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Original article

Brushing, poultice or immersion? The role of the application technique on the performance of a novel hydroxyapatite-based consolidating treatment for limestone

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ABSTRACT

A novel inorganic consolidant has recently been proposed for the treatment of carbonate stones used in architectural and cultural heritage. The consolidant is an aqueous solution of diammonium hydrogen phosphate (DAP), which penetrates inside the stone and reacts with calcite to form hydroxyapatite (HAP). This HAP-based treatment seems very promising in several respects. It is effective in enhancing mechanical properties, only slightly alters stone transport properties, causes limited color change, and involves the use of non-toxic water solvent. However, several different treatment conditions and application methods have been investigated so far in the literature and the most suitable procedure for application in situ has not been identified yet. Therefore, in this paper a systematic investigation of the effects of different application methods of the DAP solution (brushing, poultice and immersion) was carried out. After DAP application, a further step consisting in a limewater-saturated poultice, aimed at overcoming possible issues connected to the presence of unreacted DAP in the treated stone, was performed and an "application cycle" was finally proposed. The treatments were tested on artificially weathered samples of Globigerina limestone ("Franka" type), a highly porous stone typically used in historical architecture in Malta and severely affected by decay processes. Even if Globigerina limestone is usually subject to salt-induced damage in the field, in this study artificial weathering was performed by heating to induce a controlled and uniformly distributed decay in the samples, as the presence of soluble salts would have interfered with the mechanisms of penetration and distribution of the DAP solution in the substrate, which was the main research objective. The outcome of the different treatments was evaluated in terms of consolidant penetration depth, mechanical properties, microstructure, contact angle, water sorptivity and color change, with respect to the untreated samples. The newly formed phases were characterized by SEM/EDS, FT-IR and ion chromatography. Based on the results of the study, brushing seems to be the most suitable method for DAP application, as it induces significant mechanical improvement but still limited microstructural, physical and chromatic alterations. Moreover, the benefits deriving from a higher consolidant absorption, as achieved by poultice and immersion applications (which are however much more laborious on site) are not so great in terms of HAP distribution in the substrate and consolidating performances.

1. Research aims

A new inorganic consolidant for carbonate stones, based on the formation of hydroxyapatite, has recently been proposed [1]. The treatment consists in impregnating the stone with an aqueous phosphate solution, which reacts with calcite in the stone forming hydroxyapatite. Since this treatment offers several advantages with respect to currently available products for carbonate stones consolidation, in the last couple of years several studies have been carried out on the use of hydroxyapatite for stone conservation. However, the most suitable procedure for in situ application of the treatment has not been identified yet. Therefore, in this study the effects of several different application methods (brushing, poultice and immersion) were investigated and compared, in terms of consolidant penetration depth, mechanical properties, microstructure, contact angle, water sorptivity and color change, with respect to untreated stone. Moreover, to improve the effectiveness and

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the aesthetic outcome of the hydroxyapatite-based treatment, in this paper a novel method was also proposed, consisting in the application of a limewater-saturated poultice to remove unreacted phosphates remained inside the stone. The newly formed phases were characterized by SEM/EDS, FT-IR and ion chromatography. To study the mechanisms of DAP solution penetration, distribution and reaction in the substrate, tests were carried out on a "simplified system", i.e. a porous carbonate stone (Globigerina limestone from Malta, "Franka" type) artificially weathered by heating (instead of by salts, as would be the case in the field), as the presence of soluble salts inside the tested samples would make the investigated mechanisms hard to be evaluated.

2. Introduction

A novel hydroxyapatite-based treatment has recently been proposed for the consolidation of carbonate stones in cultural and architectural heritage conservation [1]. The treatment consists in impregnating the stone with an aqueous solution of diammonium hydrogen phosphate (DAP), which reacts with calcite in the stone forming hydroxyapatite (HAP). Thanks to its low viscosity, this aqueous consolidant was found to be able to penetrate deeply into the stone, causing a remarkable mechanical improvement after only 48 hours of reaction and inducing no complete pore occlusion, thus leaving sorptivity and water vapor permeability of the stone substantially unaltered [1–3]. Also considering the lack of toxicity for the operator, the HAP-based treatment looks like a promising new consolidant, able to overcome many limitations that currently available treatments often exhibit when applied to carbonate stones, and has consequently received considerable attention in the field of cultural heritage conservation [1–12]. In addition to consolidation of porous limestone [1,2] and sandstones with different carbonate contents [3,4], the HAP treatment has also been tested as protective treatment for marble against acid rain corrosion, as HAP exhibits a good compatibility with calcite in terms of crystal structure and lattice parameters (suggesting the possibility of epitaxial growth) and a much lower solubility in acid than calcite [5,6]. The results obtained so far have shown the potential of the HAP coating to significantly improve marble resistance to dissolution [5–8].

In the field of limestone consolidation, the HAP testing was carried out adopting a multiplicity of treating parameters, in terms of:

- phosphate salt used as HAP precursor. As an alternative to DAP, $(NH)_2HPO_4$, that was used in most of the studies [1–3,5,6,9,10,12], ammonium di-hydrogen phosphate (ADHP), $NH_4H_2PO_4$, with possible addition of NH_3 30% to increase the solution pH [10], and ammonium phosphate (AP), $(NH_4)_3PO_4$, [4,11] have been proposed as well;
- concentration of the phosphate solution. DAP concentrations ranging from 0.1 M up to the saturation concentration (3.7 M at 20 °C) were investigated [1,2,10]. ADHP was used with a concentration of 5% [10], while AP was used with concentrations of 5% [11] and 10% [4];
- method of application of the phosphate solution. The investigated application techniques include partial immersion for 48 hours [1,2,9], brushing until apparent refusal and then wrapping with a plastic film for 48 hours [3,9], application by poultice for 4 to 17 hours [10] and spraying [4,11].

The selection of the most effective conditions for limestone treatment is rather difficult, since each of the above-mentioned parameters plays a very important role in determining the final effects of the consolidating treatment. Indeed, with regard to the three points reported above:

- depending on the phosphate salt used as HAP precursor, the nature and the amount of the newly formed calcium phosphate phases may change. By using DAP, HAP was found to be the main reaction product, alongside some minor metastable calcium phosphate phases [1,10]. Instead, when ADHP was used, the reaction products were found to be HAP and brushite ($CaHPO_4 \cdot 2H_2O$), the latter being undesirable as it is soluble [10]. To boost HAP formation and reduce the amount of phosphate salt needed to form HAP, AP has been suggested as well;
- in the case of DAP, the improvement in dynamic elastic modulus and tensile strength was found to increase substantially for increasing DAP concentrations, which can be ascribed to the formation of a higher amount of HAP [1,2]. However, when higher concentrations of DAP are used, some unreacted DAP remains in the stone at the end of the treatment, as denoted by the presence of soluble PO_4^{3-} detected in DAP-treated stones [2], hence several strategies have been adopted to remove unreacted DAP at the end of the treatment, namely immersing DAP solution-saturated samples in de-ionized water for 3 days [1] or, after drying, immersing consolidated samples in a saturated solution of calcium hydroxide for 48 hours [2];
- the application procedure highly influences the final effects of any consolidating treatment, even for the same stone type, as widely discussed in the literature [13–15]. For instance, in the case of ethyl silicate, Paraloid B72 or a bi-component epoxy consolidant applied on four different carbonate stones, the amount of product absorbed after treatment by capillary absorption for 3 hours was found to be sensibly higher than that absorbed after brushing until apparent refusal or by immersion for 3 or 24 hours, which led to identify capillarity as a much more efficient application method than full immersion [13,14]. Nevertheless, in the case of ammonium oxalate applied to a slightly porous limestone as a protecting treatment, application by immersion resulted in a higher penetration depth than application by brushing or poultice [15]. At the same time, application by brushing for a total of 10 minutes over a period of 1 hour was found to produce a calcium oxalate layer similar to that formed after treatment by poultice for 10 hours or more [15].

In this paper, the most suitable treatment conditions were investigated in view of using HAP for limestone consolidation in situ. In particular, referring to the three aspects discussed above, the following points were considered:

- since ADHP is less effective in providing PO_4^{3-} ions than DAP and AP, but, at the same time, AP is not currently available in the European and American markets, DAP was used as the precursor for HAP;
- for increasing the treatment effectiveness, a DAP concentration of 3.0 M, close to the saturation one, was used. For preventing possible problems owing to the presence of unreacted DAP inside stone pores, after the DAP treatment samples were dried and a saturated solution of calcium hydroxide (the so-called limewater) was applied by poultice. Limewater was preferred over de-ionized water as it contains calcium ions that are expected to react with unreacted DAP (as well as other soluble calcium phosphate phases) to form additional HAP. Samples were dried before application of the poultice to promote the capillary absorption of the limewater. If the poultice were applied on DAP solution-saturated samples, the driving force for calcium ions penetration would be diffusion, which is a definitely slower process. Application by poultice was selected because it is easy to perform in the field and because the poultice is expected to extract unreacted