Conservation of marble artifacts by phosphate treatments: influence of gypsum contamination

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Abstract

The use of ammonium phosphate solutions has proven to be very promising for protection and conservation of marble. However, all the studies carried out so far have been performed on uncontaminated marble. Unfortunately, this is rarely the case in the field, because marble artifacts exposed outdoors are often affected by sulfation, i.e. formation of a gypsum crust on the surface. Because gypsum is much more soluble than calcite, the outcome of the ammonium phosphate treatment is expected to be sensibly altered by the presence of gypsum. Therefore, in this study the nature and morphology of the new calcium phosphate phases formed by reacting gypsum with aqueous solutions of diammonium hydrogen phosphate (DAP) were investigated. In particular, the effect of DAP concentration, ethanol addition (aimed at reducing gypsum solubility), and pH were explored. The result is that phase formation can be controlled by suitably tuning the above mentioned parameters. Phases with low solubility (such as tricalcium phosphate and hydroxyapatite) can be obtained by increasing the ethanol concentration, the DAP concentration or the pH. However, their formation is associated with diffused cracking, likely because of excessive growth of the new phases. Among the investigated formulations, treatment with a 0.1 M DAP solution with 30 vol% ethanol at pH=8 seems to be the most suitable one, as it leads to formation of brushite (about 30 times less soluble than gypsum), without cracking, so that a reduction in gypsum solubility in rain is expected.

Keywords: Marble; Gypsum; Black crusts; Hydroxyapatite; Protection

1 Introduction

Aqueous solutions of diammonium hydrogen phosphate (DAP, $(NH_4)_2HPO_4$)) have proven highly promising for protection and consolidation of marble [1-4]. Thanks to the reaction between the phosphate solution (also containing a calcium source) and the substrate, new calcium phosphate (CaP) phases are formed [5]. These new phases are able to improve marble resistance to dissolution in rain (thanks to their lower solubility than calcite) [2,5] and marble cohesion (thanks to their bonding action at grain boundaries) [1,4]. Ideally, the new calcium phosphate should be hydroxyapatite (HAP, $Ca_{10}(PO_4)_6(OH)_2$), which is the least soluble CaP phase in aqueous solutions at pH > 4 [5,6]. However, depending on the reaction conditions (e.g., pH [3] or addition of external calcium sources [5]), different CaP phases may form alongside HAP, such as octacalcium phosphate (OCP, $Ca_8(HPO_4)_2(PO_4)_4\cdot5H_2O$), β-tricalcium phosphate (β-TCP, $β-Ca_3(PO_4)_2$), brushite ($CaHPO_4\cdot2H_2O$), monocalcium phosphate monohydrate (MCPM, $Ca(HPO_4)_2\cdot H_2O$) and monocalcium phosphate anhydrous (MCPA, $Ca(HPO_4)_2$). These phases have sensibly different solubility in water [1], hence the exact nature of the new CaP phases is fundamental for success of the treatment.

As pointed out by some recent applications of the DAP-based treatment to some real artifacts [1,7], the possible presence of contaminants on the surface to be treated can have a significant impact on the nature of the new calcium phosphate phases formed after treatment. In fact, in the field marble is frequently contaminated with gypsum, resulting from marble sulfation induced by the high concentrations of sulphur dioxide in the atmosphere in the past decades. An example of marble affected by surface sulfation is illustrated in Figure 1. Gypsum formed on the surface of marble elements cannot always be completely removed before marble treatment. Because gypsum has a much higher solubility in water than calcite (~2.4 and ~0.014 g/l, respectively), the treatment outcome is expected to be sensibly affected by the presence of gypsum [1].

A few studies have investigated the effects of treating gypsum with aqueous solutions of DAP [7-10]. Depending on the reaction conditions (e.g. DAP concentration, pH, duration), phases with low solubility (such as β-TCP, OCP, HAP) and more soluble phases (such as brushite) have been found [7-10]. However, when high DAP concentrations were used (3.0 M [9] and 3.8 M [8]), the formation of cracks and fissures in the new calcium phosphate layer was observed [8,9].

The present study is aimed at investigating and optimizing the nature and the morphology of the new CaP phases formed starting from gypsum, by promoting the formation of phases with low solubility and preventing cracking. To this aim, the influence of several parameters (DAP concentration, pH, and addition of ethanol to reduce gypsum solubility) was investigated.

2   Materials and methods

1.1   Samples

To investigate the effect of gypsum on the nature of the new CaP phases, a simplified system was considered. Tests were carried out on specimens of gypsum pastes, produced by mixing bassanite with water (water/bassanite weight ratio 0.5). Prisms with 4×4×16 cm^3 size were cast and then, after hardening, cubes with 1 cm edge length were sawn and used for the tests.

1.2   Treatments

Samples were treated by full immersion for 24 hours in 200 ml of aqueous solutions of DAP with different formulations, designed to investigate the effects of the following parameters:

1) *Effect of ethanol (EtOH) concentration*. Because gypsum solubility in an aqueous solution can be reduced by adding ethanol to the solution [11], increasing ethanol additions to water (0, 10, 30 and 50 vol%) were explored to study the influence of decreasing calcium ion concentrations, for a given DAP concentration (0.1 M).

2) *Effect of DAP concentration*. Increasing DAP concentrations (0.05, 0.1 and 0.5 M) were explored to study the influence of phosphate ion concentration for a given calcium ion concentration (determined by an ethanol addition of 30 vol%).

Figure 1:   Example of marble decoration affected by sulfation (Monumental Cemetery in Bologna, Italy, XIX century). Beneath the gypsum surface layer (also incorporating some particulate matter), marble exhibits grain disaggregation

3) <u>*Effect of pH*</u>. Because higher pH is expected to favor formation of HAP instead of brushite [12], the effect of increasing the pH to 10 using ammonium hydroxide was investigated for increasing DAP concentrations (0.05, 0.1 and 0.2 M) and a given concentration of calcium ions (corresponding to a 30 vol% ethanol addition).

After immersion in the solutions for 24 hours, the samples were extracted and abundantly rinsed with water to remove unreacted DAP and ammonium sulfate (that is expected as a by-product [8-10]).

1.3   Characterization

The mineralogical composition of the new CaP was determined by grazing incidence X-ray diffraction (GID, Bruker D8 Discover X-Ray Diffractometer, Cu anode, incidence radiation $\theta=0.5°$, detector scan range $2\theta=3\text{-}37°$). This technique detects the composition of surface layers without interference from the substrate, thanks to the reduced penetration depth of the incoming X-rays.

The morphology of the new phases was assessed by observing the samples (after coating with carbon) using an environmental scanning electron microscope (FEI Quanta 200 FEG ESEM).

3   Results and discussion

The composition and morphology of the new CaP phases formed by reacting gypsum with a 0.1 M DAP solution with increasing amounts of ethanol are reported in Figure 2. While fewer phases were formed with no or low ethanol addition, abundant new phases were found for 30 and 50 vol% ethanol additions. The new phases were identified by GID as brushite and β-TCP, respectively. While in the case of β-TCP (50 vol% ethanol addition) diffused cracking was observed, no cracks were visible in the case of brushite (30 vol% ethanol addition). Therefore, the latter ethanol concentration was selected in the prosecution of the study.

When higher and lower DAP concentrations were explored for a fixed 30 vol% ethanol addition, the new phases reported in Figure 3 were obtained. With a DAP concentration of 0.05 M, brushite was formed, with no visible cracking. On the contrary, when the DAP concentration was increased up to 0.5 M, β-TCP formed but heavy cracking occurred.

Increasing the pH from 8 to 10 had a strong impact on the composition of the new phases (Figure 4). At DAP concentrations of 0.05 and 0.1 M, alongside brushite (the only phase formed at pH=8) also β-TCP and HAP were formed. Further increasing DAP concentration to 0.2 M (the highest concentration that did not lead to immediate precipitation at pH=10), only β-TCP and HAP were found. However, in all cases where the pH was increased up to 10, diffused cracking occurred, because of excessive

growth of the new CaP phases. Cracking also led to flaking and detachment from the substrate, which of course is undesired.
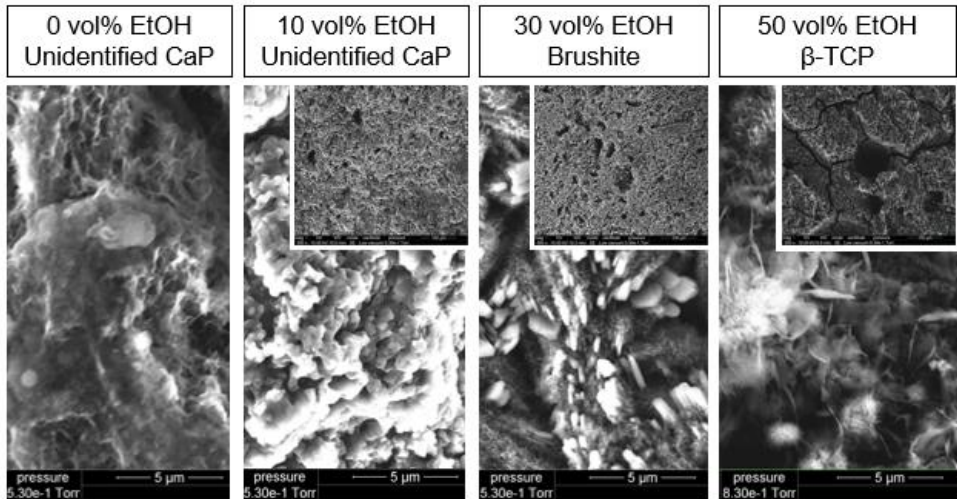

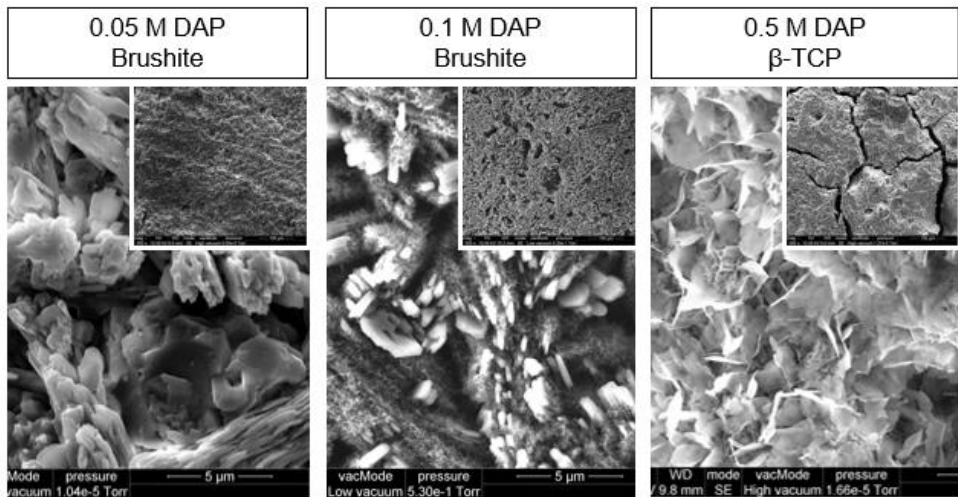**Figure 2:**   CaP phases formed by reaction with a 0.1 M DAP solution with increasing ethanol content at pH=8

Figure 3:   CaP phases formed by reaction with a DAP solution with increasing concentration at fixed 30 vol% ethanol content at pH=8
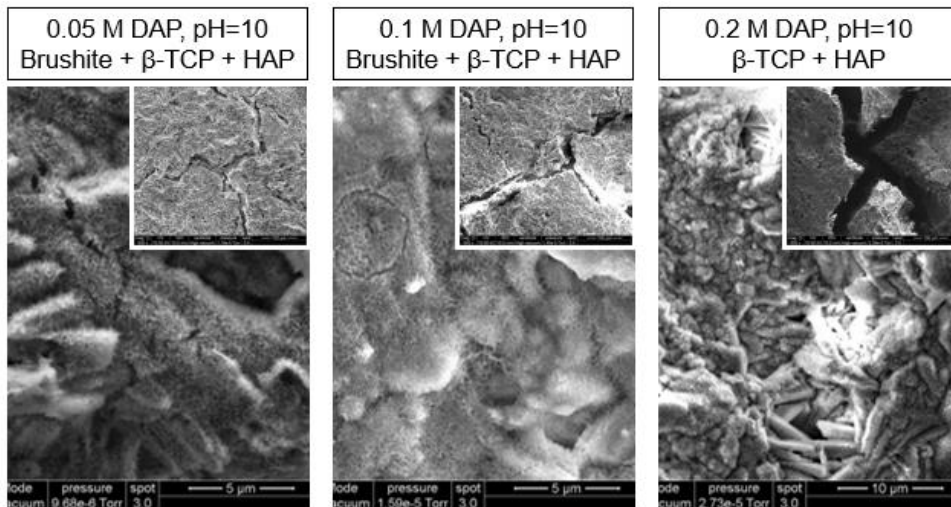
Figure 4: CaP phases formed by reaction with a DAP solution with increasing concentration at fixed 30 vol% ethanol content and pH=10

The change in composition of the new CaP phases, passing from brushite to β-TCP, when either the DAP or the ethanol concentrations were increased might seem counterintuitive, because in both cases the Ca/P ratio was diminished. In fact, a higher Ca/P ratio in the solution would be expected to favor the formation of phases with a higher Ca/P ratio (hence, β-TCP instead of brushite). However, this was not the case and the reason is thought to be the fact that brushite formation is kinetically favored, because brushite contains HPO_4^- ions (which are the main species originated from DAP dissociation), whereas HAP contains PO_4^{3-} ions (which are only a minor fraction). Accordingly, it has recently been proposed that precipitation of CaP phases follows the Ostwald's rule, i.e. the phase with the fastest precipitation rate (e.g. brushite) is preferentially formed, even if it is not the most stable phase (e.g. HAP) [9]. To verify this hypothesis, two solutions of $CaCl_2$ and DAP were prepared with Ca/P molar ratios of 10:6 (corresponding to that of HAP) and 1:1 (corresponding to that of brushite). By powder XRD it was found that very similar results were obtained in the two cases, i.e. formation of brushite and a minor amount of HAP, independently of the initial Ca/P ratio. The hypothesis that brushite formation is kinetically favored over that of HAP, basically independently of the Ca/P ratio in the starting solution, seems hence confirmed.

In any case, brushite is about 27 times less soluble in water than gypsum [1], hence its formation is expected to be beneficial. On the contrary, even if less soluble phases such as β-TCP and HAP could be obtained, their formation was always associated with diffused cracking, which would be detrimental for the treatment success. Therefore, the formulation involving 0.1 M DAP in 30 vol% ethanol at pH 8 (leading to brushite and no cracking) appears as the most promising one, among those investigated in

this study. Further tests are in progress to assess its ability to diminish the water solubility of treated gypsum. In addition to the conservation of sulfated marble, the same formulation is expected to be suitable also for the conservation of gypsum stuccoes. Further tests are in progress to assess the ability of this treatment to reduce the water solubility of gypsum stuccoes and increase their mechanical properties.

4   Conclusions

In this study, gypsum samples were treated with different aqueous solutions of DAP and the composition and morphology of the new CaP phases were investigated. The effects of ethanol addition to the DAP solution (aimed at diminishing gypsum solubility), DAP concentration, and solution pH were investigated. The results of the study indicate that it is possible to obtain phases with very low solubility (such as β-TCP and HAP) by increasing the DAP concentration, by increasing the EtOH concentration or by increasing the solution pH. However, in all these cases, the new CaP phases exhibited diffused cracking, presumably because of excessive growth of the new phases. For this reason, the formulation involving 0.1 M DAP in 30 vol% ethanol at pH 8 (leading to formation of uncracked brushite) seems like the most promising one. Indeed, as brushite is much less soluble than gypsum, a benefit in terms of reduction in dissolution in rain is expected. Treatment with the same solution with the aim of forming brushite is also expected to be beneficial in the case of gypsum stuccoes, both in terms of reduction of solubility in rain and increase in mechanical properties. Relevant experimental tests are in progress.

Acknowledgments

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