



Resistance to simulated rain of hydroxyapatite- and calcium oxalate-based coatings for protection of marble against corrosion



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ABSTRACT

Dissolution in pure and acid rain is among the main environmental degradation processes of marble. Coatings based on hydroxyapatite (HAP) have been proposed to prevent marble corrosion, providing encouraging results. In this paper, the resistance to dissolution was investigated on marble treated with different HAP-treatment formulations and compared to commercial ammonium oxalate. The ability of the coating to prevent corrosion was evaluated by performing wetting/drying cycles, by a custom-designed apparatus simulating rain. When ethanol is added to the solution used to form HAP, a significant reduction in calcium ions leached from marble is found, which is indicative of reduced corrosion.

1. Introduction

Marble is among the most used materials in historic and modern architecture, but when exposed to the outdoor environment, it experiences severe decay, mainly because of the characteristics of calcite, its main mineral constituent [1,2]. Calcite has a relatively high solubility in water (which leads to the surface recession of marble elements) [1–7] and an unusual anisotropic thermal behavior (which leads to marble sugaring at the micro-scale and bowing of marble slabs at the macro-scale) [8–10]. Reaction products that can form as a result of calcite interactions with the environment, such as gypsum and calcium nitrate, also have very high solubility, thus further causing surface recession and threatening the conservation of marble artifacts.

Dissolution and consequent surface recession of marble can occur in both acidic and neutral environment [11]. In particular, there are three main processes leading to dissolution of marble on site.

- i) Dissolution in pure rain in equilibrium with atmospheric CO₂: pH in these conditions is around 5.6, but might span from 5 to 7 in European environments [6];
- ii) Dissolution in an acidic environment, where the acidic pH results from the presence of atmospheric pollutants, such as SO₂ and NO_x, that can push the pH down to 4;
- iii) Dry deposition of gaseous atmospheric pollutants, such NO_x and, mostly, SO₂, that cause conversion of marble into more soluble products, such as gypsum and calcium nitrate, which are easily washed away by rain [12–14].

According to current data and to predictions for this phenomenon in European climates in the near future, dissolution in pure rain (the so-called Karst effect [6]) is the main mechanism. It accounts for about 50–90% of the total surface recession of carbonate stones [6].

The rate and mechanism of calcite dissolution fall into different regimes, depending on the rain pH: i) acid solutions, ii) neutral and alkaline solutions, and iii) transitional regime. The boundaries between the regimes are at about pH 4 and 5.5 for KCl solutions at 25 °C, but they might vary slightly. What changes substantially in each regime is the dependence of dissolution rate upon H⁺ concentration and presence of Ca²⁺ in solution [11]. No significant differences are expected for a pH change within the ambient range, while dissolution rate rises significantly as pH drops in the acid range and dissolution kinetics may vary significantly when switching from one regime to another.

Dissolution has caused the corrosion of several millimeters from historical surfaces in the past centuries, resulting in the damage of architectural and sculptural details, and further recession is to be expected in the future, with the consequent loss of precious material. Surface recession depends on several parameters and can be modeled by different equations (for example, according to the Lipfert equation [15], surface dissolution is dependent on the solubility of calcium carbonate in water in equilibrium with CO₂, the amount of precipitation per year, the H⁺ concentration, the deposition velocity of SO₂ and HNO₃, and the concentrations of SO₂ and HNO₃). For this reason, current data and estimates for the near future vary to a very high extent, depending on the geographical location and on the rain pH: values between 4 and 130 μm/year surface recession are predicted by Lipfert

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[15] for carbonate stones, while values of about 14 $\mu\text{m}/\text{year}$ are indicated in [6]. In the latter case, 96–99% of recession is because of the Karst effect.

For this reason, the search for a suitable protective treatment that might retard or prevent dissolution is one of the main goals in cultural heritage preservation. However, none of the currently used protectives can be considered satisfactory, because they either lack efficacy (typically, in the case of traditional inorganic products [16–18]) or efficacy and/or durability (typically, in the case of organic products [19–22]).

To overcome these limitations, treatments based on hydroxyapatite ($\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$, HAP) have been proposed for marble protection [23–25], in view of the very low solubility and dissolution rate of the mineral HAP [23,26]. Together with low solubility and slow dissolution rate, HAP has shown an excellent compatibility with calcite substrates and is non-hazardous for the operators and the environment [10,27–30], which also pushed towards its use for stone conservation. HAP can be obtained by reacting a solution of diammonium hydrogen phosphate ($(\text{NH}_4)_2\text{HPO}_4$, DAP) with calcium ions, coming from the substrate and/or externally supplied by adding CaCl_2 to the DAP solution [23–26]. Notably, no unreacted DAP, chlorides (when CaCl_2 is added to the DAP solution) or reaction by-products (such as ammonium carbonate [2]), all potentially harmful to the stone, remain after rinsing with water at the end of the treatment, as verified in previous studies by several techniques, i.e. SEM-EDS [10,26–29,32], FT-IR [24,27–29], Raman [10], and GI-XRD [32].

The advantage of the low solubility of HAP was first suggested in [23] and later evaluated in [24] and [25]: tests carried out so far on both marble powders and massive samples confirmed that HAP treatments can increase the resistance of marble to dissolution. In particular, tests performed on marble powders [24] indicated that, by adding ethanol (EtOH) to the DAP solution, it is possible to significantly enhance surface coverage while reducing cracking and porosity, because ethanol influences the hydration shell of ions in the solution, thus favoring HAP formation [24,31]. This, in turn, boosts the resistance of the samples against corrosion [31]. Moreover, superimposed layers formed at low DAP concentration were found to have a higher efficacy than one layer formed at high DAP concentration, because in this latter case the HAP layer is cracked [24].

The results of acid resistance tests carried out so far on marble powders [24] still need to be validated on massive specimens, i.e. samples of at least a few square centimeters surface, so as to get closer to the conditions of marble buildings and statues on site. In fact, the formation of HAP coatings and their resistance to dissolution in acid may differ between powders and massive specimens: in addition to the different specific surface area, in powders the coverage of each particle and its resistance to dissolution is basically independent of the behavior of the other particles; on the contrary, in massive samples each calcite grain, having a different orientation, may positively or negatively influence the surrounding grains. Indeed, on the one hand, grains with the most favorable crystallographic orientation may promote HAP nucleation and spread to the adjacent grains; on the other hand, grains with the least favorable orientation and hence poor coverage by HAP may allow acid to reach the marble substrate and trigger dissolution at the calcite-HAP interface also in adjacent grains, in spite of their good initial coverage with HAP. Therefore, in this paper the resistance to dissolution was investigated on massive samples of Carrara marble, treated with different concentrations of the DAP solution, with and without ethanol addition, and by performing single and double applications. The efficacy of the DAP-based treatments was compared to that of ammonium oxalate (AmOx), which is currently one of the most used inorganic protectives for marble [16,17,33–36].

To better reproduce the real conditions experienced by marble on site, resistance to dissolution was evaluated with a custom-designed apparatus able to simulate rain instead of using an apparatus with a finite volume of acid, as in references [24,25]. Unlike dissolution tests carried out by exposing samples to acid solutions in a beaker, which are

very useful for screening the most promising treatments, this apparatus prevents accumulation of calcium ions (that originate from marble dissolution) near the marble surface, which would reduce the dissolution rate and hence possibly influence the reliability of the results [11,24,37]. Moreover, by means of this rain simulating apparatus, it is also possible to prevent any influence deriving from the stirring rate of the solution, which might also have an impact on the dissolution rate [11], and also to reproduce the slight mechanical action of rain drops hitting the surface of the stone [38,39]. Finally, differently from references [24,25], calcium and phosphate ion concentrations were determined to measure the dissolution of the substrate and the coating, instead of pH shift over time.

2. Materials and methods

2.1. Materials

Specimens ($30 \times 30 \times 20 \text{ mm}^3$) were sawn from a single slab of Carrara marble (supplier: Imbellone Michelangelo s.a.s.). DAP (> 99%, Sigma Aldrich), calcium chloride (assay > 99.0%, Sigma Aldrich), ethanol (Fisher-Scientific) and ammonium oxalate ($\geq 99.99\%$, Sigma Aldrich) were used for the treatments. Prior to treatment and characterization, prisms were rinsed with water and ethanol to remove possible surface impurities and dried in an oven at 40 °C until constant weight.

2.2. Treatments

For each treatment, duplicate samples were used. The number of samples for each treatment was considered sufficient based on preliminary tests carried out on marble powders and $1 \times 1 \times 1 \text{ cm}^3$ cubes, for which no significant differences in surface coverage or in coating morphology, composition and acid resistance were found among different samples treated with the same procedure [24].

The conditions used are summarized in Table 1 and described in the following. Two reference samples were left untreated (*Samples "UT"*). *Samples "0.1MED"* were treated twice, the first time by total immersion for 24 h in an aqueous solution containing 0.1 M DAP + 0.1 mM CaCl_2 + 0.5 wt% EtOH, and the second time (after drying) by total immersion for 24 h in an aqueous solution containing 0.1 M DAP + 0.1 mM CaCl_2 (no ethanol was added). CaCl_2 was added to prevent dissolution of the substrate [32]. Ethanol was added only during the first treatment, because its addition to the second treatment had proven to make the layer too thick and to cause no further benefit [24]. This procedure was the most effective among those investigated in preliminary tests on powders [24]. *Samples "3M"* were analyzed for comparison's sake, using another formulation of the DAP treatment

Table 1

Labeling and description of the treatments. In the labels, "0.1M" and "3M" indicate the concentration of DAP in the treating solution, "E" indicates the addition of ethanol, "D" indicates the double application of a treatment, "AmOx" stands for treatment by ammonium oxalate.

Specimen	Treatment description	Application method
UT	Untreated	–
0.1MED	First treatment: 0.1 M DAP + 0.1 mM CaCl_2 + 0.5 wt.% EtOH	Immersion
	Second treatment: 0.1 M DAP + 0.1 mM CaCl_2	Immersion
3M	First treatment: 3 M DAP	Brushing
	Second treatment: 1.7 g/l $\text{Ca}(\text{OH})_2$	Poultice
AmOx	5 wt.% AmOx	Brushing
AmOx + 0.1 M	First treatment: 5 wt.% AmOx	Immersion
	Second treatment: 0.1 M DAP + 0.1 mM CaCl_2	Immersion

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