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An innovative phosphate-based consolidant for limestone. Part 2: Durability in comparison with ethyl silicate

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HIGHLIGHTS

- Durability of a new phosphate consolidant for limestone was investigated.
- Wetting–drying, freezing–thawing and salt crystallization cycles were performed.
- Changes in weight, dynamic modulus, tensile strength and porosity were monitored.
- Limestone samples treated with the phosphate consolidant exhibited a good behaviour.
- Comparative samples treated with ethyl silicate underwent sensible deterioration.

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ABSTRACT

The durability of a new phosphate consolidant for limestone, based on formation of hydroxyapatite (HAP), was investigated in comparison with ethyl silicate (ES). Untreated, HAP- and ES-treated samples were subjected to repeated wetting–drying, freezing–thawing and salt crystallization cycles. The weathering effects were monitored in terms of alterations in visual appearance, weight, dynamic elastic modulus, tensile strength and pore size distribution. HAP samples performed better than untreated samples and underwent less deterioration in original properties than ES samples. ES samples, subjected to salt crystallization cycles when the treated layer was still hydrophobic, experienced detachment of the consolidated layer.

1. Introduction

To overcome the limitations that commercial consolidating products exhibit when applied to porous carbonate stones, the use of a new phosphate-based consolidant has recently been proposed [1]. The innovative treatment is based on the formation of hydroxyapatite (HAP) directly inside the stone, as the reaction product between an aqueous solution of diammonium hydrogen phosphate (DAP) and the calcitic substrate [1]. So-formed HAP is able to effectively bond stone grains, thus restoring stone cohesion and improving mechanical properties [1].

In Part 1 of this study [2], the effectiveness and compatibility with the substrate of the new phosphate treatment were systematically investigated and compared with those of ethyl silicate (ES), which is nowadays the product most widely used in the field for stone consolidation. In terms of *effectiveness*, the HAP-treatment proved to be able to penetrate deep into the stone (about 10 mm, similarly to ES) and result in significant mechanical strengthening, although slightly lower than that obtained by ES (for HAP and ES, increases in dynamic elastic modulus of +47% and +61%, respectively, and in tensile strength of +27% and +47%, respectively, were obtained) [2]. Notably, the curing period is sensibly different between the two treatments, only 2 days of reaction with DAP for the HAP-treatment and nominally 1 month for ES, hence the much shorter curing time is a first advantage of the new phosphate consolidant (which however also involves a second treatment for

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24 h with a limewater poultice after DAP application, thus resulting more laborious than the ES treatment). In terms of *compatibility* with the substrate, the HAP-treatment caused very small colour change, as well as very limited alterations in pore size distribution and transport properties of liquid water and water vapour, which on the contrary were altered to a higher extent by ES [2]. In particular, HAP leaves stone water transport properties basically unaltered, which can be considered as a second strong advantage compared with ES. Indeed, ES induces temporary hydrophobicity that may last for several months after the treatment, thus impeding any water-based treatment after consolidation and possibly leading to stone exfoliation, if water and salts are trapped behind the consolidated layer.

Considering its ability to overcome the two main limitations of ES (i.e., the prolonged curing time and the temporary hydrophobicity after consolidation), the new HAP-treatment has the potential of becoming a better option for limestone consolidation compared with ES, whose performance on calcitic substrates is generally reported to be limited due to the lack of chemical bonding [1].

However, effectiveness and compatibility are only two of the main requirements that a valid stone consolidant must fulfil [3,4], as it must also guarantee a proper *durability*, intended as the ability of not losing its effectiveness as a consequence of exposure to environmental weathering processes and not giving rise to harmful products as a consequence of ageing [3]. A further important aspect, related to durability, is the possible incompatibility between the consolidated part and the unconsolidated substrate that may arise when treated stone is subjected to environmental weathering processes. Moreover a consolidant should either be reversible (i.e. it should be possible to remove it in the future), or at least should be retreatable [5,6]: the latter aspect was indirectly evaluated in Part 1 of this study [2], while the durability of the HAP-treatment is the subject of the present paper.

Similarly to the case of a consolidant's effectiveness and compatibility [2], also in the case of a consolidant's durability, aspects related to the type of weathering processes and stone parameters to be taken into consideration are not univocally identified.

Firstly, the weathering processes to be considered actually depend on the stone type on which the consolidant is applied, as well as the environmental exposure conditions, because different stone types are typically affected by different weathering processes. For instance, thermal weathering and chemical weathering originated by dissolution in rain are major issues in the case of marbles [7,8], but their effects are much less pronounced on other kinds of stone. Similarly, hygric and hydric dilatation properties induced by clays are a major weathering phenomenon in clay-bearing sandstones [9], but they have a limited influence on the durability of other lithotypes. In the case of porous limestones (on which the effectiveness and compatibility of the HAP-treatment have been evaluated in Part 1 of the study [2]), the most important and diffused weathering processes are freezing–thawing cycles and crystallization of soluble salts [10–14] (that are not equally important on scarcely porous stones such as marbles). Therefore, in the present paper, HAP-treated limestone was subjected to accelerated ageing to assess its durability against freezing–thawing cycles and salt weathering cycles. Moreover, as in the first study on the use of HAP as a consolidant for limestone the possible dissolution of newly formed soluble calcium phosphate phases was identified as a potential issue [1], in this study the durability against wetting–drying cycles was also specifically investigated.

Once defined the weathering processes that should be taken into consideration, what experimental procedures should be followed for accelerated ageing and what stone parameters should be monitored to assess the ageing impact still remain open questions. Indeed, several different national and international recommendations exist (e.g. European EN 12371 [15] and Italian UNI 11186 [16] for freezing–thawing test, European EN 12370 [17], RILEM MS-A.1 [18] and RILEM MS-A.2 [19] for salt weathering test) and several further different experimental procedures have been reported in the scientific literature, as the above-cited standards are often regarded as not fully reliable and/or effective [20]. The various methods differ in terms of experimental conditions (specimen type, salt type, salt solution concentration, drying conditions, etc.), as well as methods for assessing damage (visual inspection, measurement of weight, dynamic elastic modulus, tensile strength, porosity, etc.) [21]. The choice of the experimental conditions is very important, as they determine not only the duration of the tests, but also the type of damage induced by the tests (e.g. pulverization rather than crack formation), and hence the representativeness of the obtained results [21].

Considering all these aspects, in the present paper the HAP-treatment durability against wetting–drying, freezing–thawing and salt crystallization cycles was investigated by combining experimental conditions and assessment methods proposed in different sources, as detailed in the following. All the tests were carried out also on samples treated with ES, to obtain a sound evaluation of the possible use of HAP as a better option for limestone consolidation compared with ES.

2. Materials and methods

2.1. Stone

Globigerina limestone, a very porous stone used both in prehistoric temples and in baroque architecture in Malta, was used for the durability tests (the same lithotype was used also for assessing HAP effectiveness and compatibility [2]). Because of the specific environmental conditions in Malta (i.e., huge rising damp from the ground, containing high amounts of sulphates, and severe marine aerosol, containing high amounts of chlorides), in its natural environment Globigerina limestone is severely affected by salt weathering [22]. This makes the evaluation of the durability of Globigerina limestone to salt weathering after consolidation particularly fitting and important, in the view of conservation of real buildings and monuments made of Globigerina limestone. In the case of freezing–thawing cycles, this kind of weathering process is actually not very relevant for Globigerina limestone, as sub-zero temperatures are not frequent in Malta. However, the obtained results could be possibly extended to other porous stones with composition and microstructural features sufficiently similar to those of Globigerina limestone (carbonate content ~93 wt.%, open porosity ~40%, average pore radius ~2 μm [2]), for instance Lecce stone [23] or Noto stone [24].

For the experimental tests, cylindrical samples (5 cm height, 2 cm diameter), cubic samples (5 cm side) and prismatic samples ($7 \times 7 \times 2.5$ cm^3) were obtained from a slab of Globigerina limestone ("Franka" type [25]), quarried in the area of Qrendi and provided by Xelini Skip Hire and High-Up Service (Malta). For cubic and prismatic samples, during sawing particular attention was paid to keep trace of the original bedding planes, while cylindrical samples were core-drilled in the direction perpendicular to the bedding planes.

As recommended by Italian Recommendation NORMAL 20/85 for testing of consolidants [4] and specifically recommended in the scientific literature when the durability of consolidating treatments to salt crystallization needs to be evaluated [21], all Globigerina limestone samples used in this study were artificially weathered prior to consolidant application, with the aim of making the results as reliable as possible [1,26,27]. Preliminary artificial deterioration was performed by heating samples at 400 °C for 1 h, according to a previously developed methodology [1,26,27]. In Globigerina limestone, artificial deterioration by heating causes a sensible decrease in mechanical properties and increase in water absorption, ascribable to the formation of new nano-cracks as a consequence of calcite crystal deformation upon heating [27]. This kind of microstructural alteration is actually not fully representative of the type of deterioration that Globigerina limestone undergoes in the field, which is mainly powdering and alveolization caused by salt weathering and wind erosion. Consequently, pre-deterioration by salt crystallization might appear as more suitable to reproduce weathering conditions closer to those actually experienced in the field [28,29]. However, as discussed in detail in Part 1 of this study [2] and in the literature [7,30], pre-deterioration by accelerated salt crystallization cycles is hard to control and leads to samples heavily contaminated with salts (even after desalination), which would make the consolidant effects hard to be evaluated at this stage of research on HAP. For this reason, pre-deterioration by heating was preferred, as this procedure allows to obtain samples with homogenous and reproducible porosity and mechanical properties alteration, but free from salt contamination.