, were used. Each sample was subjected to a 25-80-25 °C heating-cooling cycle, temperature being increased/decreased with a rate of 1°C/min and maximum temperature being maintained for 1 hour. These conditions were selected to simulate temperature excursions comparable to those naturally occurring in the field [57]. The thermal expansion coefficient was calculated as the slope of the linear part of the thermal strain/temperature graph, between 30 and 80 °C.

# 2.3.3. Qualitative evaluation of additional requirements

The retreatability of the two tested consolidants, as well as their impact on human health and environment, were not investigated experimentally, as these aspects were beyond the scope of this paper. However, some preliminary indications were derived from the obtained experimental results and available literature data.

# 3. **RESULTS AND DISCUSSION**

For each investigated property, the experimental results obtained for the phosphate and silicate consolidants are firstly reported and discussed, then they are compared with the thresholds/limits available in the literature, so that pros and cons of both tested consolidants can be highlighted.

### **3.1.** Effectiveness

Weight increase. According to [30], a weight increase is positive even though not necessarily representative of consolidation efficacy. Weight increases after HAP and ES treatments are reported in Table 1. Cylinders and cubes weighed just at the end of 10 brushing applications exhibited specific product uptakes quite similar among each other, although rather different between HAP  $(1.43-1.47 \text{ kg/m}^2)$  and ES  $(0.77-0.95 \text{ kg/m}^2)$ . This can be ascribed to the differences in the two impregnating solutions (DAP and ES), in terms of density, viscosity, presence of volatile solvent, etc. Notably, even if cylinders and cubes exhibited comparable specific weight increases, their degree of saturation is remarkably different. In the case of HAP, cylinders exhibited a percentage weight increase (17.3 wt%) very close to full saturation with water (17.1 wt%, cf. § 3.2), which suggests that the DAP solution was able to fill basically all the accessible pores. Differently, cubes exhibited a percentage weight increase definitely far from saturation (1.7 wt%). In the case of ES, slightly lower values were registered, but a similar difference in the degree of saturation of cylinders and cubes is present. Considering this difference in the degree of saturation, cylindrical samples (almost entirely saturated with the consolidants) can be used to study the properties of the consolidated layer alone, while cubes (comprising both a consolidated and an unconsolidated part) can be used to study properties transition from the treated layer to the untreated substrate. The dry mass residue after curing for 1 month, during which solvent evaporation and consolidant hardening reactions took place, was sensible different for the two treatments. In particular, the final weight increase caused by ES was sensibly higher than that owing to HAP, hence a more pronounced porosity alteration is expected for the former treatment.

<u>Penetration depth</u>. For both the DAP solution and ES, a penetration depth around 7 mm was found right at the end of the treatment (Figure 2) and a uniform penetration was observed. After curing, results of MIP and FT-IR analysis (Figures 3-4 and Figure 5, respectively, commented below) indicate that penetration depth increased to at least 10 mm for both consolidants, suggesting that consolidant further penetration and distribution in the stone took place after the end of the treatment. This is owing to the fact that consolidants are absorbed quickly into larger pores and then are gradually drained into smaller pores, which may lead to significant additional penetration [16].

A penetration depth as high as possible is usually recommended for consolidants [7,8,19,30]. Anyway, what is important is that the consolidating treatment reaches the unweathered substrate. As the level of stone deterioration in most cases is reportedly about 1-2 cm [16], the penetration depth registered for both treatments can be considered as satisfactory. Moreover, consolidants are also required to distribute in the substrate in a gradual way, so as not to create crusts or abrupt changes in mechanical properties between the impregnated layer and the underlying ones [7,30,58].

Based on results of microstructural, physical and mechanical properties variations with depth, for both consolidants no abrupt transition seems to be present, as detailed in the following.

<u>Mechanical properties</u>. Based on the results of abrasion test (Table 2), both HAP and ES resulted in significant and comparable increases in abrasion resistance, thus being equally effective in enhancing stone resistance to pulverization and decohesion. Moreover, for both treatments the resistance to abrasion at a depth of 5 mm from the surface is comprised between that of the consolidated surface and that of the underlying substrate not reached by the consolidant (for which the abrasion resistance of the untreated reference was assumed), which suggests that the consolidated layer (about 10 mm thick) did not become a "monolithic" hard crust.

In terms of dynamic elastic modulus, a remarkable consolidating effectiveness was achieved for both treatments (Table 3): increases from 11.2 GPa to 16.5 GPa for HAP and to 18.1 GPa for ES were registered. Accordingly, significant increases in tensile strength were found as well (Table 3), ES causing a higher improvement (from 2.7 MPa to 4.0 MPa) than HAP (from 2.7 MPa to 3.4 MPa).

Even if Recommendation NORMAL 20/85 [30] reports that an increase in compressive strength as high as possible should be obtained after consolidation, a "moderate" increase in mechanical properties is preferable according to other sources. For instance, some authors suggest that a tensile strength increase  $\leq +50\%$  be achieved after treatment [19,59]. In this way, the treated part is prevented from "over-strengthening", i.e. formation of a hard surface crust, with excessively high mechanical properties that may lead to mechanical mismatch between the treated part and the substrate and eventually to consolidated layer detachment. However, as in general the level of deterioration of the original stone is unknown (decay might have caused a tensile strength decrease higher or lower than 50%), an alternative approach is to consider a consolidating treatment as sufficiently effective if it is able to restore the mechanical properties of the unweathered material, without exceeding them significantly [60].

If the tensile strength increase  $\leq +50\%$  threshold is considered, both HAP- and ES-treatment could be regarded as compliant with this recommendation, as they both caused tensile strength increases below +50%. However, it should be noted that artificial weathering actually caused a 10% decrease in tensile strength and a 28% decrease in dynamic elastic modulus (Table 3). Therefore, if the criterion of re-establishing the original mechanical properties without significantly exceeding them is adopted, mechanical strengthening caused by HAP ( $\Delta\sigma_t = +27\%$  and  $\Delta E_d = +47\%$ ) seems preferable over that caused by ES ( $\Delta\sigma_t = +47\%$  and  $\Delta E_d = +61\%$ ), which might lead to some mechanical mismatch between the consolidated layer and the unweathered substrate.

The high effectiveness of the investigated ES-based product on Globigerina limestone, even if the performance of silicate consolidants is reportedly rather limited on carbonate stones, may be explained considering the characteristics of both the specific ES product and the specific substrate. As for the ES product, the presence of 25 wt.% organic solvent (white spirit) and TEOS partial prepolymerization (40% monomers and 35% dimmers/trimers, to reduce evaporation) contribute to achieving a good penetration depth. Once penetrated into the stone, ES reaction with atmospheric moisture is accelerated by the presence of 1% dibutyltin dilaurate as catalyst. The presence of the solvent also has the effect of diluting ES, so that the thickness of the formed silica gel is reduced and the risk of cracking is reduced as well [16]. As for the substrate, in addition to the physical bond between the stone and the silica gel (which however may be strong), in the case of Globigerina limestone some chemical bond (although sporadic) can take place between the silica gel and quartzitic fractions naturally present in the stone, which partially contributes to enhance the consolidating action [59].

In addition to the different mechanical improvement, a further significant difference between the two treatments is the curing time required to achieve such improvement, namely 1 month for ES [16,43] and 48 hours of DAP impregnation and 24 hours of limewater poultice application for the HAP-treatment [23]. The much shorter curing can be regarded as a first important advantage of the phosphate treatment, which however requires two treatments (brushing and poulticing) while ES only requires a single treatment.

#### 3.2. Compatibility

<u>Colour change</u>. For HAP- and ES-treated samples, colour change is illustrated in Figure 6 for three exemplificative prismatic samples, while quantitative values are reported in Table 4. ES causes a very limited modification of colour parameters, while HAP is responsible for non-negligible alterations, mainly in terms of lightness ( $L^*$  parameter). Anyway, both treatments can be considered as acceptable, as they are below the threshold generally accepted for stone consolidants ( $\Delta E \leq 5$ )[21], even if in the case of HAP the corresponding colour change is visible by human eye ( $\Delta E > 3$ ) [23].

<u>Newly formed phases and secondary by-products</u>. The DAP solution is expected to react with the substrate and lead to the formation of HAP and volatile ammonium carbonate, which is not corrosive to stone [18]. Accordingly, in the FT-IR spectra of DAP-treated samples (Figure 5) bands at 564-565 cm<sup>-1</sup> and 601-604 cm<sup>-1</sup> were detected, which are compatible with bands attributed in the literature to P-O bonds of HAP [61], while no ammonium carbonate, unreacted DAP or highly soluble metastable calcium phosphate phases were found. However, it should be noted that the

possible presence of octacalcium phosphate (OCP,  $Ca_8(HPO_4)_2(PO_4)_4 \cdot 5H_2O$ ) cannot be completely excluded based on the obtained FT-IR spectra [61]. Even if formation of exclusively HAP is desirable, as this mineral is the least soluble among calcium phosphates, still formation of OCP (more soluble than HAP but still remarkably less soluble than calcite [62]) is not expected to be detrimental to the consolidating treatment success [21]. Additional investigations (including Raman spectroscopy) are currently in progress to ascertain the possible presence of OCP [63]. The absence of highly soluble metastable calcium phosphate phases was confirmed also by ion chromatography results, that detected no soluble  $PO_4^{3-}$  ions in DAP-treated samples. This can be attributed to the effectiveness of the two-step treatment adopted for HAP formation: in the first step, consisting in DAP application,  $Ca^{2+}$  ions coming from the calcitic substrate react with  $PO_4^{3-}$  ions to form HAP; in the second step, consisting in limewater-poultice application, additional  $Ca^{2+}$  ions are supplied for making metastable calcium phosphate phases and unreacted phosphate fractions form additional HAP; then, by letting the poultice dry in contact with the samples, soluble phases are removed from the stone and transported into the poultice during drying.

In terms of compatibility, intended as the quality of not having negative consequences on the original substrate [33], HAP could be considered as fairly compatible with limestone, although not being originally present in the stone. Indeed, HAP is one of minerals (alongside calcium oxalate) that constitute the so-called patinas, that have been found to develop over the centuries on the surface of carbonate stones [64]. Such patinas (for which either a natural or an anthropic origin has been suggested [64]) have been found to provide a good protective action of the underlying stone, which can be ascribed to the compatibility in crystal structure between calcite and HAP and to the good stability over time of this latter mineral (cf. § 1). Considering their protective actions (as well as their historic value), it is nowadays usually recommended that such patinas be not removed by cleaning during restoration interventions. On the contrary, it is usually recommended they be preserved as an alteration of the substrate, not having a negative effect on its conservation [65]. Different would be the case of a gypsum crust, formed over stone surface as a product of *deterioration* of stone, having no protective action but on the contrary forming at stone expenses and causing increasing deterioration, so that it could in no way be regarded as compatible.

In the case of ES, hydrolysis-condensation reactions lead to the formation of silica gel and volatile ethanol as by-product, which is not corrosive to stone [16]. Accordingly, FT-IR spectra of ES-treated samples (Figure 5) showed a marked band at 1080 cm<sup>-1</sup>, owing to Si-O-Si groups of silica gel [66]. Moreover, a slight band at 1170 cm<sup>-1</sup> was also present, especially in the deeper sample, which can be attributed to Si-O-C groups of non-hydrolyzed ES [66], even after 1 month curing. From a chemical point of view, the formed silica gel could be regarded as similar and hence

somewhat compatible with the quartzitic fractions naturally present within Globigerina limestone (at least compared to other consolidating products totally different from natural stones, such as organic polymers). However, in terms of amount and distribution of these silicatic phases, it should be noted that the natural (crystalline) quartz particles are present in small amounts and are dispersed in the carbonate fractions, while (amorphous) silica gel is concentrated in pores, where it may locally reach relatively high concentrations. Hence, the actual compatibility (non dangerousness) of the newly formed phase should be further investigated, in terms of thermal behavior, pore occlusion, etc.

<u>Microstructure</u>. The effects of the HAP- and ES-treatments on the pore size distribution of treated samples are illustrated in Figure 3 (cylindrical samples) and Figure 4 (cubic samples), in terms of both cumulative and differential pore volume. Firstly, it can be observed that alterations induced by the treatments were much more pronounced in cylindrical samples than in cubic ones, consistently with the fact that, at the end of brushing application, cylinders were almost entirely filled with consolidating solutions, while cubes were far from saturation (Table 1). In accordance with results of abrasion tests (cf. § 3.1), MIP curves of cubic samples (Figure 4) show a gradual microstructure modification, passing from the surface layer (0-5 mm) to the underlying layer (5-10 mm) to the most internal one (10-15 mm), suggesting that no surface clogging layers were formed after treatment. For the 10-15 mm layer, curves of treated and untreated samples basically overlap, which further indicates that treatments penetration depth was about 10 mm.

In the case of cylindrical samples, almost entirely consolidated, alterations in total open porosity and volume of pores within different ranges are reported in Table 5. The ES treatment partly occluded pores, especially in the surface layer of the sample: total open porosity decreased from 37.3% (untreated reference) to 30.7% (surface of the ES-treated sample). Differently, the HAP-treatment left the total open porosity essentially unaltered, even if it caused some modifications in the pore range between 0.01 and 0.2 µm (especially in the surface layer, Figure 3).

To evaluate whether the level of alterations in open porosity and pore size distribution caused by the treatments can be considered as acceptable, different indications may be found in the literature. Some sources suggest that a moderate porosity decrease and modification in pore size could be desirable [1,19,30] as this might lead to a smaller stone susceptibility to weathering. However, consolidants that do not cause pore occlusion are often recommended [16,34], to ensure that consolidation does not result in *worsening* of stone susceptibility to weathering. Adopting an approach similar to that in the case of mechanical improvement, alterations in open porosity and pore size distribution could be considered as acceptable if they tend to bring the treated stone back to the condition before weathering (that generally causes porosity increase and pore widening).

In the case of Globigerina limestone tested in this study, artificial weathering by heating caused a remarkable decrease in mechanical properties, but still no substantial alteration in porosity and pore size distribution (presumably because thermally induced cracks were formed at the nano-scale, beyond the sensitivity of MIP [40]). Therefore, the fact stone porosity was not occluded by HAP and that ES caused a decrease limited to ~15% can be regarded as a positive feature of the investigated consolidants.

Alongside the level of alteration in total open porosity, it is extremely important to evaluate the alteration in pore size distribution, as it could exacerbate some deterioration processes. According to [30], the increase in the percentage of "small" pores (having radius  $r < 1 \mu m$ ) should be as limited as possible. From this point of view, ES, although altering the total open porosity to a larger extent, led to a reduction in the volume of pores with  $r < 1 \mu m$ , while HAP caused a small increase in the volume of this range of pores (Table 5). However, the smaller the pore size, the higher the pressure caused by salt crystallization in the pore and hence the salt-related decay [1,19]. Therefore, alterations in the amount of smallest pores detectable by MIP (e.g., pores with  $r < 0.01 \mu m$ ) should be considered as well. HAP caused an increase in this latter range of pores from 0.0% to 0.4% near the surface and to 0.1% at a depth of 5 mm. Therefore, especially in the case of ES, a possible increase in stone sensitivity to salt crystallization and freezing-thawing cycles cannot be excluded, which makes specific experimental tests necessary to deeply elucidate this aspect. The results of salt crystallization tests and freezing-thawing tests are reported in Part 2 of this study [29].

*Physical properties*. The effects of the two treatments on stone behaviour, in terms of contact angle ( $\alpha$ ) and time for water absorption ( $t_a$ ), are reported in Figure 7 and Table 6. HAP caused an increase of both parameters, but the contact angle of treated samples remained below the 90° conventional threshold between hydrophilic and hydrophobic behaviour. On the contrary, after consolidation with ES, treated stone definitely acquires a hydrophobic behaviour, as denoted by the contact angle (remarkably above the 90° threshold) and time for water absorption (largely increased with respect to the untreated reference). This hydrophobicity is caused by the presence of residual ethoxy groups (also detected by FT-IR analysis) that remain in the stone until hydrolysis-condensation reactions have completed, which may take as much as 6-7 months [16].

In accordance with contact angle results, sorptivity measured one month after the treatment results significantly different for the HAP- and ES-treatments. As illustrated in Figure 8, HAP does not significantly alter water sorptivity and water absorption (Table 6). On the contrary, ES-treated samples exhibit an initial hydrophobic behaviour: for about 24 hours since the beginning of the sorptivity test, water absorption is negligible (Figure 8). Then, water uptake sharply increases and,

after 7 days, the final water absorption is substantially similar to that of the untreated reference (Table 6). This behaviour is due to the fact that prolonged contact with water causes complete hydrolysis of residual ethoxy groups [43].

Reductions in water absorption and water sorptivity after consolidant application are regarded as positive according to some authors, as far as water vapour permeability remains unaltered [7,19,30]. However, hydrophobicity caused by stone consolidants has some drawbacks, firstly because it may lead to stone exfoliation, if some water source is present behind the consolidated layer, and also because it delays or even makes it impossible to apply water-based treatments after consolidation (e.g., application of water repellents or the so-called "*scialbatura*", i.e. application of a thin layer of coloured mortar over stone) [16]. For these reasons, according to several authors [16,22,34], consolidants that do not alter water transport properties may be preferable in the on-site practice and in some situations (e.g. northern climates) hydrophobic consolidants are actually inadvisable [16].

During the temporary hydrophobic behaviour of ES-treated stone (lasting up to 6-7 months [16]), the issues recalled above may arise. Conversely, HAP preserves stone hydrophilic behaviour at any time after the treatment and causes no substantial alteration in stone sorptivity, so it seems more compatible and hence preferable over ES. Anyway, ES-induced hydrophobicity is only temporary, hence possible methods for accelerating ES hydrolysis-condensation reactions may represent a very important advance to develop a fully ES-based compatible treatment [24,43].

In terms of water vapour permeability, which should be not blocked after consolidation so that stone is allowed to "breathe" [7,19,30], both HAP and ES gave good results. As reported in Table 6, both treatments left the water vapour diffusion resistance coefficient substantially unaltered, in compliance with the requirement of maintaining water vapour permeability as high as possible [30]. It should be noted that the performance of ES-based treatments with respect to stone breathability may change significantly depending on the specific product used: according to literature, commercial ES-based products may cause decreases up to 40% [59]. Moreover, in the case of salt crystallization, stone breathability is not sufficient for preventing damage, as a high evaporation rate may even lead to high amounts of salts deposited inside the stone [16]. This further underlines the important fact that, after consolidation, stone ability to exchange *liquid* water with the environment must be preserved. This was investigated experimentally by measuring the drying behaviour of untreated and treated samples. As illustrated in Figure 9, both treatments caused very little changes to the stone drying rate, which can be regarded as a very positive feature. However, it should be noted that the behaviour of ES-treated stone changes significantly over time as curing proceeds. For instance, as illustrated in Figure 9 for a sample treated with ES left to cured for only 1

week before the beginning of the test, the drying rate is remarkably lower, compared to ES-treated sample cured for 1 months. This may cause durability issues before curing is completed and, therefore, the durability of ES-treated samples cured for only 1 week before weathering cycles was experimentally investigated in Part 2 [29].

Thermal cycles. The thermal expansion of untreated and treated samples as a function of temperature is illustrated in Figure 10. The untreated sample exhibited a maximum thermal expansion  $\epsilon_{max} = 0.16$  mm/m, a thermal expansion coefficient of  $\alpha_t = 3.2 \times 10^{-6} \text{ °C}^{-1}$  and a residual strain  $\varepsilon_{res} = -0.02$  mm/m. The fact that, after reaching 80°C, once returned to room temperature the untreated sample exhibited a contraction is not uncommon for porous limestones. For instance, for limestones subjected to 30-80-30 °C thermal cycles residual shrinkage has been reported, which was attributed to vaporization of even firmly adherent water molecules, made possible by the slow heating rate [67]. In the case of the consolidated samples, the thermal behaviour should be as similar as possible to that of the untreated stone, in order to avoid mismatches that could lead to cracking or flaking [7,16,30]. The ES sample exhibited a behaviour very similar to the untreated reference, while in the case of the HAP sample some differences could be observed (Figure 10 and Table 6). In particular, the HAP sample exhibited a lower thermal expansion coefficient ( $\alpha_t = 1.6 \times$  $10^{-6}$  °C<sup>-1</sup>) and a higher residual strain ( $\epsilon_{res}$  = -0.05 mm/m). To evaluate whether such differences between untreated and HAP-treated samples should be considered as potentially negative for the treatment compatibility, a search was carried out in the literature about modifications in thermal behaviour of natural stones subjected to consolidating treatments. While no results were found specifically for Globigerina limestone, some useful data were found for Carrara marble consolidated with products based on ES and poly-methyl-methacrylate (PMMA) [68]. After heating to 65 °C, increases in residual strain of ~0.04 mm/m for ES and ~0.2 mm/m for PMMA were found, with respect to the untreated marble reference [68]. Such increases were regarded as "minor" and "large", respectively [68]. Considering that the above-mentioned residual strain increase of ~0.04 mm/m was regarded as "minor" in the case of Carrara marble, which is known to be very sensitive to thermal weathering [57], it seems reasonable to assume that the residual strain increase of 0.03 mm/m found in this study after consolidation with HAP can be regarded as minor as well, also considering that no particular sensitivity to thermal cycles is known for Globigerina limestone. In any case, additional tests on a larger number of samples seem opportune. Moreover, it should be also borne in mind that all the samples used in this study had been artificially weathered by heating at 400 °C before being re-heated to 80°C. Since the most severe thermal degradation is usually experienced when a certain temperature is reached for the first time, while subsequent cycles at the same temperature (or lower) have a much more limited effect [40,68], the thermal behaviour of

samples tested in this study is probably different from that of previously unheated samples. Hence, additional tests on unconsolidated and consolidated samples, preliminarily weathered by alternative methods other than heating, seem opportune as well. The possible compatibility issues related to thermal behaviour should be also specifically investigated in case the HAP-treatment is applied to marbles, for which thermal weathering is actually one of the main causes of degradation [57,69].

# 4. DISCUSSION OF ADDITIONAL REQUIREMENTS

#### 4.1. Expected retreatability

Both HAP and ES, as any other inorganic consolidant, give *irreversible* products, the stability of hydroxyapatite and silica gel formed inside the pores after treatment actually being one of the strong points of these consolidants. However, they are both *retreatable* consolidants.

The HAP-treatment, preserving stone hydrophilic behaviour and not occluding pores, allows the DAP-treated stone to be further treated with either the same consolidant or a different one. This aspect has been recently investigated in [24], where some additional benefit was registered in case of double application of DAP-solution (apparently not all the internal surface of pores had reacted after the first DAP application) and in case of DAP application followed by ES (the bond between the newly formed silica gel and the HAP-covered substrate was found to be mechanical in nature, without formation of chemical bonds). In theory, HAP-treated stone may also be re-treated with calcium carbonate-forming consolidants (e.g., lime); in this case, possible chemical bonding between the newly formed CaCO<sub>3</sub> and the HAP substrate is expected, just like epitaxial growth of HAP over calcite.

In the case of ES-treatment, the initial hydrophobic behaviour of treated stone prevents any water-based consolidant (e.g., DAP solution) to be applied for a period of at least several months. Afterwards, stone can be re-treated with consolidants (also water-based), as pores are not completely occluded.

#### **4.2.** Impact on human health and environment

Consolidants are required not to give rise to by-products or evaporation of substances that could either be hazardous for the operator's health or for the environment [16,52].

ES has a reduced toxicity and volatility with respect to other products and its reaction products (silica gel and ethanol) are harmless for human health and environment [51]. However, ES is normally applied in organic solvent (often white spirit), which can constitute up to 25% of the product in commercial formulations [58]. Organic solvents are VOCs (volatile organic compounds)

and can be toxic for human health and environment. For these reasons, many commercial products are today solvent-free [16], which however may have some drawbacks on their effectiveness. However, in general the best way to reduce the amount of VOCs is the use of consolidants applied in aqueous solution, as in the case of the HAP-treatment.

The DAP solution, being water-based and giving rise to ammonium carbonate, carbon dioxide and water as by-products, is not dangerous for the environment and the operator. According to its MSDS, there are some risks connected to the use of DAP, such as irritation to skin, eyes or breathing apparatus. However, exposure limits are not established for the operators as proper personal protective equipment is considered as sufficient to safely handle the product.

# 5. CONCLUSIONS

In this study, a systematic comparison was carried out between HAP and a commercial ESbased product for consolidation of Globigerina limestone subjected to preliminary artificial weathering. Based on the obtained results, the following conclusions can be derived:

- 1. In terms of *effectiveness*, both treatments were able to reach an adequate penetration depth (about 10 mm) and distribute uniformly in the stone. Both treatments caused a remarkable increase in mechanical properties, actually higher in the case of ES. The good performance of ES on Globigerina limestone, in spite of its carbonate composition, can be attributed to the characteristics of both the specific ES product (presence of organic solvent, presence of catalyst, TEOS partial pre-polymerization) and the specific substrate (naturally containing small amounts of quartz). Even if the mechanical improvement caused by both treatments was lower than the +50% tensile strength increase recommended by some authors as a maximum threshold to avoid "over-strengthening", still after treatment with ES stone mechanical properties resulted remarkably higher than those of the unweathered reference. This suggests that some mechanical mismatch between the consolidated layer and the unweathered substrate may take place in the case of ES. In addition to not causing "over-strengthening", the HAP-treatment also has the advantage of being effective after only 48 hours of impregnation with the DAP solution and limewater-poultice application for 24 hours, while ES requires curing for namely 1 month. However, the HAP-treatment involves 2 steps (brushing with the DAP solution and application of limewater poultice), which partly complicates on-site operations, compared to ES that only requires a single treatment.
- 2. In terms of *compatibility*, both treatments caused chromatic alterations lower than the commonly accepted threshold for stone consolidants and caused no formation of dangerous by-

products. Both treatments caused only limited alterations in total open porosity and pore size distributions, which were actually more pronounced in the case of ES (especially in terms of increase in percentage of pores with radius  $r < 0.01 \mu m$ ). Even if both treatments exhibited water capillary absorption after 7 days, water vapour permeability and drying rate substantially similar to those of untreated references, still ES is responsible for making treated stone temporarily hydrophobic, as denoted by the increase in contact angle (above the hydrophobicity threshold after 1 month curing) and the negligible water absorption for the first 24 hours of contact with water. This hydrophobic behaviour, owing to incomplete hydrolysis of ES, may last in the field for several months, during which the drying rate is sensibly reduced, risks related to water trapped behind the hydrophobic layer may arise and water-based restoration interventions are impeded. Consequently, the temporary hydrophobic behaviour of ES-treated stone constitutes a strong limitation of this consolidant. On the contrary, HAP leaves the treated stone hydrophilic at any time, hence this treatment seems preferable from the compatibility point of view.

It should be highlighted that the obtained results are valid for the specific ES-based product used in this study, while different commercial products may lead to significantly different outcomes, as a consequence of different product formulations, in terms of solvent presence, solvent type, degree of TEOS pre-polymerization, catalyst, etc.

Based on the results reported in this paper, HAP can be considered as a very promising method for consolidation of porous limestone, able to overcome limitations currently exhibited by ES in terms of effectiveness (prolonged curing time) and compatibility (temporary hydrophobicity). To fully evaluate the potential of HAP as a substitute for ES for consolidation of porous limestone, the durability of the phosphate treatment to wetting-drying, freezing-thawing and salt weathering cycles (again in comparison with ethyl silicate) was evaluated in Part 2 of this study [29].

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**Table 1.** Product absorbed after brushing 10 times and dry mass residue after curing for 1 month of cylindrical and cubic specimens (values are averages for 6 cylinders and at least 2 cubes, standard deviations in brackets).

		Product absorbed after brushing 10 times		Dry mass residue after curing for 1 month	
		Specific amount [kg/m <sup>2</sup> ]	Percentage amount [wt%]	Retained/absorbed specific amount [%]	
HAP	cylinders	1.47 (±0.02)	17.6 (±0.3)	3.4	
	cubes	1.43 (±0.01)	1.7 (±0.1)	5.2	
ES	cylinders	0.95 (±0.01)	13.7 (±0.2)	42.1	
	cubes	0.77 (±0.14)	0.9 (±0.2)	46.7	

**Table 2**. Weight loss after abrasion test, measured at a depth of 0 and 5 mm from the treated surface. Values are averages for 2 samples (difference from maximum and minimum values in brackets).

Depth	$\Delta wt [mg/mm^2]$			
	UNTR	HAP	TEOS	
0 mm	0.16 (±0.01)	0.10 (±0.03)	0.10 (±0.01)	
5 mm	0.16 (±0.01)	0.12 (±0.00)	0.11 (±0.01)	

**Table 3**. Mechanical properties, untreated and treated samples:  $E_d$  = dynamic elastic modulus;  $\sigma_t$  = tensile strength. For comparison's sake, values of unweathered samples (UNWEATH, not subjected to artificial weathering) are reported as well. Values are averages for 6 samples, standard deviations in brackets.

	UNWEAT	UNTR	НАР	ES	
$E_d$ [GPa]	15.6 (±0.3)	11.2 (±0.5)	16.5 (±0.4)	18.1 (±0.1)	
$\sigma_t$ [MPa]	3.0 (±0.3)	2.7 (±0.3)	3.4 (±0.2)	4.0 (±0.2)	

**Table 4.** Results of spectrophotometry on untreated and treated samples:  $L^* = black \div white; a^* = red \div green; b* yellow \div blue; <math>\Delta E = color change$  ( $\Delta E = 3$ : human eye detection limit**Errore.** L'origine riferimento non è stata trovata.;  $\Delta E = 5$ : threshold accepted for stones subjected to conservation treatments).

	L*	<i>a</i> *	<i>b</i> *	$\Delta E$
UNTR	72.89	9.28	18.06	-
HAP	68.92	10.81	19.39	4.45
ES	72.11	9.99	18.85	1.32

**Table 5.** Microstructural properties of untreated and treated samples, taken at a depth of 0-5 mm and 5-10 mm from the treated lateral surface of cylindrical samples: OP = open porosity; pores with  $r > 1 \mu m =$  volume of pores with radius coarser than 1  $\mu$ m/sample volume; pores with  $r < 1 \mu m =$  volume of pores with radius smaller than 1  $\mu$ m/sample volume; pores with  $r < 0.01 \mu m =$  volume of pores with radius smaller than 0.01  $\mu$ m/sample volume. By summing up the volume of pores in the various ranges, the sample total open porosity is obtained.

	OP	Pores with $r > 1 \ \mu m$	Pores with $r < 1 \ \mu m$	Pores with r < 0.01 $\mu$ m
	[v/v%]	[v/v %]	[v/v %]	[v/v %]
UNTR	37.3	25.7	11.6	0.0
HAP 0-5 mm	35.1	23.0	12.1	0.4
HAP 5-10 mm	37.7	25.5	12.2	0.1
ES 0-5 mm	30.7	21.8	8.9	0.7
ES 5-10 mm	31.8	23.5	8.5	0.5

**Table 6.** Physical and thermal properties of untreated and treated samples:  $\alpha = \text{contact angle}$ ;  $t_a = \text{time for}$  absorption; AC = absorption coefficient;  $WA_{24h} = \text{water absorption after 24 hours of capillary suction}$ ;  $WA_{7d} = \text{water absorption after 7 days of capillary suction}$ ;  $\mu = \text{water vapor diffusion resistance coefficient}$ ;  $\varepsilon_{\text{max}} = \text{maximum thermal expansion}$ ;  $\varepsilon_{\text{res}} = \text{residual strain}$ ;  $\alpha_t = \text{thermal expansion coefficient}$ . Values of  $\alpha$ ,  $t_a$ , AC,  $WA_{24h}$  and  $WA_{7d}$  are averages for at least 2 samples (standard deviations in brackets).

		UNTR	НАР	TEOS
α	[°]	32.3 (±12.1)	74.4 (±3.4)	114.3 (±3.8)
t <sub>a</sub>	[ms]	684 (±195)	3957 (±2417)	> 1 hour
AC	$[(mg/cm^2)/s^{0.5}]$	21.2 (±0.6)	14.8 (±2.6)	0.1 (±0.0)
$WA_{24h}$	[wt%]	15.3 (±0.1)	15.0 (±0.1)	0.3 (±0.1)
WA <sub>7d</sub>	[wt%]	17.1 (±0.1)	16.5 (±0.1)	17.5 (±0.4)
μ	-	7.3	7.8	7.4
ε <sub>max</sub>	[mm/m]	0.16	0.09	0.14
ε <sub>res</sub>	[mm/m]	-0.02	-0.05	-0.03
$\alpha_t$	[10 <sup>-6</sup> °C <sup>-1</sup> ]	3.2	1.6	3.2



Figure 1. Example of use of Globigerina limestone in historical architecture in La Valletta (Malta) and details of severely weathered architectural elements.



**Figure 2**. Penetration depth of the two treatments, as assessed by fracturing freshly treated samples (the zone reached by the consolidants are darker than the substrate).



**Figure 3**. Pore size distribution of untreated and treated cylindrical samples (for each condition, two samples were analyzed, collected at a depth of 0-5 and 5-10 mm from the treated surface).



**Figure 4**. Pore size distribution of untreated and treated cubic samples (for each condition, three samples were analyzed, collected at a depth of 0-5, 5-10 and 10-15 mm from the treated surface).



**Figure 5**. FT-IR of untreated and treated samples. For treated samples, two measurements were performed, at a depth of 0-5 mm and 5-10 mm from the treated surface.



Figure 6. Color change after treatment.



Figure 7. Contact angle of untreated and treated samples.



Figure 8. Water sorptivity of untreated and treated samples.



**Figure 9**. Drying rate of untreated and treated samples. For comparison's sake, a sample treated with ES and left to cure for only 1 week before the beginning of the test was also considered (for this sample, the initial moisture content is notably lower than for the other samples, as the ES-treated layer is still hydrophobic and so it cannot be saturated with water).



Figure 10. Thermal expansion of untreated and treated samples.