



Penetration depth and redistribution of an aqueous ammonium phosphate solution used for porous limestone consolidation by brushing and immersion



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HIGHLIGHTS

- Redistribution of a consolidant might occur after application in porous materials.
- Redistribution was here investigated for an innovative hydroxyapatite-consolidant.
- Two different application methods (brushing and immersion) were considered.
- Application and drying determine penetration depth and amount of hydroxyapatite.
- Application of a limewater poultice is effective in removing soluble compounds.

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ABSTRACT

When consolidants are applied to porous stones, redistribution may occur inside the pore system after the treatment application, which influences their final penetration depth and performance. In this paper, the kinetics of redistribution were investigated for a 2-step hydroxyapatite-based consolidant, applied by brushing and immersion. The results of the study indicate that both the application method and the drying phase are crucial in determining the final penetration depth, the amount of hydroxyapatite that forms and the redistribution kinetics. In all cases, the limewater poultice applied during the second step of the treatment proved to be effective in removing soluble compounds.

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1. Introduction

The penetration depth of consolidants is one of the key parameters that influence their efficacy, as it determines their ability to reach the unweathered substrate. The final amount and distribution of the consolidant are also important features in determining the outcome of consolidation, as the formation of a superficial, over-consolidated crust might lead to detachment, whereas a smooth gradient in properties between the consolidated

layer and the unconsolidated substrate is ideal [1–3]. However, the consolidant penetration and distribution inside the stone are known to be dependent on a multitude of parameters, including the competition between capillary absorption and solvent evaporation, the pore system of the material, the viscosity and surface tension of the consolidant and the solvent, the presence and size of solid particles possibly suspended in the consolidant and the reaction mechanisms of the consolidant [1–19]. The limited penetration depth (owing to reasons such as too fast a reaction, agglomeration of particles or too short a pot life) is one of the main disadvantages of many organic and inorganic consolidants.

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When a consolidant is applied to a porous stone, it penetrates because of capillary suction. Absorption occurs in different stages, as the liquid first enters large pores and then is gradually drained into finer and finer ones, resulting in a progressive increase of the penetration depth after the consolidant application, as envisaged in the literature [4,14]. After drying, the consolidant forms a layer on pore surfaces and toroidal drops at concavities, such as grain junctions [4]. In a previous study [3], the Authors investigated the penetration depth of ethyl silicate (the most widely used stone consolidant) in a highly porous substrate (*Globigerina* limestone) and found that the final penetration depth significantly differs from that assessed right at the end of the treatment application, increasing from 6–7 mm to 12–13 mm due to consolidant redistribution. This redistribution is dependent on wetting of the pore walls, hence the presence of contaminants or particles inside the stone or on the surface, such as biofilms (that accumulate mainly on the surface) or salt deposits (that can accumulate both on the surface and inside the pores), may play an important role. In fact, they can reduce the uptake of the consolidating solution by blocking the pores, limiting their accessibility or changing their surface roughness. The process is further complicated by the fact that the migration of a liquid inside a porous material causes displacement of the fluids already inside the pores, whenever these fluids are immiscible. This may be the case of organic solvent-based consolidants (like ethyl silicate) if they are applied to materials containing water inside the pores. In the case of water-based consolidants, air might resist penetration by water and thereby affect the distribution of the consolidant; at the same time, the application of a water-based consolidant could cause water to displace air, water behaving as the wetting fluid, thus influencing the distribution of the consolidant in the porous network [14].

In the present paper, the redistribution after application was investigated for a consolidating treatment based on formation of hydroxyapatite (HAP), which has recently received a considerable attention as one of the most promising inorganic consolidants for stones containing carbonate fractions [16–22]. HAP was originally conceived for protection of marble, considering the extremely low solubility and dissolution rate of HAP compared to calcite [22–24]. In addition, the consolidating ability of HAP in the case of weathered limestone [16,17,25–27] and marble [28,29] was investigated, with very promising results. The treatment substantially consists in the application of a water solution of a phosphate salt (usually diammonium hydrogen phosphate, DAP) that reacts with calcium ions (either deriving from micro-molar dissolution of the substrate or externally added) to form HAP inside the micro-cracks and pores among calcite grains. This newly formed HAP is able to bond chemically to calcite grains and heal micro-cracks, thus re-establishing cohesion between grains and improving mechanical properties. Since the treatment is based on water and no particles are present (not even at the nano-scale), the treatment is able to penetrate deeply into the substrate and distribute evenly, as further discussed in the paper.

Several recipes for the HAP-treatment have been proposed through the years, in terms of the nature of the phosphate precursor, its concentration, the reaction time and the application technique [16,17,20,23]. In the present study, we focused on the treatment procedure based on application of a 3 M DAP solution, followed (after drying) by application of a cellulose poultice impregnated with limewater [25–28]. The limewater poultice is meant to dissolve the unreacted DAP that may be still present inside the pores, thus inducing formation of additional HAP. During drying, as the poultice is left in contact with the stone, the poultice is meant to cause extraction of any remaining unreacted DAP, that (being dissolved in limewater) is transported towards the drying surface.

The study of the redistribution of the HAP-based consolidant was considered as particularly important for the following reasons:

- the HAP-based treatment involves two soaking steps (application of a DAP solution and then application of a limewater poultice [25]) and two drying steps, each of which might influence the distribution of the treating solutions and of the reaction products;
- the treatment with the DAP solution might involve the formation of several metastable phases instead of HAP [16,24,30–34], due to changes in pH or ammonia evaporation [22,34]. Formation of soluble phases might occur while the consolidant migrates inside the stone, thus making the effects of redistribution even more important;
- the insight derived from the present study could be relevant also for other water-based treatments.

The redistribution mechanisms are also expected to depend on the application procedure of the consolidant. In a previous study [25], the effectiveness and compatibility of the HAP-based treatment were found to be significantly affected by the application technique. In fact, application by immersion resulted in increased HAP-formation, higher penetration depth and greater increase in mechanical properties of the stone, compared to application by brushing; however, it also resulted in more significant microstructural and aesthetic modifications. In addition, the thickness of the final consolidated layer (i.e. the depth of the region in which HAP was present at the end of the treatment curing) was found to be different from the thickness of the layer initially impregnated by the consolidating solution. In particular, it was higher for brushing. This finding suggests the need to better investigate how capillary absorption, evaporation and reaction of the ‘fresh’ consolidant jointly act in the different steps of the HAP-based treatment, which is the subject of the present paper. In the practice of monument conservation, consolidant application is normally carried out by brushing, as immersion is scarcely feasible (apart from small and/or entirely confinable objects). However, application by immersion allows evaluation of the efficacy of a treatment and is widely used in laboratory studies, so it can be considered as a benchmark for other application techniques.

To evaluate the consolidant redistribution, several aspects were investigated. Firstly, it was determined to what extent DAP redistribution occurs in the stages following the application. Two different application procedures, involving either continuous or discontinuous supply of the consolidant, namely immersion and brushing, were examined to test the differences in penetration depth and in HAP formation deriving from different capillary absorption mechanisms during soaking. Then, considering that the proposed procedure consists of different steps, involving different soaking and drying phases (each possibly influencing the distribution of DAP and reaction products), the distribution of the consolidant and the unreacted DAP solution at different depths in the stone was evaluated at each treatment stage. Particular attention was also devoted to investigating the possible formation of metastable intermediate phases (which might occur during the HAP-formation reaction), at each step. Finally, the efficacy of applying a limewater poultice, to boost formation of HAP and remove unreacted DAP and soluble phases [25], was systematically investigated.

2. Materials and methods

2.1. Materials

Testing was carried out on *Globigerina* limestone (labeled as GL, typically used in historic architecture in Malta), a soft organogenic limestone which suffers from deep deterioration and is hence an ideal target for HAP-based consolidation. Due

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