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CONSOLIDATION OF SUGARING MARBLE BY HYDROXYAPATITE: SOME RECENT DEVELOPMENTS ON PRODUCING AND TREATING DECAYED SAMPLES

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Abstract

Consolidation of sugaring marble (i.e., marble affected by granular disaggregation) still lacks fully effective solutions. Consequently, the use of an innovative phosphate-based treatment, aimed at bonding calcite grains by formation of hydroxyapatite at grain boundaries, has recently been proposed. In this paper, firstly a novel method for producing artificially decayed marble samples, by contact with a heating plate, is proposed. Then, some results are presented about the effectiveness and the compatibility of two different formulations of the phosphate treatment, differing in terms of concentration of the phosphate precursor (3.0 M or 0.1 M aqueous solutions of diammonium hydrogen phosphate, DAP), possible ethanol addition to the DAP solution and number of DAP solution applications (1 or 2). The results of the study point out that the new weathering method allows to obtain specimens with a gradient in microstructural and mechanical properties with thickness, just like naturally weathered samples. Both phosphate treatments were able to significantly improve marble cohesion, without causing significant changes in thermal behaviour and aesthetic appearance after treatment. The addition of small quantities of ethanol to the DAP solution seems to be a very promising method for favouring HAP formation and improving the treatment performance.

Keywords: Grain loss; Thermal ageing; Thermal diffusivity; Calcium phosphates; Ethanol.

1 Introduction

The so-called "sugaring" of marble is a degradation phenomenon that consists in grain detachment and loss, leading to severe alteration of the original morphology of architectural elements and sculptures. As an example, sugaring affecting carved marble decorations in the Monumental Cemetery in Bologna (Italy, XIX century) is illustrated in Figure 1.

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Figure 1: Sugaring marble in the Monumental Cemetery in Bologna, Italy (XIX century).

Sugaring originates from cyclical thermal excursions that outdoor marble elements experience. Daily temperature variations cause anisotropic deformation of calcite grains of which marble is composed, with the result that micro-cracks open at grain boundaries and grains start to detach (Siegesmund *et al.*, 2000).

In spite of the wide diffusion of this weathering phenomenon, no fully satisfactory treatment for effectively and durably stopping marble sugaring has been developed yet. Organic polymers exhibit limited compatibility and durability, alkoxysilanes give modest mechanical improvement and long-term performance, lime-based treatments (also at the nano-scale) are affected by low penetration depth and effectiveness, ammonium oxalate provides insufficient consolidation and long-term protection (Sassoni and Franzoni, 2014b).

For this reason, an innovative inorganic phosphate treatment has recently been proposed for sugaring marble consolidation (Sassoni *et al.*, 2015). The phosphate treatment, originally proposed for limestone consolidation (Sassoni *et al.*, 2011) and marble protection (Naidu and Scherer, 2014), is based on the reaction between the calcitic substrate and an aqueous solution of di-ammonium hydrogen phosphate (DAP) to form hydroxyapatite (HAP).

Results obtained so far on the use of HAP for consolidation of sugaring marble are extremely promising, in terms of both effectiveness and compatibility of the new treatment (Sassoni *et al.*, 2015). However, further research is still needed, because:

(i) Experimental tests on the HAP-treatment have been mainly carried out on marble samples artificially weathered by heating at 400 °C for 1 hour in oven, according to a procedure previously developed by the authors (Sassoni *et al.*, 2011; Franzoni *et al.*, 2013; Sassoni and Franzoni, 2014). This procedure proved to be effective in producing samples with characteristics very similar to those of naturally sugaring samples, namely with increased open porosity and coarsening of the pore size, with respect to the unweathered condition. However, samples produced in that way are *entirely* decayed, whereas naturally weathered samples exhibit a *gradient* in microstructural and mechanical properties, the superficial part being highly damaged and the inner part being basically undamaged. As one of the goals of consolidation is to restore cohesion in the decayed part of a stone, so as to bring it back to the condition before weathering, the use of artificially weathered samples with a gradient in properties is a very important aspect for studying new consolidants (Lubelli *et al.*, 2015).

(ii) A recent study by the Authors has shown that the addition of ethanol (EtOH) to the aqueous DAP solution, used to react marble to form HAP, is able to significantly improve HAP formation (Graziani *et al.*, *in press*). EtOH addition resulted in better coverage of marble surface by HAP and a reduction in cracking of the HAP layer, as well as a reduction in the DAP concentration, hence a beneficial effect is expected also in the case of sugaring marble consolidation.

Therefore, in the present study some preliminary results are presented about:

(i) a new methodology to produce artificially weathered marble samples with a gradient in microstructural and mechanical properties;
(ii) the effects of adding ethanol to the aqueous DAP solution, in terms of consolidating efficacy and compatibility with the substrate.

2 Materials and Methods

2.1 Marble

Carrara marble was used for the tests, considering its wide diffusion in historic architecture and sculpture. For tests on artificial weathering, samples with 2.5×2.5×5 cm^3 dimensions (provided by BasketweaveMosaics.com, USA) were used. For tests on the phosphate treatments effects, samples with 2×2×3 cm^3 dimensions (provided by Imbellone Michelangelo s.a.s., Italy) were used.

2.2 Artificial weathering of marble samples

For producing a gradient in marble properties, samples were put in contact with a heating plate already at 350 °C, as illustrated in Figure 2. Four thermocouples, put in contact with sample surface at various distances from the heating plate (0, 10, 25 and 50 mm) and connected to a pc, were used to continuously record the temperature reached by the sample at different heights from the plate. To identify the most suitable time of heating, the method described in the following was used.

Assuming that the heat flow from the heating plate is one-dimensional (which is the case if sample sides are covered with an insulator, so that heat losses are prevented), the equation governing the heat flow is:

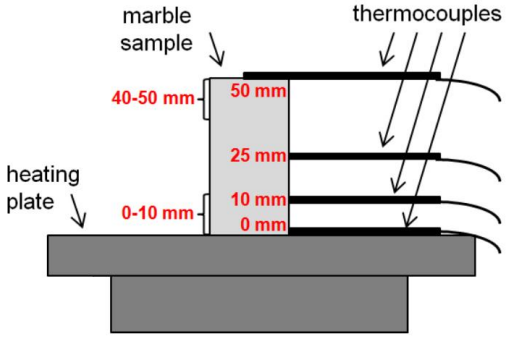

Figure 2: Experimental set-up for accelerated ageing of marble samples

$$\frac{\partial T}{\partial t} = \frac{\partial}{\partial x}\left(k(x,t)\frac{\partial T}{\partial x} \right) \quad (1)$$

where T is the temperature, t is the time, x is the distance from the heating plate and k is marble thermal diffusivity. It can be demonstrated, for the case of constant k, that the sample top at 50 mm from the heating plate is not subject to warming (and hence a gradient in sample properties can be expected) if the time of heating is limited to:

$$t \leq \frac{0.1H^2}{k} \quad (2)$$

where H is the sample height. To estimate the time of heating, preliminary tests were carried out to determine the thermal diffusivity of Carrara marble (no reference value was found in the literature). A 5 cm side cubic sample was placed in contact with the heating plate (initially cold) and then heated from 24 °C to 270 °C, heat losses being prevented insulating sample's lateral sides with a porous stone and top with a glass fibre board. Temperature variations at different heights from the heating plate (0, 10, 20, 30, 40 and 50 mm) were measured as a function of time, by means of six thermocouples inserted inside purposely drilled holes. By fitting the $T(x,t)$ curves measured at different heights from the plate to a numerical solution of Eq. (1), $k(x,t)$ was found to vary parabolically with temperature, decreasing from 1.6×10^{-6} m^2/s at 24 °C to 4.0×10^{-7} m^2/s at 270 °C. A very good fit was obtained to $T(x,t)$ measured at each of the thermocouples, so this model can be used in the future to simulate arbitrary heating procedures. The details of these calculations will presented in a future publication. The decrease in k with T is thought to be a consequence of microcracks opening as temperature increases. Using Equation (2), with H = 5 cm, the times of heating corresponding to the limiting values of k were calculated and times of about 2.5 and 10 minutes were obtained.

The effects of heating samples by contact with the heating plate at 350 °C for 5 and 10 minutes were evaluated by comparing the two parts of the sample at 0-10 mm and at 40-50 mm from the plate (hence, respectively, directly in contact with the plate and at the opposite side, Figure 2). This comparison was performed in terms of ultrasonic pulse velocity (*UPV*) and elastic modulus (E) determined by nanoindentation test. *UPV* was measured, before and after heating, by transmission method, using a PUNDIT commercial instrument with 54 kHz transducers and a rubber couplant between the sample and the transducers. E was calculated as the slope of the unloading part of the force-displacement curve obtained by subjecting the marble sample to the following loading cycle: loading to 400 μN, holding, unloading. The loading cycle was performed using a Digital Instruments AFM with integrated nanoindentation capability.

2.3 Consolidation of marble samples

As optimization of the novel weathering procedure is still in progress (cf. § 3.1), samples to be treated with the phosphate consolidants and untreated references were preliminarily artificially weathered by heating at 400 °C for 1 h in oven, according to a procedure previously developed by the Authors (Sassoni *et al.*, 2011; Franzoni *et al.*, 2013). Two treatment conditions were considered:

(i) "3.0 M DAP". These samples were firstly treated with a 3.0 M solution of DAP (Sigma-Aldrich, reagent grade) and de-ionized water, applied by brushing 15 times. At

the end of brushing application, the samples were wrapped in a plastic film to prevent solution evaporation and left to react for 48 hours. Then, they were unwrapped, rinsed with water and left to dry. Finally, they were treated with a saturated solution of calcium hydroxide (Sigma-Aldrich, reagent grade) in de-ionized water (so-called limewater), applied by poultice. The poultice was prepared using limewater and dry cellulose pulp (MH300 Phase, Italy) with a weight ratio 6:1. After wrapping in a plastic film for 24 hours and then drying, samples were ready for characterization tests.

(ii) "0.1 M DAP with 0.5 wt% EtOH + 0.1 M DAP". These samples were treated according to the method recently proposed by Graziani *et al.*, *in press*. As a first step, samples were treated by immersion in a 0.1 M DAP solution with addition of 0.5 wt% EtOH for 24 hours. After rinsing with water and drying, samples were then subjected to a second treatment with a 0.1 M DAP solution, again applied by immersion. After drying, samples were ready for tests.

The consolidating efficacy of the two treatments was evaluated in terms of increase in *UPV*, with respect to the untreated references. *UPV* was selected as it is very sensitive to healing of microcracks and is hence frequently adopted to assess the efficacy of stone consolidants (Weiss *et al.*, 2002). *UPV* was measured with a Matest commercial instrument with 55 kHz transducers, using a rubber couplant between the samples and the transducers.

The compatibility of the two treatments was evaluated in terms of alterations in thermal behaviour and aesthetic appearance. As marble decay is mainly induced by thermal excursions, the evaluation of the thermal behaviour of consolidated marble is very important (Ruedrich *et al.*, 2002). Untreated and treated samples (30×9×7 mm^3) were subjected to the following thermal cycle, using a push-rod dilatometer Netzsch mod. 402 E (Netzsch-Geratebäu GmbH, Selb, Germany): (i) heating from room temperature to 80 °C at 1 °C/min, (ii) isothermal dwell for 1 hour at 80 °C, (iii) cooling to room temperature at 1 °C/min. The maximum heating temperature was chosen to simulate environmental conditions experienced in the field (Siegesmund *et al.*, 2000). The residual strain after cooling to room temperature (ε_r) was considered. The aesthetic alteration was evaluated in terms of colour change, defined as $\Delta E = (\Delta L^{*2} + \Delta a^{*2} + \Delta b^{*2})^{1/2}$. The colour parameters L*a*b* (L* = black÷white, a* = red÷green, b* yellow÷blue) were measured using a Spectrophotometer CM-2600d, Konica Minolta Sensing.Inc.

3 Results and Discussion

3.1 Artificial weathering

For marble samples put in contact with the heating plate initially at 350 °C for 5 and 10 minutes, a remarkable temperature gradient is present inside the samples, as illustrated in Figure 3 (left). The thermocouple in contact with the sample and the plate registers a temperature of 312-335 °C after 5 and 10 minutes, respectively (both temperatures being lower than the initial one because contact with the sample lowers the plate temperature). At a height of 10 mm from the plate the temperature is sensibly lower (106-117 °C, respectively). At the top of the sample (50 mm height) the temperature is still quite close to ambient temperature after 5 minutes (42 °C) and a little higher after 10 minutes (53 °C).

Correspondingly to this temperature gradient, a significant gradient in mechanical properties was registered.

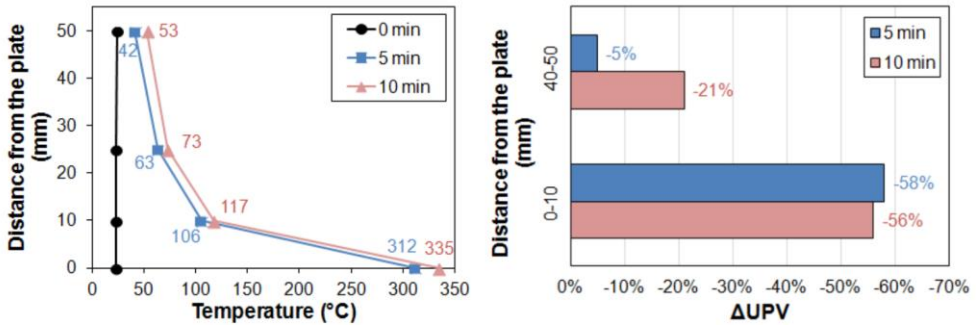

Figure 3: Effects of accelerated ageing: temperature (left) and UPV variation (right) at different heights from the heating plate after 5 and 10 minutes .

In terms of *UPV*, decreases with respect to the initial condition are reported in Figure 3 (right). In the sample part close to the plate (0-10 mm), a strong *UPV* decrease is registered after 5 minutes (-58%). When contact with the plate is increased up to 10 minutes, a similar *UPV* decrease is recorded in this sample part (-56%). However, the situation is quite different at the top of the sample (40-50 mm from the plate). While after 5 minutes only a minor *UPV* decrease is registered (-5%), in agreement with the limited temperature reached in this layer (42 °C), after 10 minutes a non-negligible *UPV* decrease (-21%) is registered also in this layer, in agreement with the higher temperature reached (53 °C).

Based on these results, a time of heating of 5 minutes seems to be the most suitable, as it allows to obtain a marked gradient in *UPV* across sample thickness, without significantly altering properties at the extremity of the sample far from the plate. Accordingly, in the sample heated for 5 minutes a marked difference (-75%) was registered also in terms of elastic modulus *E* determined by nanoindentation, between parts at 0-10 mm and 40-50 mm from the heating plate.

However, results reported above were obtained for a sample that had been heated over the plate without insulating the sides and the top, so that some heat loss was experienced. Consequently, conditions for calculating the time of heating using Equations (1) and (2) were not strictly respected. For samples subjected to artificial weathering with thermal insulation, an even more pronounced gradient in temperature and hence in microstructural-mechanical properties is expected. Tests involving insulated samples are currently in progress. On these samples, a systematic evaluation of mechanical property alteration as a function of the distance from the heating plate will be carried out by nanoindentation. Being a non-destructive technique (causing only nanometric damage to calcite grains), it will be possible to derive profiles of sample elastic modulus *E* after artificial weathering and after consolidation by the phosphate treatment.

3.2 Consolidation

The effects of the two consolidating treatments are summarized in Table 1. Both treatments proved to be highly effective in restoring marble mechanical cohesion, being able to bring *UPV* almost back to the value before artificial weathering (3.2 km/s).

Table 1: Effects of the two consolidating treatments.

Specimen	UPV (km/s)	ε_r (mm/m)	ΔE*
Untreated	0.6	0.24	-
3.0 M DAP	2.9	0.23	1.5
0.1 M DAP with 5 wt% EtOH + 0.1 M DAP	2.2	0.16	1.1

Between the two treatments, that involving a higher DAP concentration allowed to achieve a higher *UPV* increase. However, it is remarkable that the treatment involving EtOH addition allowed to achieve a comparable increase in *UPV*, notwithstanding the much lower (30 times) concentration of DAP used. This can be ascribed to the beneficial effect of: (i) adding EtOH, that according to some studies favours HAP formation (Lerner *et al.*, 1989); (ii) applying double treatments, that allow to achieve a better coverage of calcite grains, without causing excessive growth of the HAP film (Graziani *et al.*, in press).

In terms of thermal behaviour after consolidation, both treatments gave good results, causing a residual strain after the heating-cooling cycle less than or equal to that of the untreated reference (Table 1). This is very important, because if an increase in residual strain were found, an increase in sensitivity to thermal cycles should be expected (Ruedrich *et al.*, 2002). Notably, the residual strain of the sample treated with EtOH addition is very close to the value exhibited by marble before artificial weathering (0.15 mm/m). This is a positive feature, as stone consolidants should ideally modify the properties of decayed stone so as to bring them back to the condition before decay.

In terms of aesthetic appearance, the two consolidating treatments exhibited a good compatibility (Table 1), in both cases leading to a colour change ΔE^* lower than the threshold commonly accepted for stone consolidants ($\Delta E^* = 5$) and even lower than the human eye detection limit ($\Delta E^* = 3$). The ΔE^* caused by the treatment with EtOH addition was actually lower than the other treatment, which can be ascribed to the lower DAP concentration involved by this treatment condition.

4 Conclusions

In the present paper, some recent developments were reported on the production of artificially weathered samples for testing of consolidants and on the effects of two different formulations of the hydroxyapatite-based treatment for consolidation of sugaring marble. Heating marble samples by contact with a heating plate at 350 °C for 5 minutes proved to be an effective way to produce samples with a marked gradient in mechanical properties (just like naturally weathered marble), namely an *UPV* decrease of - 58% at a distance f 10-20 mm from the plate and basically no damage at a distance of 40-50 mm. As for consolidation, the double treatment involving the addition of a very small quantity of ethanol to a DAP solution with low concentration (0.1 M DAP) produced a significant mechanical improvement, with only minor alterations in thermal behaviour and aesthetic appearance. This suggests that ethanol additions to the DAP solution are a very promising method for favouring HAP formation and improving the treatment performance.

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