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10 years of marble conservation by ammonium phosphate: laboratory and field data on protection, consolidation and mitigation of bowing

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Abstract

This paper presents a brief review of the use of ammonium phosphate solutions for the conservation of marble artworks. First, the idea behind the treatment is presented and the studies aimed at optimizing the treatment parameters are summarized. Then, the treatment ability to protect marble from dissolution in rain, to consolidate weathered marble and to mitigate bowing are reviewed. Finally, some field studies are presented.

Keywords: Marble, Hydroxyapatite, Dissolution, Acid rain, Protective coatings, Thermal weathering, Sugaring, Bowing

Introduction

To face the lack of commercial products able to combine effectiveness, compatibility and durability when applied to carbonate stones, ammonium phosphate was proposed 10 years ago for stone consolidation and protection (Matteini et al., 2011; Naidu et al, 2011; Sassoni et al, 2011). As sketched in Figure 1, the idea is to form calcium phosphates (CaP) as the reaction product between the substrate and an aqueous solution of a phosphate salt that the stone is treated with (Sassoni et al., 2011). Among CaP, hydroxyapatite (HAP, $Ca_{10}(PO_4)_6(OH)_2$) is the most preferable mineral, as it is the least soluble CaP at pH>4.

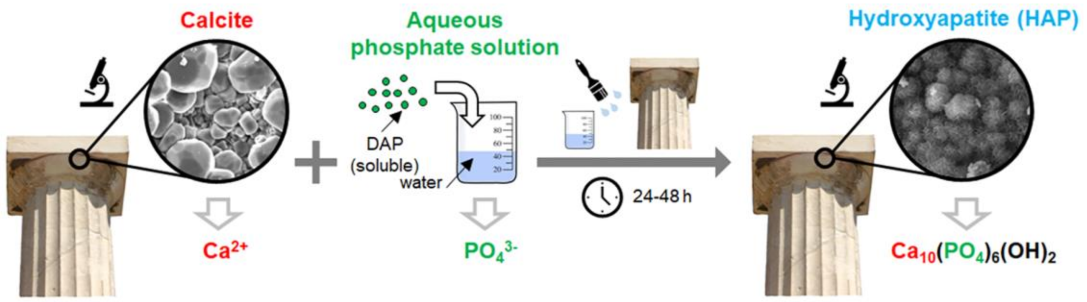

Figure 1: Scheme illustrating the idea of the ammonium phosphate treatment (Sassoni, 2018).

The ammonium phosphate treatment was inspired by the ammonium oxalate (AmOx) treatment, proposed by Matteini in the '90 (Matteini, 1994). By treatment with AmOx, protective patinas of calcium oxalate (CaOx) can be formed over stone in a few hours. However, the effectivness of so-formed CaOx has been found to be lower than hoped, likely because CaOx is only slightly less soluble than calcite and its crystal structure is different from that of calcite (Sassoni et al., 2011).

Because HAP is orders of magnitude less water soluble than calcite but still has a crystal structure and lattice parameters very close to those of calcite (Naidu & Scherer, 2014), if a continuous coating of HAP can be formed over the marble surface, effective protection against dissolution in rain can be achieved (Naidu et al., 2011). Moreover, by HAP formation inside the cracks among calcite grains, mechanical properties of marble and porous limestones can be improved (Sassoni et al., 2011).

The present paper reviews the most important findings on the use of ammonium phosphate for the conservation of marble, in terms of optimization of the treatment parameters and evaluation of its protective and consolidating ability, also for mitigation of bowing.

Optimization of treatment parameters

The role of several parameters has been systematically investigated:

(1) nature of the phosphate precursor. Diammonium hydrogen phosphate (DAP, $(NH_4)_2HPO_4$) is commonly used as phosphate precursor. Other ammonium phosphate salts have been investigated with the aim of favoring HAP formation (the more PO_4^{3-} ions are produced by the salt dissociation, the better), but the nature of the phosphate precursor is substantially indifferent if the pH of the aquous solution is controlled (Naidu & Scherer, 2014).

(2) concentration of the phosphate solution. DAP concentrations ranging from 0.1 M up 3 M are commonly used (Sassoni, 2018). The rational is that the higher the DAP concentration, the higher the amount of PO_4^{3-} available to form HAP. However, as the DAP concentration increases, the thickness of the HAP layer also increases, with increased microcrack formation and porosity (Figure 2) (Sassoni et al., 2018c). The DAP concentration can be reduced with satisfactory results if alcohol is added to the solution (Figure 2), as detailed in the following. Reducing the DAP concentration also has the positive effect of reducing the amount of unreacted fractions and the formation of by-products, so that rinsing with water at the end of the treatment is sufficient to remove undesired fractions. On the contrary, when highly concentrated DAP solutions are used, application of a limewater poultice after treatment with DAP is recommended, so that all unreacted fractions are reacted and/or removed from the stone and transported into the poultice during drying (Sassoni, 2018).

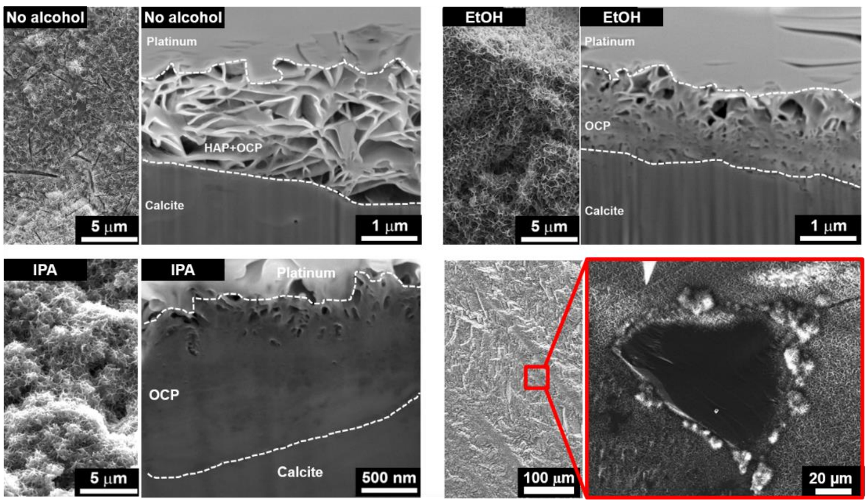

Figure 2: Top views and cross sections of marble samples treated with DAP solutions, with and without alcohol addition, and detail of a grain remained uncoated after treatment ("No alcohol" = 1 M DAP+1 mM $CaCl_2$; "EtOH" = 0.1 M DAP+0.1 mM $CaCl_2$ in 10 vol% ethanol; "IPA" = 0.1 M DAP+0.1 mM $CaCl_2$ in 10 vol% isopropanol) (adapted from Sassoni et al, 2018c).

(3) solution pH. The higher the pH, the higher the amount of PO_4^{3-} ions produced by DAP speciation, which favors HAP formation. However, coatings formed at high pH (10 or 11) exhibited increased tendency to crack, because of excessive growth of the CaP film. Therefore, the use of DAP solutions with no pH adjustment (pH ≈ 8) is usually preferred (Sassoni et al., 2018c).
(4) treatment duration. Treatment for 24-48 h is usually adopted, as after this time protective coatings continuosly cover the marble surface and sufficient mechancial consolidation is achieved (Naidu & Scherer, 2014; Sassoni et al., 2011). Nonetheless, succesful treatments for as short as 3 h have been reported (Ma et al, 2017).
(5) addition of calcium sources. Several ionic additions (CO_3^{2-}, Sr^{2+}, Mg^{2+}, Al^{3+}) have been tested to modify HAP formation, but the most significant benfit was found when Ca^{2+} ions were provided direclty into the DAP solution (Naidu & Scherer, 2014). This provides continuous coatings in a shorter time, while also preventing the dissolution of the substrate. Among different calcium sources, $CaCl_2$ in molar ratio of 1:1000 with respect to DAP has given the best results (Naidu & Scherer, 2014). Ca^{2+} addition also has the effect of favoring formation of a different CaP minerals besides HAP, namely octacalcium phosphate (OCP). OCP is more water soluble than HAP, which is not ideal, but still less soluble than calcite, so its formation is not detrimental for the treatment success (Naidu & Scherer, 2014).
(6) addition of alcohols. Addition of alcohol to the DAP solution allows to obtain much denser coatings (Figure 2) (Graziani et al., 2016; Sassoni et al., 2018c). This is thought to be due to alcohol molecules being able to weaken the hydration sphere of phosphate ions in solutions, thus making them more reactive to form CaP. IPA is more effective than ethanol, because its bigger molecule is adsorbed less tightly onto the calcite surface, so the surface reactivity is higher compared to EtOH adsoprtion (Sassoni et al., 2018c).
(7) composition of the new CaP phases. Alongside (or even instead of) HAP also other CaP may be formed, such as OCP when a calcium source or alcohols are added to the DAP solution. As long as the water solubility of these CaP phases is lower than that of calcite, their formation is expected to be favorable Actually, if their formation is linked to an improvement in the coating continuity and density, their formation is actually preferable. When Mg is present in the substrate (e.g. dolomitic marbles), formation of magnesium phosphates needs to be carefully checked as they may interfere with CaP formation (Sassoni, 2018).

Protection

The need to protect marble from dissolution in rain originates from the slight solubility of calcite in water, which may lead to the loss of inscriptions and carved elements after prolonged exposure. To protect marble from dissolution in rain, the CaP coatings need to be less soluble than calcite, continuous, pore- and crack-free, not significantly altering the marble color. All these requirements can be met if CaP coatings are formed with the addition of alcohols into the DAP solution (Figure 2). The protective efficacy of various DAP formulations was found to be as follows (Figure 3): AmOx < DAP with no alchol addition < DAP with EtOH < DAP with IPA (Sassoni et al., 2018c). Compared to the untreated reference, DAP-treated samples reach the same level of pH after about twice as much time. By extrapolation, the lifetime of a marble monument could be virtually doubled if a DAP-based treatment is applied. However, protection is still not complete (Figure 3), because some grains remain uncoated after treatment, even though the surrounding grains are perfectly covered with the CaP coating (Figure 2). This is thought to be a consequence of the unfavorable crystallographich orientation of these grains, over which the coating development is inhibited. New strategies to overcome this limitation are currently being investigated (e.g., the use of templates or other organic additions). Notably, the color change after treatment by any of the DAP formulations is below the common acceptability limit (CIELAB $\Delta E^*=5$), in most cases being actually below the visibility limit ($\Delta E^*=2.3$) (Sassoni, 2018).

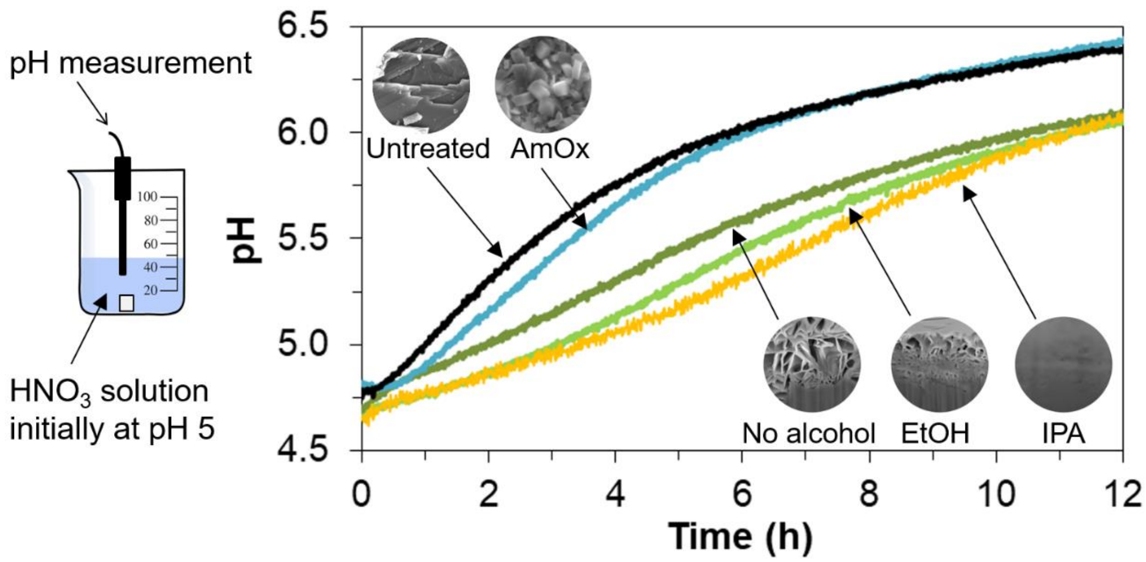

Figure 3: Protective efficacy of DAP treatments in comparison with ammonium oxalate (same label meaning as in Figure 2) was assessed by measuring the increase in pH over time of an acidic solution, resembling slightly acidic rain, where marble samples were separately immersed. The solution pH increases as marble is consumed, so the lower the curve, the higher the protective efficacy (adapted from Sassoni et al, 2018c).

Consolidation

The need to consolidate marble mainly arises from thermal weathering caused by the anisotropic deformation of calcite grains upon heating (Siegesmund et al, 2000). This results in formation of microcracks at the grain boundaries, the phenomenon being worsened by the possible presence of moisture in the stone. The ability of DAP solutions to increase marble cohesion and mechancial properties has been investigated on several types of artificially weathered samples, including compacted powders, samples heated in an oven (uniformly weathered) and samples heated on a hot plate (differentially weathered) (Sassoni, 2018). For this latter type of samples, the consolidating efficacy of various DAP formulations was found to be as follows (Figure 4): DAP with no alchol addition > AmOx > DAP with EtOH ≈ DAP with IPA (Sassoni et al., 2018c). Treatment with a highly concentrated DAP solution (with no alcohol addition) brought the highest increase in marble cohesion because, in this case, the presence of pores in the newly formed CaP is not as detrimental as in the case of protective films, provided that the tip of cracks among calcite grains is succesfully sealed. Less concentrated DAP solutions with alcohol addition caused lower mechancial strengthening, but still marble cohesion was fully recovered after double treatment. The penetration depth of the DAP solution obviously varies with the marble porosity and deterioration state, reaching at least 20 mm in highly deteriorated marble (Sassoni et al., 2015). When tested on naturally weathered marble, the consolidating efficacy of DAP solutions was confirmed. Actually, formation of HAP was found to be promoted in naturally weathered marble, because of the presence of some gypsum deposits (providing additional calcium ions) and because of the higher surface roughness (which favors HAP nucleation) (Sassoni et al., 2015).

Mitigation of bowing

Bowing affects thin marble slabs, typically used as gravestones or cladding elements, which experience differential thermal weathering across the slab thickness. The ability of DAP solutions to *arrest* bowing of already bowed slabs and to *prevent* bowing of fresh slabs has been investigated (Sassoni et al., 2018a). As illustrated in Figure 5, pre-bowed slabs subjected to any of the DAP treatments experienced reduced bowing, compared to untreated marble. On the contrary, marble treated by AmOx exhibits much higher bowing, which is likely to be attributed to the thermal properties and stiffness of CaOx. In the case of not pre-bowed slabs, treatment with DAP before exposure to the thermal cycles was able to reduce the bowing significantly (Figure

5). The benefit of the DAP treatment arises from newly formed CaP being able to increase marble mechanical properties, without complete pore and microcrack occlusion. In this way, when consolidated marble experiences a temperature variation, some deformation of the calcite crystals can occur without stress and without microcrack formation at grain boundaries.

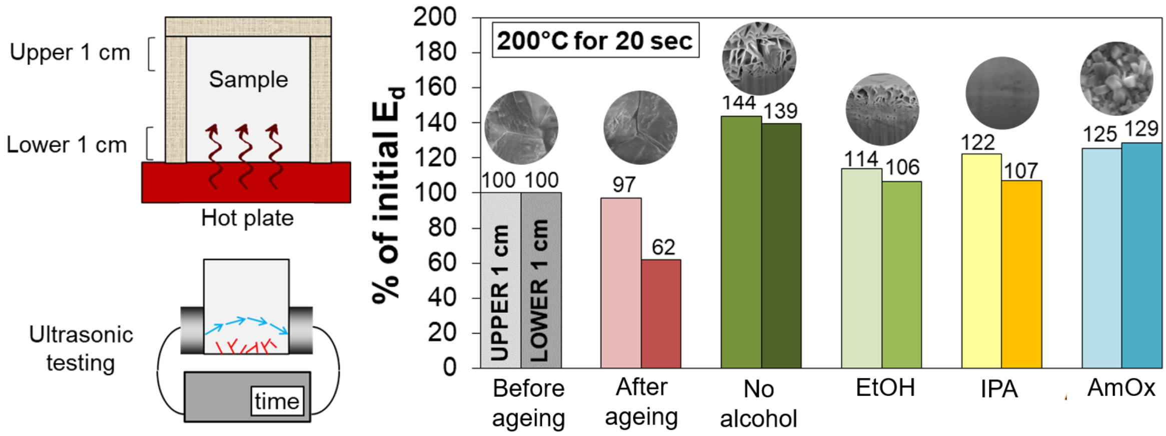

Figure 4: Consolidating efficacy of DAP treatments in comparison with ammonium oxalate (same label meaning as in Figure 2) was assessed using ultrasound velocity to determine the dynamic elastic modulus (E_d) of specimens preliminarily artificially aged by contact with a hot plate, which induced near-surface formation of micro-cracks (adapted from Sassoni et al, 2018c).

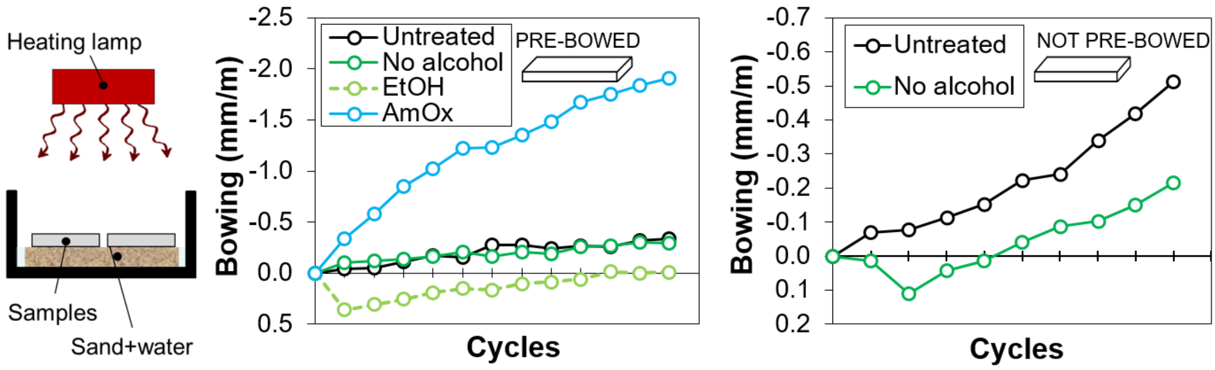

Figure 5: Ability of DAP treatments and ammonium oxalate (same label meaning as in Figure 2) to arrest and prevent bowing. Bowing was measured after 20-90-20 °C thermal cycles in wet conditions (adapted from Sassoni et al, 2018a).

Other functions

The DAP treatment has also been investigated for transformation of gypsum into less soluble CaP, which can be of interest for the conservation of marble affected by formation of a surface gypsum crust and gypsum-based stuccoes (Sassoni, 2018). Moreover, the addition of photocatalytic nano-TiO_2 into DAP solutions was investigated to provide marble surfaces with durable self-cleaning ability, by embedding nano-TiO_2 into insoluble HAP coatings (Sassoni, 2018).

Field applications

The DAP treatment is currently being applied on an increasing number of real artworks but only a few applications to case studies have been reported in the scientific literature so far. A good performance 1 year after the treatment has been reported for a rock-cut chamber tomb in Cyprus, treated with 1 M DAP for 3 h (Ma et al., 2017). A good consolidating ability, with minor color alterations, was found also in the case of a monumental tombstone in Bologna (Italy), treated with 3 M DAP for 72 h, followed by application of a limewater poultice for 48 h (Scherer et al., 2018). Additional field testing is in progress, including a sculpture in the park of the Royal Palace in Versailles (France), but the relative data have not been published yet.

Conclusions

All the results obtained so far in the laboratory on the use of ammonium phosphate solutions for marble conservation have been very encouraging, which has pushed the first field applications onto real case studies. Only a limited number of field studies have been reported in the scientific literature so far, but the high potential of the treatment has been confirmed.

References

Graziani G., Sassoni E., Franzoni E., Scherer, G.W. 2016. Hydroxyapatite coatings for marble protection: Optimization of calcite covering and acid resistance. Appl. Surf. Sci. 368, 241–257, doi: 10.1016/j.apsusc.2016.01.202

Ma X., Balonis M., Pasco H., Toumazou M., Counts D., Kakoulli I. 2017. Evaluation of hydroxyapatite effects for the consolidation of a Hellenistic-Roman rock-cut chamber tomb at Athienou-Malloura in Cyprus. Construct. Build. Mater. 150, 333–344, doi: 10.1016/j.conbuildmat.2017.06.012

Matteini M., Moles A., Giovannoni S. 1994. Calcium oxalate as a protective mineral system for wall paintings: methodology and analyses, III Int. Symp. Conservation of Monuments in the Mediterranean Basin, ed. V. Fassina, H. Ott, F. Zezza, 155-162

Matteini M., Rescic S., Fratini, F., Botticelli, G. 2011. Ammonium phosphates as consolidating agents for carbonatic stone materials used in architecture and cultural heritage: Preliminary research. Int. J. Archit. Herit. 5, 717–736, doi: 10.1080/15583058.2010.495445

Naidu S., Blair J., Scherer G.W. 2016. Acid-resistant coatings on marble. J. Am. Ceram. Soc. 99, 3421–3428, doi: 10.1111/jace.14355

Naidu S., Sassoni E., Scherer G.W. 2011. New treatment for corrosion-resistant coatings for marble and consolidation of limestone, in Stefanaggi M., Vergès-Belmin V. (Eds), “Jardins de Pierres – Conservation of stone in Parks, Gardens and Cemeteries”, Paris (F) 22-24 June 2011, p. 289-294, ISBN: 2-905430-17-6

Naidu S., Scherer G.W. 2014. Nucleation, growth and evolution of calcium phosphate films on calcite. J. Colloid Interface Sci. 435, 128–137, doi: 10.1016/j.jcis.2014.08.018

Sassoni E. 2018. Hydroxyapatite and Other Calcium Phosphates for the Conservation of Cultural Heritage: A Review, Materials, 11, 557, doi: 10.3390/ma11040557

Sassoni E., Andreotti S., Scherer G.W., Franzoni E., Siegesmund S. 2018a. Bowing of marble slabs: Can the phenomenon be arrested and prevented by inorganic treatments? Environ. Earth Sci. 77, 387, doi: 10.1007/s12665-018-7547-7

Sassoni E., Graziani G., Franzoni E. 2015. Repair of sugaring marble by ammonium phosphate: Comparison with ethyl silicate and ammonium oxalate and pilot application to historic artifact. Mater. Des. 88, 1145–1157, doi: 10.1016/j.matdes.2015.09.101

Sassoni E., Graziani G., Franzoni E., Scherer G.W. 2018c. Calcium phosphate coatings for marble conservation: Influence of ethanol and isopropanol addition to the precipitation medium on the coating microstructure and performance. Corros. Sci. 136, 255–267, doi: 10.1016/j.corsci.2018.03.019

Sassoni E., Naidu S., Scherer G.W. 2011. The use of hydroxyapatite as a new inorganic consolidant for damaged carbonate stones. J. Cult. Herit. 12, 346–355, doi: 10.1016/j.culher.2011.02.005

Scherer G.W., Franzoni E., Sassoni E., Graziani G. 2018. Phosphate consolidants for carbonate stones, APT Bulletin: The Journal of Preservation Technology, 49, 61-68, https://www.jstor.org/stable/26502504

Siegesmund S., Ullemeyer K., Weiss T., Tschegg, E.K. 2000. Physical weathering of marbles caused by anisotropic thermal expansion. Int. J. Earth Sci. 89, 170–182, doi: 10.1007/s005310050324