

SYNERGIC USE OF AMMONIUM OXALATE AND DI-AMMONIUM PHOSPHATE IN THE PROTECTION AND CONSOLIDATION OF CARBONATE MATERIALS

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Abstract

The aim of this this research is to verify the suitability of some treatments based on ammonium oxalate and ammonium phosphate for the consolidation and protection of the internal entrance of Palazzo Verità Montanari (1583) in Verona, made of Avesa Stone. Different application protocols of the two products have been compared (the product alone, in mutual sequence, in mixture). The efficacy and limitations of the treatments are discussed on the basis of the results obtained with various types of diagnostic analyzes, invasive and non-invasive, as part of a laboratory experimentation carried out on specimens of the same carbonate stone.

Keywords: Conservation; Consolidation; Ammonium Oxalate; Di-Ammonium Phosphate; Carbonate Materials

Introduction

The present research concerns an experimentation carried out on several possible consolidation treatments to be adopted for the conservation of the internal entrance of Verità Montanari Palace (1583) in Verona. The Palace was commissioned to an unknown author by Giacomo Verità, to commemorate and glorify his father, Gerolamo Verità, a well-known political figure and the first Veronese poet that use the vernacular in his writings [1-2]. The internal entrance of the Palace was realized in Avesa stone, an organogenic limestone.

The consolidation of ancient architectural stone façades is one of the most delicate tasks in the conservation of stone artefacts. Consolidation, in fact, is an intrinsically irreversible operation and before deciding which treatments to use – whose materials will remain permanently inside the stone - severe and critical attention is required.

Once the stones have been quarried and shaped to be finally put in place, they will continue the natural decay process already begun in the outcrop [3-4]. The laying of a stone implies a new context in which the stone is subjected to new stress, sometimes in contact with other materials with different physical-chemical-mechanical characteristics that may accelerate the natural process of alteration or that may trigger new decay phenomena. The decay of stone materials manifests in different ways (scaling, pulverization, etc.), depending not only on the environmental conditions but also on the intrinsic stone characteristics related with the genesis

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(magmatic, metamorphic and sedimentary), the mineralogical composition (silicatic, carbonate, chalky, phosphatic etc) and the stone structure. Furthermore, in the recent decades, the climate change with its sudden variations in temperature, precipitation and wind, accelerated some types of deterioration processes (e.g. saline crystallization) or sparked off new decay phenomena [5].

The only way to safeguard the buildings and monuments stone heritage is to guarantee a continuous maintenance in order to counteract the decay processes and to avoid the development of new ones [6]. Maintenance/conservation interventions must not only be limited to the constituent materials but also to the context in which they are inserted, for example the control of biological growth in archaeological sites or the proper functioning of systems designed to protect the building from atmospheric agents (roofs, rainwater control systems, etc).

The conservation interventions for stone materials include cleaning, consolidation and protection procedures, not always in this order and not always necessary all of them as they are depending on each specific case. The most suitable procedures are always targeted taking into account the best result with the lowest invasiveness [7-8]. As for consolidation, restorers and scientists have studied products and treatments since the first restoration interventions but the results have not been always encouraging. Nevertheless there has been more and more attention towards products that are compatible, durable, sustainable for the environment and non-toxic to humans [9]. The action of a consolidating treatment is to restore cohesion to the material but, caution must be taken in order not to induce a final "cohesion" higher than the one of the unaltered material. This means that the consolidated material must be mechanically compatible with the rest of the stone. Furthermore, a good consolidant must have a suitable chemical compatibility with the material on which it is applied, without giving rise to harmful by-products or triggering new decay processes [7-8]. Moreover, the penetration inside the stone material should be deep enough in order to reach the sound material and, therefore, not to give rise to sharp variations of cohesion. Other important aspects to be considered for a stone consolidant are the treatment must not give rise to significant colour changes; it should allow the application of a new treatment (even with another product) without compromising the result; it should maintain the stone characteristics of liquid water permeability in order to minimize the formation of harmful salts sub-florescences.

Hardly a consolidating product will have all these characteristics but, inevitably, each treatment will favour some characteristics rather than others.

Usually, the consolidating products are divided into two large classes, the organic ones (generally synthetic polymers) and the inorganic ones. These products are applied in liquid form (solution or suspension) to be able to impregnate the stone [7]. Consolidation of the stone material occurs according to different mechanisms, among which solvent evaporation and special chemical reactions (more frequently for inorganic) are prevalent. Consolidating agents are usually applied on the surface of the material by brush, poultices, spray, pipette, less frequently by immersion, and are drawn into the material by capillarity.

Treatments based on organic polymeric products, such as vinylic, acrylic and epoxy resins, were widely used in the past, because of their ease of use, good adhesive properties and strengthening ability [10-11]. However, their behaviour over time has proven to be substantially unsatisfactory, because of their limited penetration depth, their tendency to change colour, their sensitivity to UV light, their scarce compatibility and their generally low durability, but mainly because of their high conflictual behaviour in case of porous stone materials affected by soluble salts, a very recurrent situation of the architectural and archaeological heritage.

Certainly, the treatments based on inorganic products are interesting for their compositional affinity with stones [12-14].

In order to better frame the case of Verità Palace in Verona, a focused review on the inorganic consolidation treatments describes and analyzes in the following paragraphs the various available alternatives.

a. Lime-water. A saturated solution of calcium hydroxide $\text{Ca}(\text{OH})_2$ (lime water) is applied to the surface of a stone or a fresco painting. The evaporation of water leads to the deposition of calcium hydroxide which in the presence of atmospheric carbon dioxide (CO_2), is

converted into calcium carbonate (CaCO_3) [15]. The consolidating action is similar to the setting process of a lime mortar. This treatment has long been used to protect and consolidate porous materials [12, 16] such as, above all, frescoes and wall paintings, and in general where the thicknesses involved are reduced [16, 17]. There is no agreement about its real efficacy in stone consolidation because of the low water solubility of calcium hydroxide (about 1.65g/L at 20°C), fact that requires to repeat the treatment many times. This action would transfer a too large amount of water to the stone matrix, causing salts movement and consequent efflorescences. Another drawback is an anti-aesthetic effect due to frequent surface bleaching. Furthermore, a further problem encountered especially in the case of stone conservation concerns the poor penetration of calcium hydroxide inside the stone hampered by the production of a hard compact surface layer.

b. Nano dispersions of $\text{Ca}(\text{OH})_2$ in alcohols (both ethanol and iso-propanol), usually known as Nanolimes are an alternative to the multiple application of lime-water. This type of treatment was designed to increase the adherence of the paint layer in the case of wall paintings, with interesting results [18]. Alcohols promote a slower sedimentation rate than water, and therefore affect the kinetics of carbonation and CaCO_3 polymorph selection [18, 19]. The results of application of nanolimes on stones are often controversial. In fact, if compared to lime water, nanolimes are more concentrated solutions of $\text{Ca}(\text{OH})_2$, ensuring a greater consolidating effect but, their penetration into the stone depth seems to be generally problematic [20]. It is possible to partially overcome this drawback with multiple applications of the diluted product or by applying it with the help of Japanese paper but it is not clear if, taking these precautions the consolidation effect on stones is still preserved. Furthermore, bleaching problems are also often mentioned.

c. Barium hydroxide treatment is part of the process known as Ferroni-Dini Method from the name of its creators who proposed and applied it in the late '60s to remedy the damage caused on frescoes by sulphation specially after the flood of Florence in 1966 [13]. The method involves a first phase of desulfation obtained with a poultice of a water solution of ammonium carbonate $(\text{NH}_4)_2\text{CO}_3$ in cellulose powder which, thanks to a double exchange reaction with calcium sulphate, it allows both its dissolution and the formation of calcium carbonate (CaCO_3). In the second phase barium water (a saturated solution of barium hydroxide) is used, which leads to the formation of insoluble, stable barium sulphate (BaSO_4). In the same time, the excess of barium hydroxide reacts with atmospheric CO_2 and gives rise to barium carbonate (BaCO_3). Barium carbonate gradually precipitates inside calcium carbonate crystals of the plaster, binding them with a very similar crystallographic structure. The consolidating action is strengthened by a second reaction between $\text{Ba}(\text{OH})_2$ and CaCO_3 through the formation of $\text{Ca}(\text{OH})_2$ followed by its carbonation [13]. Barium hydroxide is scarcely compatible with tempera and oil mural paintings, because of its high alkalinity and also with copper containing pigments, such as malachite and azurite, due to their vulnerability to the action of ammonia developed by ammonium carbonate [13]. Barium hydroxide water solutions have also been used for the consolidation of stones and mortars always based on the same reactive mechanisms [15, 21]. Some authors have found a predominantly superficial consolidation with the formation of a hard layer attributed to a too rapid carbonation of $\text{Ba}(\text{OH})_2$ which hinders the penetration of the solution in depth. It is likely, instead, that this is due to an incorrect method of application, i.e. by applying the barium water directly to the stone, instead of by means of a poultice, as it should be. Anyway, studies have been carried out to slow down the carbonation of barium by adding urea to the solution [22] but the results on the consolidating effect are contrasting [23].

d. Alkaline earth and semimetal alkoxides are another group of inorganic based treatments. Among them are calcium alkoxides, acting as precursors of the corresponding carbonate. Calcium alkoxides react in presence of atmospheric moisture and carbon dioxide, leading to the precipitation of nano-structured metal carbonates and alcohols [24]. The characteristics that would make these products interesting are the consolidating efficacy, compositional compatibility with carbonate rocks, an increased durability against decay, the possibility of carrying out new treatments (retractability), the easy and safe handling during

applications. Their poor solubility and volatility are negative aspects, which ensues in a low amount of precipitated carbonates in each application.

e. The *ammonium oxalate-based* treatment was developed in the '90s at the Opificio delle Pietre Dure of Florence starting from observations made in the '80s on calcium oxalate patinas that are naturally present on stones and on their protective and acid-resistant properties [25, 26]. The potential formation of calcium oxalate in an artificial way was later investigated in the same institution. Unlike calcium oxalate, which is formed spontaneously in natural patinas, mostly in various colours, from light yellow to amber, to black, following the incorporation of atmospheric particulate, the artificially formed calcium oxalate is completely colourless. It forms according to the following reaction:



The treatment based on the above reaction has been found to provide a good passivating anti-acid protective action to the carbonates stone surfaces (such as marble and many limestones) [27] with several positive aspects such as: high compatibility of the product with calcium carbonate, high durability, retractability also after many years, without accumulation, restoration of colour saturation [28]. Consolidating properties were also subsequently reported on different marbles and limestones due to the formation of whewellite with an increasing of the surface hardness and maintaining the water transport properties of the stone [29, 30]. However, the increase in mechanical strength is only superficial (about 1mm) due to a poor penetration of the solution inside, probably due to an excessive reaction rate between calcium carbonate and ammonium oxalate solution. Since the 2000, ammonium oxalate entered in the practice of conservation of ancient monuments, artefacts, architectural stone façades, decorated façades, frescoes, mosaics.

f. *Ethyl-Silicate-based* consolidants are very effective on silicate stones, such as quartzitic sandstone, due to their chemical compatibility. It is usually applied via brushing or by spraying and it penetrates via capillary suction. Over time, atmospheric water replaces the ethyl OC_2H_5 groups with $-\text{OH}$ hydroxyl groups. This process is known as hydrolysis, and it is very slow, taking six to eight weeks to complete. In this period the surface is hydrophobic preventing any water-based interventions after consolidation. The loss of hydrophobicity of the surface signals the end of the hydrolysis process and it is the beginning of the condensation process of the oligomers to form a silica gel. The chemical bond that forms between the hydroxyl groups of the silicate stones and the silica gel, confers the consolidating power to this treatment. The absence of such hydroxyl groups on carbonate stones does not make it suitable for such type of materials. In that case the treatment is only filler and not a "binder"[31]. However, this treatment is also applied to carbonate stones with more or less positive results (mainly depending on the presence of silicate components in the stone) and in this sense, with the help of nanotechnologies, attempts have been made to make it more similar to these materials [32]. The most important property of ethyl silicate is the depth of penetration inside the material which, with suitable dilutions, is appropriate not to form hard surface layers [33, 34]. This is due to the fact that at the moment of application it is not yet a consolidant but an organic liquid not dissimilar to alcohol, which does not interact with the stone and therefore can freely flow inside without impediments. Hydrolysis and consolidation will take place after several months, when it has already penetrated even for more centimetres. On the other hand, two negative effects were noted in commercial ethyl silicate products: crack formation during the drying process and formation of dense fragments of gel inside the stone [33]. The latter can significantly decrease the transmission of water vapour through the stone by closing the porosity and thus allowing the vapour to condense inside the stone. In fact, ethyl silicate is one of the most widely used products in stone conservation and for this reason it has been the subject of studies to implement its properties and reduce the negative aspects [10, 34-37].

g. *The treatments based on nano products* are similarly to nanolime, being developed with suspensions of nanoparticles like silica, calcium oxalate, apatite etc. The addition of these nano-particles to ethyl silicate would lead to an increase in performance in terms of effectiveness (consolidating power) and reduction of negative effects (cracking due to the shrinkage of silica gel during curing [32, 38-43]). Furthermore, in the case of the mix composed

by nanolime + ethyl silicate, the hydraulic compounds may form from the reaction between free calcium ions and silicic acid with considerable consolidating action [15, 42, 43]. These treatments get some limitations in their application due to the poor penetration inside the stone and due to the possibility to give rise to whitening phenomena.

h. Alkaline activation or geopolymerisation is an innovative method of consolidation based on the dissolution of clay minerals by highly alkaline solutions (NaOH, KOH) and with the consequent formation of mineralogical phases such as zeolites, which are minerals not subject to swelling and with earth-cementing action. It has been mainly tested on earthen materials and in laboratory as possible impregnating agent on stones [44]. It is also of some interest for producing mortars for restoration [45-49]. Recently it was introduced for the in situ consolidation of the Alhambra earthen walls [50-52].

i. Ammonium Phosphates. To address the lack of an effective consolidating agent for limestones, starting from the consolidating action of ammonium oxalate (said to be insufficiently deep) an ammonium phosphate-based treatment was developed, with the formation of calcium phosphates, according to a reaction mechanism very similar to that of ammonium oxalate [53, 54]: soluble ammonium phosphate + calcium carbonate \rightarrow calcium phosphate + NH_3 + CO_2 + H_2O . This reaction occurs via a dissolution/precipitation process at ambient temperature and pressure. The calcium phosphates that forms would coexist with calcium carbonate, a situation that already exists in important natural structures such as the mammals bones and the shells of some marine organisms, demonstrating the full compatibility between the two compounds [53]. Unlike ammonium oxalate, three ammonium phosphates are potentially available: mono-, di- and tri-ammonium-phosphates $(\text{NH}_4)\text{H}_2\text{PO}_4$, $(\text{NH}_4)_2\text{HPO}_4$ and $(\text{NH}_4)_3\text{PO}_4$. Among these, various preliminary studies carried out in the laboratory have led to select as the best appropriate the di-ammonium phosphate (DAP) [53, 54]. The consolidating effect of di-ammonium-phosphate is based on the formation of calcium phosphates crystals which are deposited mainly on the internal walls of naturally formed micro-cracks in a degraded stone material, creating connecting micro-bridges, with consequent rebuilding of cohesion [53]. Several calcium phosphates can be formed, depending on the reaction conditions, although most of them are very insoluble. Among these, the prevalent species are hydroxyapatite $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ and octa-calcium phosphate $\text{Ca}_8(\text{HPO}_4)_2(\text{PO}_4)_4 \cdot 5\text{H}_2\text{O}$ [53]. Despite the high solubility in water (~ 690 g/l at 20°C), the treatment with di-ammonium-phosphate, on ancient monuments is applied at low concentration (5-7% w/v and recently also lower), however sufficient to obtain good consolidation results. This is also because of the full absence of toxicity of di-ammonium phosphate that is a well-known fertilizing agent. The latter property, however, where conditions of humidity or water stagnation exist, can favour the growth of microflora in the treated stone. This drawback has been overcome by combining the water solution of DAP to a small percentage of a suitable biocide (such as benzalkonium chloride or other similar quaternary ammonium salts) [55]. The potential of this treatment (good compatibility with the carbonate matrix, good consolidating effect, possibility of having solutions in different percentages, absence of chromatic alteration), have made it the object of thorough studies and many experiments before being used (since 2010) for the re-consolidation of marble statues, architectural façades and degraded mortars [20, 53-54, 56-63].

As regard the consolidation and protection of the internal entrance of the Palace Verità Montanari realized with the Avesa stone, in this research, laboratory investigations on this type of stone are presented, aimed to define the most suitable treatment for the problematics encountered on this case of study. The decay problems are related to a natural predisposition of this stone to alteration due to its high porosity (23%), low cohesive properties and the presence of a certain amount of clay minerals. All these factors favour the interaction with water and salts dissolved in it, leading to different types of alterations (intergranular decohesion, sulfation and formation of black crusts (Fig. 1), as a consequence of the saline crystallization, frost and thaw action and attack of the carbonate matrix by atmospheric acid pollutants.



Fig. 1. Details of the decorated sub-frame of Palazzo Verità Montanari in Verona (fotos from 2016) with (a) calcium carbonate recrystallization phenomena and (b) black dendritic crusts (Lucrezia Campana, credits)

According to the experience gained by our research group in time [13, 26-29, 58, 64-65] and pursuing the double conservative goal of protection from acid agents and of consolidation, some treatments based on ammonium oxalate, di-ammonium phosphate and their combinations were proposed, and their effectiveness was firstly investigated through laboratory researches. In particular, the novelty consists in the possibility of combined treatments to induce a better penetration inside the stone material, and therefore a better consolidation effect. The efficacy of the above treatments was assessed with good results through different techniques such as: colour measurements, water absorption capacity, drilling resistance, SEM/EDS, and XRD. The results obtained in this first phase were aimed at identifying the most appropriate treatments for the *in situ* application

Materials and methods

The effectiveness of the treatments was verified through invasive and non-invasive diagnostic investigations.

Stone treatments

Avesa stone is an organogenic limestone of Eocene age that crops out extensively in Val d'Avesa, part of the Lessina area, a hilly-mountainous area north of Verona. Morphologically, the surface of the stone is rough due to the fossil-presence. From the point of view of physical properties, the stone has a porosity index of 23%, a bulk volume of 2.00-2.20g/cm³ and a compressive strength of 220-280kg/cm² [66]. The experimentation was carried out in laboratory on 5×5×1cm and 5×5×2cm of sound Avesa stone specimens which, after cutting, were washed and dried in a desiccator (with silica gel and RH 4%) till a constant weight.

As consolidating products, ammonium oxalate (Sinopia Restauri) and di-ammonium phosphate 94% purity (Chemical Franke S.R.L.) was chosen. Both products were diluted to 5% in deionized water. Benzalkonium chloride (Antichità Belsito), with a final concentration of 3% was added to di-ammonium phosphate solution in order to avoid the development of biodeteriogens. All the applications were carried out by poultice, dispersing the solutions in cellulose powder, and keeping them in contact with the stone surface for suitable times.

In order to obtain a more objective assessment of the treatment to be adopted, it was decided to compare five different protocols with the use of the two consolidating agents in aqueous solutions: individually, in a mixture and in sequence.

The treatments that were tested are listed below and their characteristics are reported in Table 1. For each treatment, 3 specimens of Avesa stone were used and 3 additional specimens were left as an untreated reference.

AmOx- ammonium oxalate;

DAP (+BAC) - di-ammonium phosphate (+ benzalkonium chloride);

MIX- mix of ammonium oxalate and di-ammonium-phosphate (+BAC);

AmOx → **DAP** (+BAC) - ammonium oxalate followed by di-ammonium phosphate (+BAC);

DAP (+BAC) → **AmOx** -di-ammonium phosphate followed by ammonium oxalate.

It is expected that the combined treatments, applied in sequence, react at different levels of the stone. For example, in the case of the AmOx → DAP, the AmOx should consume (reacting) a part of the Ca of the calcite present on the surface, so that the subsequent DAP treatment would react mainly in depth. Likewise with DAP → AmOx, where it would be the AmOx to penetrate and react in depth.

Table 1. Treatments

Kind of treatment	1 st treatment	Contact time (h)	2 nd treatment	Contact time (h)*
	Concentration (W/V)		Concentration (W/V)	
AmOx	5%	24	-	-
DAP	5% DAP (+ 3% BAC)	24	-	-
MIX	5% DAP (+ 3% BAC) + 5% AmOx	24	-	-
AmOx → DAP	5% AmOx	24	5% DAP (+ 3% BAC)	24
DAP + BAC → AmOx	5% DAP (+ 3% BAC)	24	5% AmOx	24

* after 24 of poultice, the specimens were placed in a stove at 40 °C until constant dry weight was reached. Then they were washed for 10 minutes with distilled water. They were then returned to the stove at 40 °C until constant dry weight was reached (i.e. when the difference between two successive weighings at an interval of 24 h was not greater than 0,1% of the specimen mass)

Mineralogical composition and petrographical study

The mineralogical composition was determined through X-ray diffraction (XRD) (X’Pert PRO diffractometer by PANalytical, equipped with X’Celerator detector and HighScore software) according to the following operative conditions: CuKα1= 1.545Å radiation, 40kV, 30mA, 2θ = 3-70°).

Petrographic analysis was carried out on thin sections with a transmitted light microscope under crossed Nichols (Zeiss AXIO Scope A1).

Colour measurements

Colour variations induced on treated and untreated specimens were determined with a X-Rite Color Munki adopting the CIE L* a* b* method [67-70] for calculating the colour parameters. According to this method, the colour of a surface is described by three parameters: L* (0 to 100) represents the lightness, a* is related to the red-green colour impulse and b* is related to the yellow-blue colour impulse [71-73].

The total colour change is summarized by the ΔE* parameter calculated by the following equation:

$$\Delta E^* = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{1/2},$$

where: ΔL* = (L*_{treated} - L*_{not-treated}); Δa* = (a*_{treated} - a*_{not-treated}); Δb* = (b*_{treated} - b*_{not-treated}).

Colour variations that determine a ΔE* greater than 3 are perceptible to the naked eye. Nine measurements were taken for each treatment using a mask to always position in the same test area.

Capillary water absorption test (UNI 10859:2000)

The Water Absorption Test by capillarity was performed according to the UNI 10859: 2000 norm [69] on 3 Avesa stone specimens (5×5×1cm) for each treatment, previously subjected to dehydration in a desiccator (with silica gel and RH 4%) until reaching a stable weight. Then, the specimens were introduced into a microclimatic chamber at a constant temperature of 23±2°C and placed in contact with a source of liquid water through a flat surface consisting of absorbent paper filters. Through the filters, the stone materials have absorbed increasing amounts of water depending on the contact time. The specimens were weighed at regular intervals 0, 10, 20, 30, 60 minutes, and 2, 4, 6, 24 hours and every 24 hours for more days. The test was continued until the difference in weight between one measurement and the

next was less than 1% (in the present case for 8 days). At the end of the test it was possible to calculate the water absorption reduction by capillary (WAR %) in accordance with the UNI 10859: 2000 standard [74] as follows:

$$\text{WAR (\%)} = 100 \cdot (Q_1 - Q_2) / Q_1,$$

where: Q_1 = amount of water absorbed by the not-treated specimen at the end of the test; Q_2 = amount of water absorbed by the treated specimen at the end of the test.

In addition to WAR calculation, the absorption curves were also realized as a function of time and the Capillary Absorption Coefficient (CA) was calculated according to the indications of the most recent UNI EN 15801:2010 standard [75].

Drilling resistance measurements tests

The consolidating action induced by the various treatments was assessed by measuring the resistance to drilling with the Drilling Resistance Measurement System (DRMS) [76-78]. The following operating conditions were used: 300 rpm speed of rotation, 10mm/min forward speed of the bit, 10mm depth of the hole. A Fischer carbide-tipped masonry drill bit, for stone and concrete, with a 5mm diameter was used. Three measurements were taken for each Avesa stone specimen, treated and not treated.

Verification of the presence of neo-formation compounds

The presence of neo-formation compounds after the treatments with di-ammonium phosphate (such as, in particular, amorphous calcium phosphates) was verified by SEM/EDS microanalysis (XL30 PHILIPS with EDAX, mod. Falcon), and not by XRD due to the limit of this technique not allowing to identify microcrystalline, low crystalline and amorphous compounds. However, the XRD technique was used in the case of the treatments based on ammonium oxalate using the same conditions as for the mineralogical characterization.

Results

The treatments performance was evaluated taking into account the physical changes occurred in the treated specimens, investigated through methods such as the Colorimetry, Water Absorption by Capillarity, and Drilling Resistance (DRMS). Moreover, the possible presences of neo-formed compounds (calcium oxalate and calcium phosphates) was assessed by XRD and SEM/EDS.

Mineralogical composition and petrographic study

The petrographic observation of the Avesa stone in thin sections pointed out the presence of Nummulites, Discocyclins and Heterostegines fossils (benthonic foraminifera) bound by a mainly micritic carbonate matrix with a little amount of clay in the interstices of fossils. According to *R.J. Dunham* [79], the rock can be classified as packstone (grain-supported fossiliferous limestone) (Fig. 2).

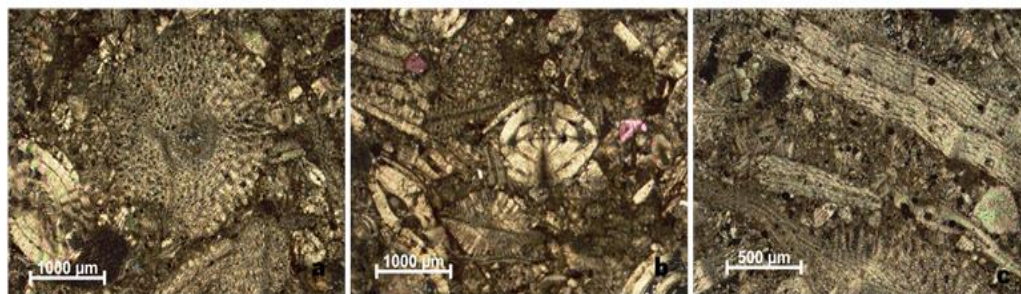


Fig. 2. Thin sections of Avesa stone with Discocyclins (a, xpl), Nummulites (b, xpl) and crushed shells with clay impurities (c, xpl).

The XRD analysis indicates that the stone is composed mainly by calcite with little amount of quartz and clay minerals.

Colorimetry

The averages of the measured values L^* , a^* and b^* , the differences between the average values of treated and untreated samples and the ΔE results are shown in Table 2 and Figure 3. In the case of the AmOx→DAP protocol, the ΔE variation is slightly lower than the other treatments.

Table 2. The main values of the parameters used to assess the degree of stone surface color change (ΔE) after the application of the treatment

Treatment	L^*	a^*	b^*	ΔL^*	Δa^*	Δb^*	ΔE^*
Reference	78.77±0.29	3.05±0.18	15.29±0.57	-	-	-	-
AmOx	73.47±1.07	4.06±0.36	17.32±1.15	-5.30	1.01	2.04	5.77
DAP (+BAC)	73.32±1.21	3.96±0.25	15.79±0.62	-5.45	0.91	0.50	5.54
MIX	73.26±0.96	4.18±0.51	16.60±1.13	-5.51	1.13	1.31	5.78
AmOx→DAP (+BAC)	74.59±1.22	3.76±0.47	13.91±1.40	-4.18	0.71	-1.38	4.46
DAP(+BAC)→AmOx	73.23±1.47	3.63±0.47	14.70±0.67	-5.54	0.59	-0.59	5.60

The colour variations (Fig. 3) are essentially due to a significant decreasing of the luminance (L^*), while the a^* and b^* values remain close to those of the reference specimens. This variation of L^* makes the treated specimens darker than those not treated. This is the consequence of a minor light scattering determined by the neo-formation products that reduce the natural roughness of the stone, decreasing the diffuse reflection of the light that consequently increases its absorption [64].

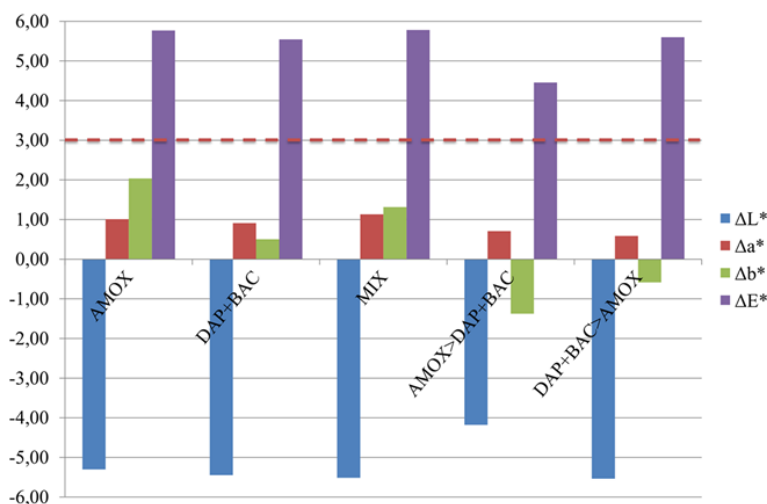


Fig. 3. ΔL^* , Δa^* , Δb^* and ΔE^* calculated for the different treatments.

Capillary water absorption test

Table 3 shows the average values of the water absorption reduction (WAR) of the treated samples compared to the untreated ones, and the capillary absorption coefficient (CA). Figure 4 shows the capillary absorption curves. The higher the WAR% value, the lower the water absorption capacity that results after the treatment. The lower the value of CA, the lower is the absorption speed.

Table 3. The values obtained for the Water Absorption Reduction (WAR) and Capillary Absorption Coefficient (CA) parameters

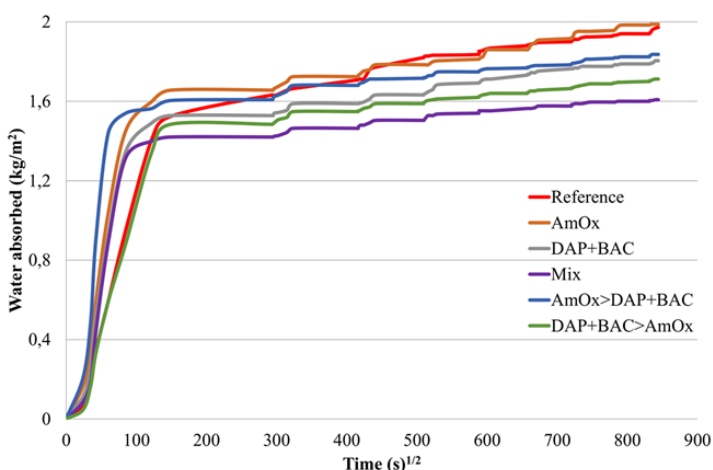
Treatment	WAR (%)	CA (kg/m ²)/s ^{1/2}
Reference	-	0.0081±0.0008
AmOx	-0.8±0.3	0.0112±0.0007
DAP (+BAC)	8.5±1.0	0.0109±0.0005
MIX	18.5±1.2	0.0105±0.0007
AmOx →DAP (+BAC)	6.9±0.9	0.0128±0.0006
DAP(+BAC)→AmOx	13.2±1.1	0.0078±0.0005

MIX is the treatment that most reduced the water absorption capacity (WAC), with a WAR of 18.5%, followed by DAP→AmOx and then by DAP, by AmOx→DAP and finally by AmOx.

The slightly negative value obtained for the specimens treated with AmOx would indicate that the treatment had no effect on the water absorption, being similar to the reference.

As regards the capillary absorption coefficient, it turns out that the specimens treated with DAP→AmOx and the reference are the slowest to absorb at the beginning of the test (first 2 minutes), followed by the specimens treated with MIX, then with DAP, then with AmOx and finally with AmOx→DAP.

Therefore the CA data are in partial discordance with those of WAR. However, an attentive observation of the absorption curves allows explaining this apparent discrepancy (Fig. 4).

**Fig. 4.** Water absorption curves

- the initial absorption speed of the untreated samples is similar to that of the samples treated with DAP→AmOx, and is the slowest, but when the curve flexes because an almost steady state has been reached, the untreated samples continue to absorb while the DAP→AmOx curve, at the plateau, is almost parallel to the time axis indicating that water absorption has practically stopped;

- the specimens treated with MIX have a slightly higher initial speed than the reference but they reach the almost stationary regime at shorter times with a smaller amount of absorbed water that remains the same even at the end of the test;

- the specimens treated with DAP behave in a similar way to the MIX but they arrive at the almost stationary regime in longer times and with greater amounts of absorbed water than the MIX;

- the specimens treated with AmOx at the beginning of the test quickly absorb water and reach the almost stationary regime at times similar to those of the reference but with higher amounts of absorbed water in such a way that at the end of the test the amount of adsorbed water is similar to the reference samples;
- the specimens treated with AmOx→DAP at the beginning of the test are those that absorb faster than all the others reaching the almost stationary regime first so that at the end of the test the amount of water absorbed is slightly lower than the reference specimens.

Drilling resistance measurement tests

Table 4 shows the values of the DRMS measurements performed on the treated and untreated specimens, expressed as the average of the values in the following measuring range: 0-10mm, 0-1mm, 1-10mm. The 0-1mm measuring range is where the tip starts working and whose values often have little diagnostic significance.

The average drilling profiles (Fig. 5) are certainly more interesting than the average resistance data because they give indications on the distribution of the treatment inside the material, on the presence of a hard surface crust due to the concentration of the treatment, and on the homogeneity of the stone material.

Table 4. Drilling resistance results

Treatment	Depth range (mm)	Drilling resistance (N)			
		Sample 1	Sample 2	Sample 3	Average
Reference	0-10	10.88±3.67	12.69±4.50	12.64±3.63	12.07±4.03
	1-10	11.46±3.28	13.58±3.71	13.10±3.20	12.71±3.51
	0-1	5.81±2.85	4.75±2.42	8.57±4.54	6.38±3.67
AmOx	0-10	13.87±3.40	9.97±2.41	16.07±3.70	13.30±4.08
	1-10	14.44±2.64	9.95±2.06	16.60±3.04	13.66±3.80
	0-1	9.20±5.08	10.32±4.54	12.06±5.90	10.53±5.18
DAP(+BAC)	0-10	13.27±3.08	9.33±1.65	10.85±2.79	11.15±3.04
	1-10	13.85±2.25	9.59±0.94	11.02±2.54	11.49±2.69
	0-1	8.20±4.27	7.26±3.75	9.69±4.26	8.38±4.10
MIX	0-10	14.24±3.71	11.67±4.45	13.59±3.55	13.17±4.06
	1-10	14.51±3.19	11.34±3.86	13.79±2.96	13.21±3.61
	0-1	12.55±6.70	15.22±7.59	12.57±7.09	13.45±7.02
AmOX>DAP(+BAC)	0-10	15.10±3.78	9.96±2.76	13.86±3.92	12.97±4.14
	1-10	16.10±2.03	10.17±2.50	14.22±3.43	13.50±3.67
	0-1	6.74±4.49	8.43±4.21	11.26±6.41	8.81±5.32
DAP(+BAC)→AmOx	0-10	20.12±5.35	16.70±3.15	21.30±5.08	19.37±5.01
	1-10	21.16±4.14	17.31±2.07	22.52±3.29	20.33±3.94
	0-1	11.25±6.08	11.62±5.36	10.95±5.45	11.27±5.46

In the first 3mm from the surface all treatments showed higher values of drilling resistance than those of the untreated specimens, fact that indicates the formation of a crust and a consolidation effect within this stone depth. Above this depth (3mm), the DRMS values of the treated specimens become more similar to those of the untreated ones, fact that is related with the penetration in depth of the treatment. For example, the DAP→AmOx treatment shows values that remain constantly high, even higher than the untreated specimens.

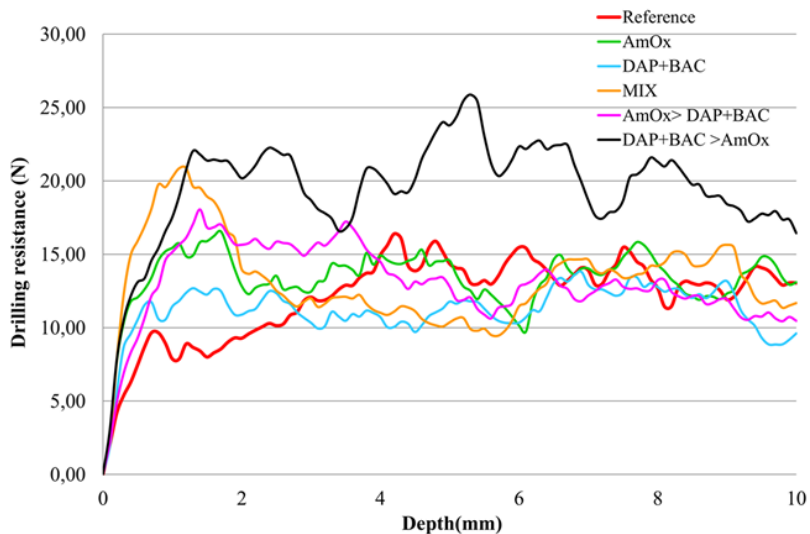


Fig. 5. Drilling resistance profiles

In particular, the drilling profiles of the specimens treated with AmOx, and AmOx→DAP tend to decrease quite gradually towards the values of the untreated while the MIX treatment, after an initial peak in the first 2mm, decreases much more rapidly.

Verification of the presence of neo-formation compounds

Fig. 6 shows the XRD spectrum of a sample taken by scratching the surface of the specimen treated with MIX. Among the treatments utilizing AmOx, this is the only one in which calcium oxalate have been identified in the Whewellite crystalline form, a compound that could be expected as a product of treatment. It is likely that in other cases calcium oxalate is poorly crystalline or microcrystalline and therefore not detectable with this technique.

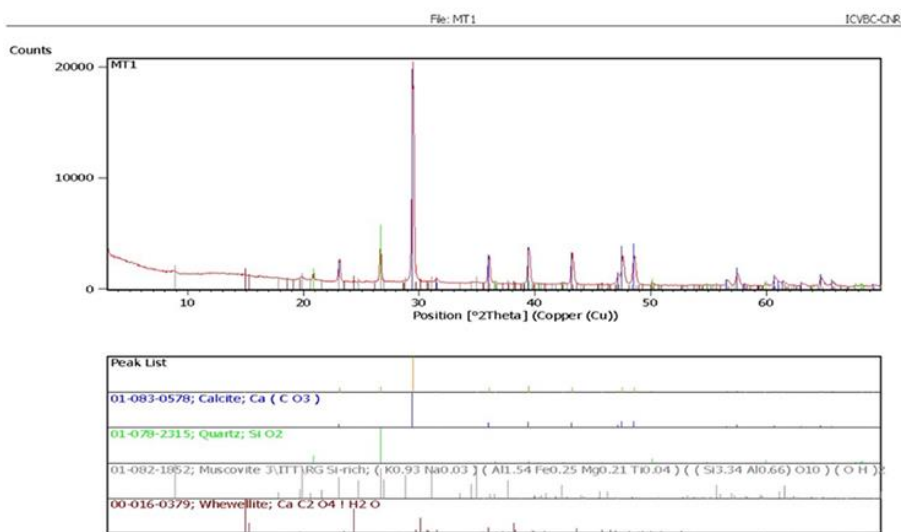


Fig. 6. XRD spectrum from a sample treated with MIX 5% for 24 h.

The presence of calcium phosphates, that are the predictable neo-formation products in the case of the DAP treatments, was not evidenced by using the XRD technique because they are often amorphous and in very little amount. As a matter of fact, taking into account the porosity of Avesa (23 %) and the percentages amount of the two agents together, after complete evaporation of water, it is expected a concentration of 1.15% of solid product in the stone for each agent. This should be theoretically the percentage (but perhaps even less) of the newly formed products dispersed in the stone pores (whether they are oxalates or calcium phosphates), below the limit of detectability of the instrument.

The SEM/EDS was an alternative for the examination of the DAP containing treatments (DAP, MIX, AmOx→DAP, DAP→AmOx). The phosphorus maps and the EDS analysis graphs are shown in figure 7.

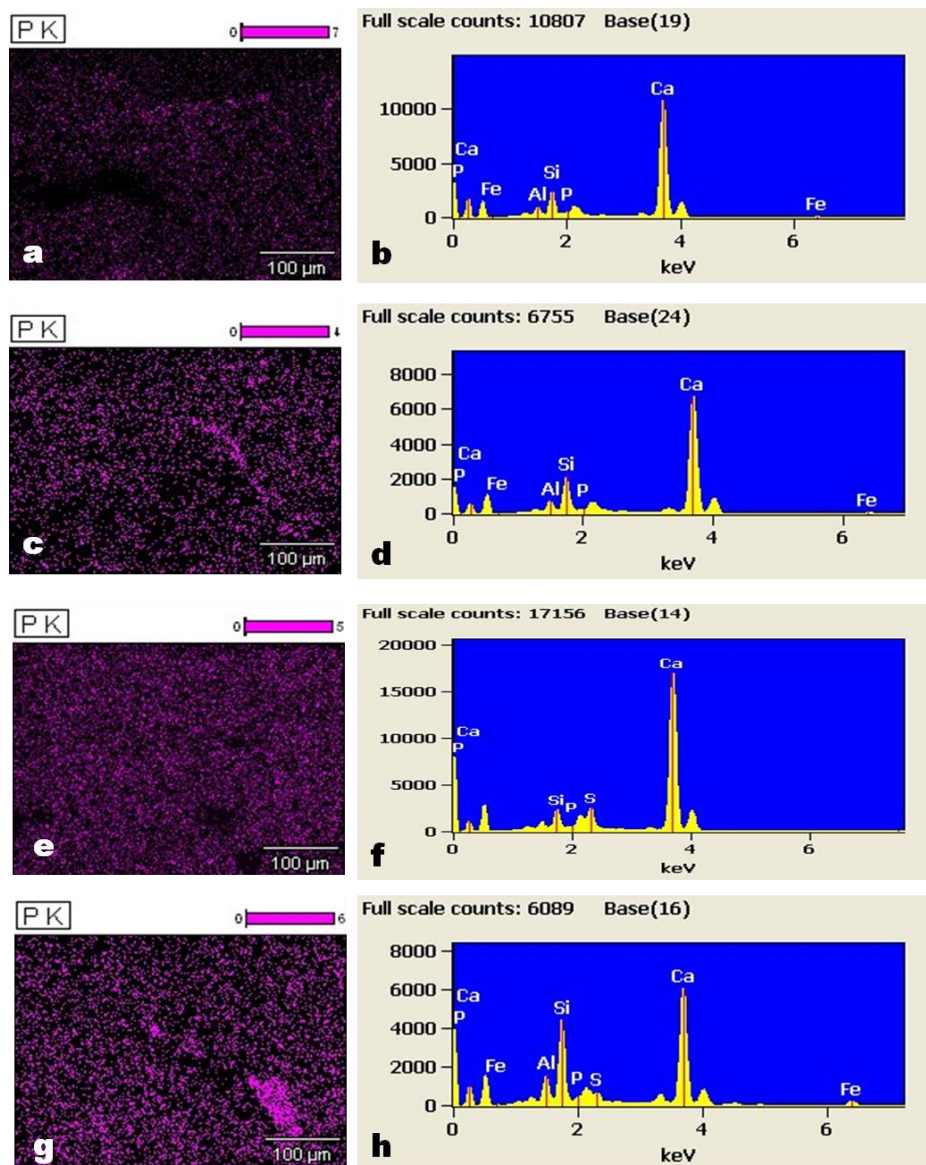


Fig. 7. Phosphorous maps (a, c, e and g) and EDS analysis (b, d, f and h) respectively for DAP, MIX, AmOx→DAP and DAP→AmOx treatments

The results presented in the figure 7 demonstrate a clear presence of calcium phosphates for the DAP→AmOx treatments (both map and EDS), AmOx→DAP (EDS), DAP+AmOx (map). A lower presence is recorded in the case of DAP alone.

Discussion

A thoughtful analyse of the obtained results was made and it is detailed below for every single treatment.

AmOx this treatment does not seem to have clearly changed the properties of the stone except for a variation in colour (darkening) with a perception of wet effect. A slight increase in drilling resistance in the very first millimetres was observed. The water absorption capacity is practically unchanged, also considering the heterogeneity of the material. There is no evidence of formation of calcium oxalates by XRD. This is attributed to a limit of detectability of the analytical technique used.

DAP (+BAC) this treatment shows a behaviour similar to the previous one (AmOx), with a darkening of the stone surface and a slight increase of drilling resistance in the first millimetres. The slight decrease in water absorption capacity, similarly to AmOx, could be linked to the heterogeneity of the stone rather than to the effect of the treatment. The SEM/EDS analysis showed a low presence of calcium phosphates.

MIX this treatment, like the previous two, induces a similar effect on colour (darkening). It causes a noticeable variation compared to the untreated both in the water absorption capacity and in the drilling resistance. These two data are in agreement because the profile of the drilling resistance shows the formation of a hard surface layer and the absorption test indicates that this layer has a reduced permeability to liquid water. This treatment is the only one that makes it possible to identify the presence of calcium oxalate via XRD. Calcium phosphates are also present (SEM/EDS analysis).

AmOx→DAP (+BAC) this treatment shows a slightly lower colour variation than the others but still with a colour saturation effect. The water absorption test showed a slight decrease in the amount of water absorbed at the end of the test, although no slowing down of the absorption rate was evidenced at the beginning. This datum is in agreement with the drilling resistance test which shows an increase in the first 4mm after which the trend is in line with the untreated reference. The formation of calcium oxalate has not been ascertained with XRD but calcium phosphates were identified by SEM/EDS. This treatment could be interesting because, although the depth of penetration is limited to 4mm, it does not lead to an excessive increase in the resistance of the material compared to the untreated.

DAP (+BAC)→AmOx the colour changed as in the case of the previous treatments, while the water absorption rate decreased in the first minutes, as well as the total amount of adsorbed water decreased at the end of the test. This datum is consistent with the increase in material cohesion (observed throughout the DRMS analysis) leading to a more compact matrix and therefore presumably with a lower permeability to liquid water compared to the untreated one. Also, for this treatment calcium oxalates were not identified by XRD, but calcium phosphates were identified by SEM. This treatment is particularly promising because it is the only one that reveals an increased resistance to drilling well distributed in depth, without the formation of a hard surface layer. The drilling resistance measured for this treatment, which is the higher among the different treatments, is considered to be excessive, fact that requires to moderate its action by decreasing to 4.0 or 3,5%, the concentration of the two agents (used at 5%).

Conclusions

This research made possible to verify the efficacy of some inorganic treatments based on Ammonium Oxalate (AmOx) and/or Di-ammonium-Phosphate (DAP) applied on the Avesa stone, a calcareous lithotype historically used in Verona. These treatments have been selected

thanks to some specific properties (compatibility, durability, minimal invasiveness, re-tractability, modest or zero toxicity) generally absent in the products of polymeric organic nature. The experimentation was not limited to the use of the two single products but wanted to deepen their use, comparing them according to five different application protocols: alone, in mixture and in mutual sequence. Low concentration solutions (5%) have always been used, respecting the principle of minimum invasiveness. The investigation was particularly significant in highlighting, beside the product, the importance of the application protocol.

In this regard, a sequential application of the combined products was tested in order to promote a first consumption of the calcium of the most superficial calcite (reaction between AmOx or DAP), favouring a more in depth reaction of the subsequent treatment (DAP or AmOx). This hypothesis was verified as true for the two treatments applied in sequence but not for the mix in which the formation of a hard surface crust was highlighted.

In conclusion the most effective and adequate treatments resulted to be DAP(+BAC)→AmOx and AmOx →DAP (+ BAC) with a good distribution and homogeneity inside the stone, the first up to 1cm, the second up to 4-5mm. They are possible protocols for the conservation treatments of deteriorated Avesa stone monuments, such as the Verità Palace in Verona.

In perspective, similar investigations should be also carried out for other categories of carbonate stones in order to check the effective adequacy of these inorganic treatments.

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