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An innovative phosphate-based consolidant for limestone. Part 1: Effectiveness and compatibility in comparison with ethyl silicate

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HIGHLIGHTS

- No fully satisfying consolidant for carbonate materials currently exists.
- An innovative phosphate treatment has recently been proposed.
- In this paper, the new treatment was compared to a commercial ethyl silicate.
- Effectiveness and compatibility of the two consolidants were investigated.
- The new phosphate treatment exhibited several advantages over ethyl silicate.

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ABSTRACT

For consolidation of weathered carbonate materials (such as marble, limestone and lime-based mortars) no fully satisfactory treatment currently exists. In this paper, an innovative phosphate treatment was investigated as a possible consolidant for limestone and compared with a commercial ethyl silicate (ES). The two treatments were evaluated in terms of effectiveness (i.e., ability to restore cohesion and mechanical properties, by measuring penetration depth, dynamic elastic modulus, tensile strength, resistance to abrasion) and compatibility (i.e., lack of any negative consequence on the original substrate, by assessing mechanical match, colour change, new phases composition, pore size distribution, water and water vapour transport properties, drying rate and thermal behaviour). The phosphate treatment proved to be very promising, being able to overcome some ES limitations.

1. Introduction

Porous materials used in historic and modern buildings, such as natural stones, bricks and mortars, are exposed to weathering processes (e.g., salt crystallization [1,2], freeze–thaw cycles [3], dissolution of soluble fractions [4]) that seriously threaten their durability. Due to weathering, these materials undergo progressive alterations in microstructural and physical properties (namely increases in open porosity, water absorption and sorptivity), that generally result in a decrease in mechanical properties [5,6]. As a consequence, especially in the case of historic buildings belonging to Cultural Heritage, it has become common practice to apply consolidants (i.e., products that penetrate deep enough into the weathered material to bind loose grains, improve their cohesion and adhesion to the sound substrate [7–11]) and/or repair mortars (i.e., mortars used for filling cracks or replicating lacking parts [12]).

Consolidants are usually distinguished in organic products (mainly acrylic and epoxy resins) and inorganic products (mainly alkoxysilanes, lime-based and barium hydroxide-based) [7–9,13]. Organic consolidants have been found to be in general scarcely compatible with the inorganic substrates and affected by low durability [14,15], hence research has recently mainly focused on inorganic consolidants. Among these latter, ethyl silicate (ES) has proved to be a rather satisfactory consolidating product for silicate materials, such as quartzitic sandstones and bricks [16,17], thanks to its ability of chemically bonding to the substrate and thanks to

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its stability. On the contrary, in the case of carbonate materials, such as marble, limestone, calcareous sandstone and lime-based mortars, no fully satisfactory consolidating treatments are currently available. Indeed, ES is less effective on carbonate materials, because in this case only physical–mechanical bonding to the substrate takes place [16], while lime-based consolidants, although compatible with carbonate substrates, are generally affected by low efficacy, low penetration depth and slow carbonation [18]. As a result, ES is currently the most widely used consolidant also for carbonate stones, in spite of its limited efficacy on this kind of substrate, mainly due to the lack of more suitable and effective alternatives [19].

A potentially good alternative to ES for carbonate stone consolidation is an innovative phosphate-based treatment that has recently been proposed [18]. The core idea is that stone can be consolidated thanks to the formation of hydroxyapatite (HAP, $Ca_{10}(PO_4)_6(OH)_2$) inside pores and micro-cracks between grains. HAP can be formed from the reaction between Ca^{2+} ions coming from dissolution of calcite grains and PO_4^{3-} ions coming from an aqueous solution of diammonium hydrogen phosphate (DAP), that is the product with which stone is impregnated [18]. With respect to existing commercial consolidants, the HAP-treatment is highly innovative for several reasons: (i) the product with which stone is impregnated (the aqueous DAP solution, free from any organic solvent) has viscosity similar to that of water and contains no particles (not even at the nano-scale), hence it is able to overcome limitations in penetration depth and effectiveness often exhibited by existing consolidants, e.g. nano-limes [20]; (ii) the binding mineral that forms from the reaction between DAP and the calcitic substrate (HAP) is expected to bond chemically to the stone [21], thus overcoming limitations exhibited by existing consolidants that bond to carbonate stones only physically-mechanically, such as ethyl silicate [16]; (iii) HAP is expected to be highly compatible with calcite, thanks to the similarity in crystal structure and lattice parameters between the two minerals, and also highly durable, thanks to its very low solubility and very slow dissolution rate [18,21]; (iv) the treatment causes no dramatic pore occlusion [18]. For these reasons, in the last few years several studies have been aimed at developing the HAP-treatment for consolidation of porous stones with different mineralogical composition and porosity [22–26] and for protection of marble against dissolution in acid environment [21,27,28], in both cases giving promising results.

In particular, previous papers by the authors and other groups were mainly aimed at optimizing the treatment conditions, so as to favour HAP formation and enhance the treatment efficacy. Several different methods to boost HAP formation have been proposed (e.g., use of different phosphate salts, cationic additions, pH control, limewater poultice application, etc.) and research is currently still progress [18,21–28]. The cited studies mainly focussed on specific aspects, such as composition of the new calcium phosphate phases, mechanical improvement and alterations in water transport properties. However, no comprehensive laboratory study on the treatment effectiveness, compatibility and durability has been reported yet, to the authors' best knowledge.

Therefore, in the present study the first attempt to evaluate the performance of the HAP-treatment from a 360-degree perspective is presented, comprising *all* the main requirements that stone consolidants must fulfil (namely, effectiveness, compatibility and durability). For the HAP-treatment, the parameters and application procedure recently proposed by the authors in [23] were adopted. Even if HAP-treatment conditions may be optimized in the future and hence be changed with respect to those adopted in the present study, still a comprehensive evaluation of the treatment performance at the present state of research, at least in laboratory conditions, is of fundamental importance. The obtained results are expected also to provide essential inputs for further treatment optimization and improvement. For example, unsatisfactory findings on the HAP-treatment durability might even result in the need of substantially modifying the treatment parameters.

The study is articulated in two parts: Part 1 (the present paper), dealing with the HAP-treatment effectiveness and compatibility, and Part 2 [29], dealing with durability. Moreover, to evaluate whether the HAP-treatment can actually be considered as a promising alternative to ES for consolidation of porous limestone, all the tests were carried out also on ES-treated samples and results obtained for the two consolidants were systematically compared.

Although relatively easy in principle, achieving the research objectives describe above is more challenging than it seems. Firstly, this is because each of the previously mentioned requirements is a complex and articulated concept, as summarized in the following [16,30–32]:

1. *Effectiveness:* The consolidant must be able to penetrate homogenously deep into the stone, so as to reach the unweathered substrate, and to induce mechanical improvement of the treated stone, so that stone resistance to weathering processes is enhanced [7,8,30].
2. *Compatibility:* The newly introduced materials must not have negative consequences on the original substrate, in a broad sense [33]. Firstly, the treatment must cause neither short-term or long-term alterations of stone aesthetical aspect, such as darkening, colour change or wet appearance [30,32]. Moreover, the consolidant must not give rise to formation of by-products harmful for the stone [8,30] or evaporation of toxic components dangerous for human health [16]. In terms of microstructural and physical properties of the stone, some reduction in open porosity and water sorptivity is to be expected or may even be desirable [19,30]. However, consolidants that clog pores and/or dramatically alter stone transport properties should be avoided, because, in case liquid water and water vapour are blocked behind the treated layer, exfoliation of stone might occur, when the trapped water is subject to freezing or soluble salt crystallization [7,8,16,34]. For these reasons, the water vapour permeability of stone must be preserved, to allow it to "breathe", and the drying rate of treated stone should be altered as little as possible, to reduce the risk of treatment failure [19,30]. Furthermore, the consolidating treatment should induce a gradual variation in stone properties with depth, so that no superficial hard crust is formed after treatment but a gradual transition is assured [7,8]. Finally, the thermal expansion coefficient of the consolidant must be similar to that of the treated stone, so as to avoid possible damage induced by a mismatch in thermal behaviour [7,30].
3. *Durability:* The consolidant effectiveness should not be lost as a consequence of exposure to environmental weathering processes and the consolidant itself must not give rise to harmful products as a consequence of ageing [8].

According to conservation principles, a further requirement of stone consolidants is reversibility, i.e. it should be possible to undo a consolidation treatment at some future date [7,16]. However, this is not feasible in practice for stone consolidants, apart from thermoplastic organic resins by dissolution in solvents. Even in this latter case, it is however unlikely that the consolidant is completely removed from stone pores and the treated stone would likely be damaged by consolidant removal [30]. Consequently, stone consolidants are usually required to be at least retreatable, i.e. it should be possible to re-treat the stone with either the same or a different consolidant in the future [16].

A further reason that makes it a very challenging task to evaluate the effectiveness, compatibility and durability of a consolidant

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