

Preliminary study on the use of ammonium phosphate for the conservation of marble-imitating gypsum-stuccoes

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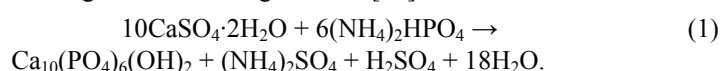
Abstract: In this study, a novel method for consolidation and improvement of resistance to water of gypsum-stuccoes was preliminarily investigated. The idea is treating gypsum with an aqueous solution of diammonium hydrogen phosphate (DAP, $(\text{NH}_4)_2\text{HPO}_4$) to form hydroxyapatite (HAP, $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$), which has much lower solubility than gypsum. Tests carried out on gypsum paste samples, manufactured to resemble historic stuccoes, showed that, after treatment with the DAP solution, a significant improvement in mechanical properties was achieved and brushite ($\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$) was formed (alongside some other by-products, that can be removed by an additional poultice treatment). Even if brushite is more soluble than HAP, still its formation is expected to be beneficial for stuccoes conservation, as brushite is significantly less soluble than gypsum.

Introduction

Since antiquity, gypsum-based stuccoes have been frequently used to imitate precious white or colored marbles, when the use of real marbles was not possible, because transport from faraway quarries was too costly [1,2]. While gypsum stuccoes generally exhibit good durability in indoor environments, they may exhibit severe durability issues when exposed outdoors (intentionally, such as in Islamic art [3], or after events such as a building's roof collapse [1]). In particular, stuccoes can suffer dissolution and pulverization, because of gypsum's high solubility in water, with consequent surface recession and loss of decorations when stuccoes are exposed to rain, condensation or rising damp [4]. However, also very low relative humidity and high temperature may lead to decay of stucco [5]. To enhance durability of stucco, in ancient times it was common practice to add organic compounds (such as sugars, glycerin and citric acid) to reduce gypsum solubility [6] and to use fats and proteins (such as animal blood, egg whites and casein) to achieve water-repellent properties [7-9]. Nonetheless, gypsum-stuccoes exposed outdoors are often in need of consolidation and protection, as illustrated for instance in Figure 1. Since

traditional consolidants and protectives (e.g. TEOS and polymeric products) have proved to have serious limitations when applied to gypsum-stuccoes, there is a need to develop new consolidating and protecting treatments specifically tailored for gypsum [4].

In this paper, a possible new strategy for the conservation of gypsum stuccoes was investigated. The idea is to use an aqueous solution of diammonium hydrogen phosphate (DAP, $(\text{NH}_4)_2\text{HPO}_4$) to react with gypsum and form hydroxyapatite (HAP, $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$), according to the following reaction [10]:



Since HAP has solubility in water about 4 orders of magnitude lower and dissolution rate about 7 orders of magnitude slower than gypsum [11,12], the formation of HAP on the surface and inside pores of gypsum stuccoes is expected to improve resistance to dissolution and pulverization.

The inspiration for the present study came from research carried out by the authors in the last few years on the use of ammonium phosphate solutions for the conservation of carbonate stones, such as marble and limestone [11,13-15]. In the case of stone, the phosphate treatment is intended to form HAP starting from calcite, with the aim of providing protection against dissolution in rain (HAP being less soluble and having slower dissolution rate than calcite) and mechanical consolidation (HAP being able to bind loose calcite grains). Starting from this background, the interaction of the ammonium phosphate solution with gypsum present in calcareous stones (as the result of stone sulfation) has recently been taken into consideration by the authors [15] and also other groups investigated the possible conversion of gypsum layers to stable phases [16]. Similarly, the use of ammonium phosphate solutions to transform gypsum into less soluble calcium phosphates was proposed in the past for the desulfation of lime paint layers [17]: encouraging results were obtained, even if phase control remained quite challenging [17].

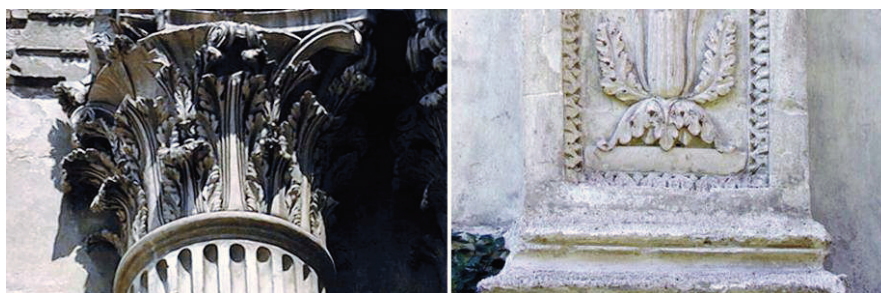


Fig. 1 Stuccoes exposed outdoor in the church of San Francesco in Fano (Italy, XIX cent.)

Materials and Methods

Samples

Samples of gypsum stuccoes were manufactured as in historic recipes. Pure gypsum binder (so-called "*scagliola*", $\text{CaSO}_4 \cdot 1/2\text{H}_2\text{O}$) and water (water/gypsum weight ratio 0.5) were used to prepare $4 \times 4 \times 16 \text{ cm}^3$ prisms, without any aggregate addition. After hardening, 12 cubic samples (4 cm side) and 12 cylindrical samples (5 cm height, 2 cm diameter) were obtained from prisms by sawing and core-drilling respectively.

Half of the samples were treated with the ammonium phosphate solution, while the other half were left untreated and used as reference. The same treatment conditions previously proposed for carbonate stones [11,13] were adopted also for gypsum stuccoes, in order to have a preliminary indication of the reactivity of gypsum to ammonium phosphate solution and to evaluate its ability to bind gypsum crystals. Samples were treated with a 1 M aqueous solution of DAP (Sigma Aldrich, reagent grade), applied by brushing until apparent refusal. After wrapping in a plastic film for 48 hours (to avoid DAP solution evaporation), samples were characterized in terms of changes in mechanical properties and morphology and composition of the new phases.

Characterization techniques

The consolidating ability of the phosphate treatment was evaluated by determining the increases in dynamic elastic modulus (E_d), compressive strength (σ_c) and tensile strength (σ_t) after consolidation. E_d was calculated as $E_d = \rho v^2$ where ρ is sample density and v is the ultrasound velocity, measured across cubic samples using a Matest instrument with 55 kHz transducers. σ_c was measured on cubic samples, using an Amsler-Wolpert loading machine (maximum load 100 kN). σ_t was measured by Brazilian test on cylindrical samples, using an Amsler-Wolpert loading machine (maximum load 10 kN).

The mineralogical composition of the newly formed phases was analyzed using a Bruker D8 Discover X-Ray Diffractometer. Grazing incidence diffraction (GID, incidence radiation $\theta=0.5^\circ$, detector scan range $2\theta=5-55^\circ$) was performed on untreated and treated samples, both on the treated surface and at 1 mm depth. Thanks to the reduced penetration of the incoming radiation with $\theta=0.5^\circ$ (amounting to a few hundreds of nanometers from sample surface), it was possible to obtain information on new phases formed on the sample's surface.

The morphology and the elemental composition of untreated and treated samples, at different depths from the treated surface, were analyzed by an environmental scanning electron microscope (FEI Quanta 200 FEG ESEM) equipped with an energy dispersive x-ray spectroscopy device (Oxford Instruments EDS probe).

Results and Discussion

After treatment, a significant mechanical improvement was found (Table 1), which suggests that gypsum crystals were more effectively bonded after consolidation. Three different phases were detected by GID after treatment (Figure 2). Accordingly, three different morphologies with different elemental composition were assessed by ESEM/EDS on the treated surface (Figure 3).

Brushite ($\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$) was found as the reaction product between Ca^{2+} ions coming from gypsum dissolution and PO_4^{3-} ions from DAP dissolution (Figure 2). Crystals containing Ca and P but not S, identified as brushite, are visible in the upper left part of Figure 3. A further magnification is reported in Figure 4. Formation of brushite starting from gypsum was reported also by Snethlage et al. [17], who however detected brushite when gypsum was reacted with ammonium di-hydrogen phosphate (ADP) at $\text{pH}=6.5$, while HAP was formed when gypsum was reacted with DAP at $\text{pH}=9.0$. Nonetheless, in the present study no HAP peaks were detected after reacting gypsum with DAP. A possible reason for this may be the evolution of pH during reaction (not measured in this study).

Table 1 Mechanical improvement after consolidation (E_d = elastic modulus, σ_c = compressive strength, σ_t = tensile strength. Values are averages for 6 samples, standard deviation in brackets).

	Untreated	Treated	Increase [%]
E_d	9.1 (± 0.1)	9.5 (± 0.1)	+5%
σ_c	15.0 (± 1.9)	22.2 (± 0.9)	+48%
σ_t	2.8 (± 0.3)	3.3 (± 0.4)	+16%

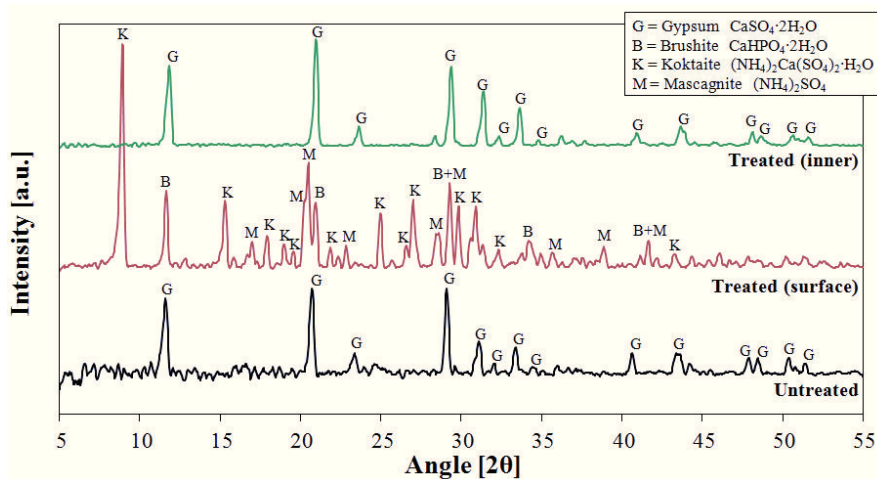


Fig. 2 XRD spectra of untreated and treated samples at different depths

According to Ishikawa et al. [19], during reaction between gypsum and the DAP solution pH progressively decreases, as a consequence of H_2SO_4 formation expected according to reaction (1). If pH decreases below 4, then brushite becomes more stable than

HAP (brushite solubility being lower than that of HAP for $\text{pH} < 4$ [19]), so that precipitation of brushite instead of HAP may occur. This may have been the case in the present study. Formation of HAP instead of brushite is expected to be achieved by controlling the reaction pH. This work is currently in progress. Nevertheless, even if brushite is more soluble than HAP for $\text{pH} > 4$ (which is the case of rainwater) [18], still brushite has much lower solubility than gypsum in the same pH range [19], hence brushite formation is expected to be beneficial for gypsum-stuccoes conservation.

As expected from reaction (1), ammonium sulphate ($(\text{NH}_4)_2\text{SO}_4$, also known as the mineral mascagnite) was formed as a by-product (Figure 2). Crystals containing N and S, but not Ca and P, identified as ammonium sulphate, are visible in the lower right part of Figure 3 and, at higher magnification, in Figure 5. Formation of ammonium sulphate, reported also by Sneath et al. [17], makes a second treatment necessary after DAP application, to remove ammonium sulphate by poulticing. If not removed, ammonium sulphate may be dissolved and re-crystallize inside the stucco pores, causing stress. The issue of removing reaction by-products does not take place in the case of carbonate stones, because in this case volatile ammonium carbonate is formed by reaction of DAP with calcite [11].

In addition, an unexpected new phase was detected by GID, i.e. koktaite ($(\text{NH}_4)_2\text{Ca}(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$) (Figure 2). Crystals containing N, Ca and S but not P, identified as koktaite, can be observed in the center of Figure 3. Consistent with what reported in the literature, they exhibit needle-like shape. Koktaite is thought to have formed because of the large amount of Ca^{2+} ions coming from gypsum dissolution, which probably caused formation of koktaite instead of ammonium sulphate. As it is reported to be highly water soluble, koktaite is expected to be easily removed by poulticing, just like ammonium sulphate.

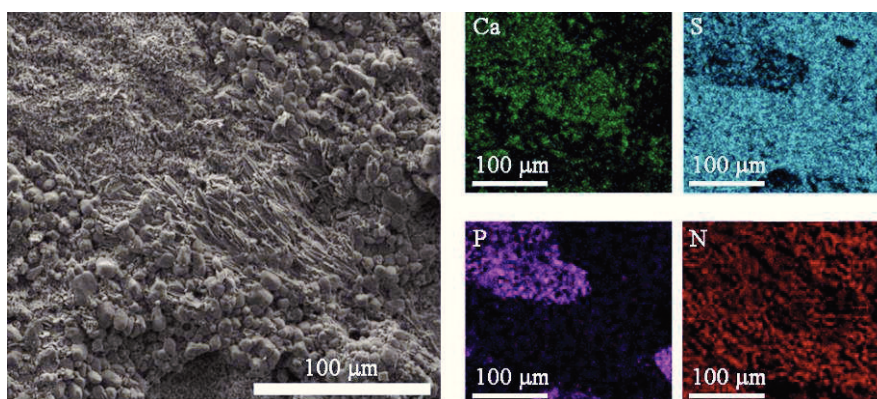


Fig. 3 ESEM image and EDS maps of treated surface (magnification 1000 \times)

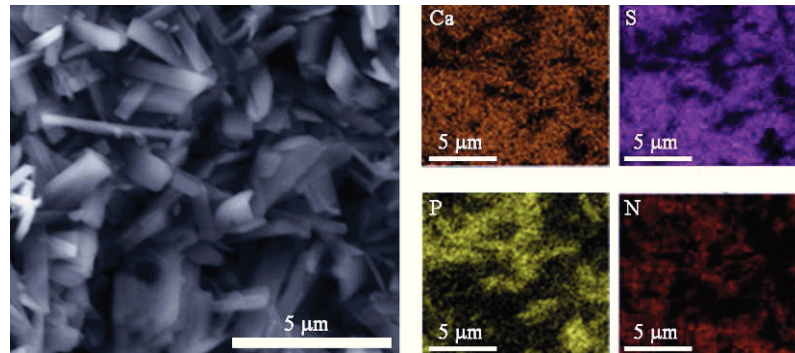


Fig. 4 ESEM image and EDS maps of brushite crystals (magnification 20000×)

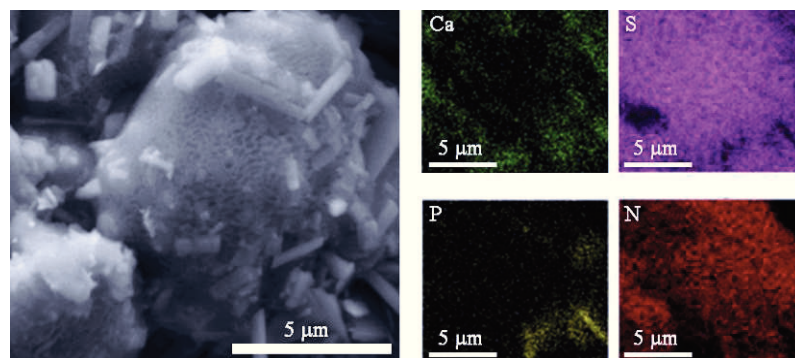


Fig. 5 ESEM image and EDS maps of ammonium sulphate crystals (magnification 20000×)

Notably, at a 1 mm depth from the surface apparently no new phase was present and only gypsum was detected by GID (Figure 2). This was confirmed also by ESEM/EDS on cross sections of treated samples, revealing P presence for a few hundreds of microns from the treated surface (Figure 6) but not much deeper into the substrate (image not shown). These findings suggest that a rapid reaction took place between the DAP solution and gypsum, so that formation of brushite (as well as other phases) was limited to sample surface. However, a significant improvement in mechanical properties was found after consolidation (Table 1), which cannot be a consequence of new phases formation only on the surface. A possible explanation for this is that, after application of the DAP solution, formation of new calcium phosphate phases was limited to the sample surface, but some dissolution and re-crystallization of gypsum inside the pores took place, resulting in increased bonding of gypsum crystal and hence increased mechanical properties. That is, the gypsum might have healed itself upon exposure to water. Additional tests are in progress to verify this hypothesis.

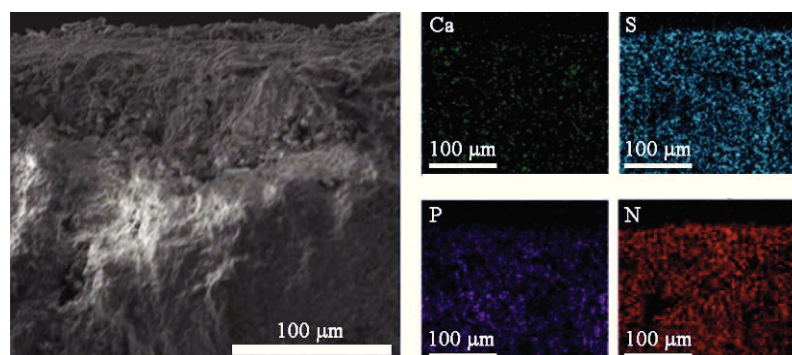


Fig. 6 ESEM image and EDS maps of a treated sample cross section (magnification 1000×)

Conclusions

Preliminary results reported in this paper about treatment of gypsum-stuccoes with a 1 M DAP aqueous solution seem encouraging. After treatment, a significant mechanical improvement was found. Several new phases were detected on the treated surface, namely brushite, ammonium sulphate and kokaite. Brushite, being sensibly less soluble than gypsum, is expected to increase the stuccoes resistance against dissolution in rain. However, further studies are in progress to favor formation of HAP instead of brushite, as HAP is less soluble in the range of rain pH. This goal is expected to be achieved by controlling the reaction pH. By also controlling gypsum solubility (e.g. by adding ethanol to the DAP solution to reduce the water content), kokaite formation is expected to be reduced. Further tests are also in progress to verify whether gypsum dissolution and re-crystallization inside pores may have contributed to mechanical improvement. These ongoing studies are also expected to provide useful insights for phosphate treatment of sulphated carbonate stones, such as marble affected by black crusts. In this case, sulfuric acid formation during reaction between the DAP solution and gypsum is not expected to be a major issue, as preliminary tests have shown only minor changes in pH, which always remained above 7.

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