Corrosion Resistance Surface Treatment for Marble | 2013-07

Princeton University

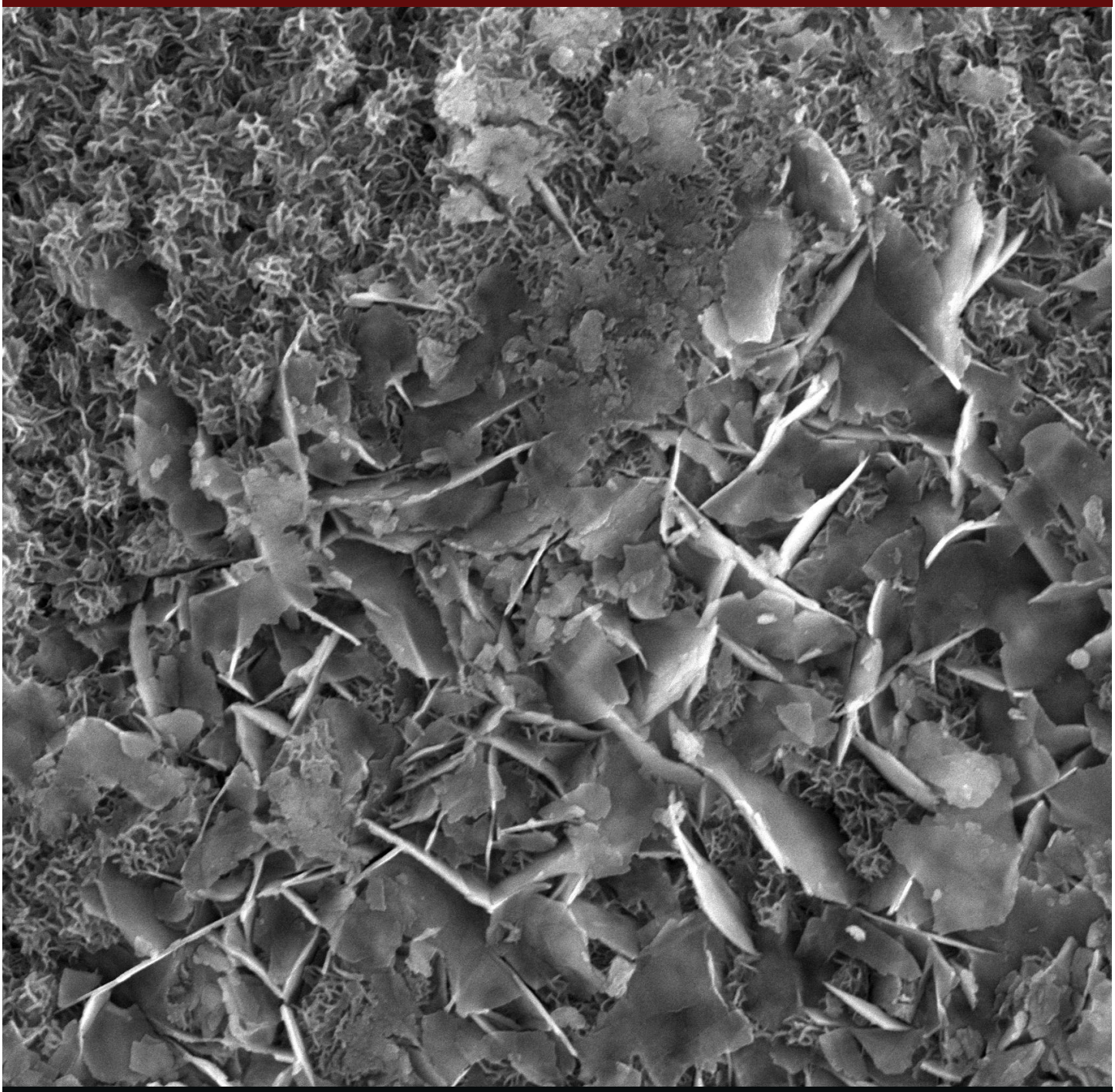

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Table of Contents

Executive Summary 3

Introduction 4

Experimental Procedure 4

Materials 4

Methods 5

Results and Discussion 7

Consolidation 7

Acid Resistance 9

Nucleation and Growth 12

Conclusions 17

Publications resulting from this grant 18

Acknowledgments 19

References 19

Executive Summary (400 words)

Marble is used in many of our most precious monuments and sculptures, but it deteriorates when exposed to water, owing to its relatively high solubility. Consequently, researchers have sought methods to enhance the durability of marble through the use of environmentally friendly chemical treatments. A particularly promising route, introduced by our research group, is to expose marble to a solution of an ammonium phosphate salt, which results in the formation of an invisibly thin coating of hydroxyapatite (HAP), which is the very durable mineral in tooth and bone. In the present study, we explored several aspects of the application of this chemistry. The phosphate salt chosen was diammonium hydrogen phosphate, which produces coatings about ten microns thick in one day. The solution is nontoxic and reasonably inexpensive, and the rate of reaction is satisfactory for field application by brushing or poulticing. By adding small concentrations of a calcium salt to the solution, the rate of formation is enhanced, and dissolution of the marble substrate is suppressed. Unfortunately, the acid resistance conferred by the film is far less than expected, because the film remains porous. Future work will attempt to eliminate the porosity by using organic templates to control the growth process.

The performance of the phosphate treatment as a consolidant for marble and limestone has proved to be exceptionally good. After being damaged by thermal treatment, the dynamic modulus of marble and limestone is returned to its original value by a single treatment with the phosphate consolidant. Direct comparison shows that it is superior to commercial silicate consolidants. Moreover, the HAP treatment does not substantially reduce the moisture transport through the stone, and does not confer hydrophobicity. Therefore, we expect this procedure to become widely used for treatment of weathered carbonate stones.

For quartzitic stones, silicate consolidants are superior, but they render the stone hydrophobic, which prevents moisture transport and hinders additional treatments, such as application of mortars or renders. We discovered that the hydrophobicity of the consolidated stone could be strongly reduced by a simple rinsing with an aqueous solution containing only about 16% ethanol. This allows the stone to be made hydrophilic within a week or two of consolidation, without excessive release of VOCs. We expect this procedure to be of great interest to conservators.

Introduction

The study supported by NCPTT Grant MT-2210-12-NC-08 culminated in a series of tests of the acid resistance of marble treated with hydroxyapatite (HAP) [Naidu and Scherer 2012; Naidu et al. 2013a], as well as oxalate [Matteini 2011], tartrate [Weiss et al. 2000], and silicate coatings [Wheeler 2005; Scherer and Wheeler 2009] that have been discussed in the literature. The dissolution rate studies were complemented by detailed analysis of the nucleation and growth process of hydroxyapatite on calcite; those results, which are summarized here, are the subject of a detailed publication that is in preparation [Naidu and Scherer, 2013]. In addition, the performance of HAP as a consolidant for limestone and marble, alone and in combination with silicate consolidants, has been investigated [Naidu et al. 2013b].

Experimental Procedure

Materials

Most tests were performed on Indiana limestone and Carrara marble obtained from Pasvalco (Closter, NJ). Indiana limestone (IL) is composed mainly of calcite ($CaCO_3$, > 97%) and minute amounts of $MgCO_3$, Al_2O_3 and SiO_2. Most of the calcite is in the form of calcite-cemented oolites, with trace amounts of sparry crystals. IL has a porosity of approximately 14% (Perry et al. 1954). IL samples used in this study were core-drilled cylinders with a diameter of 2 cm and a height of 5 cm. Carrara marble is white, fine-grained calcite with porosity of about 0.5%.

The diammonium hydrogen phosphate (DAP) (puriss. p.a. >99%) and calcium chloride ($CaCl_2 \cdot 2H_2O$, assay >99.0%) were both purchased from Sigma-Aldrich, their concentrations made up with demineralized water. Conservare® OH-100, which consists of small oligomers of tetraethoxysilane, was obtained from ProSoCo, Inc. and diluted in a volumetric ratio of

ethanol:water = 1:3 before application. This was done as undiluted Conservare was found to form cracks inside the stone [Scherer and Wheeler 2009]. Ammonium oxalate was obtained from XX while ammonium hydrogen tartrate (HCT) and HCT rinse were obtained from ProSoCo. The HCT rinse consists of limewater, which was expected to react any leftover HCT solution.

For spectral analysis, commercial HAP nanopowder (< 200 nm, > 97% purity) was obtained from Sigma-Aldrich. Trimethylethoxysilane (TMES, > 98%) was obtained from Sigma-Aldrich, sodium hydroxide (NaOH, ACS reagent grade > 97%) from ACROS and hydrochloric acid (HCl) from EMD Chemicals. Deuterium oxide (D_2O, >99.9% purity) was purchased from Cambridge Isotope Laboratories, Inc.

Ethanol solvent (200 Proof) was manufactured by Decon Labs, Inc., decane (99.5% purity) from Fisher-Scientific and hexane (assay >98.5%) from EMD Chemicals. The HNO_3 was purchased from Sigma-Aldrich.

Methods

For the study of acid resistance, the stones were coated by immersion in solutions of DAP (with or without addition of $CaCl_2$), Conservare OH, ammonium oxalate, or HCT. After curing, samples were introduced into a stirred beaker of water at a given pH, and the change in pH was monitored continuously. Before and after acid exposure, the surface was examined by SEM to evaluate the extent of coverage, the composition was analyzed by EDX, and the crystal orientation was determined using electron back-scattered diffraction (EBSD). Details are provided in Naidu et al. (2013a).

For the study of consolidation, the stone samples were first damaged by heating, following a procedure developed by our group (Sassoni et al. 2011; Franzoni et al. 2012). The

stones were then treated by immersion and dried at room temperature under a flow of air from a fan. The treatments are summarized in Table 1. The acoustic velocity was measured with a PUNDIT device (CNS Farnell) using 54 kHz transducers. To measure sorptivity, cylindrical Indiana limestone samples were suspended from a balance and a water dish was raised slowly until contact with the bottom of the sample was established. Mass increase was then continuously recorded by a computer data acquisition system (DASYLab) and the sorptivity, *S* calculated from the initial linear portion of a plot of (mass change)^2 versus time. Details are provided in Naidu et al. (2013b).

Table 1: Description of treatment conditions

Sample	Treatment conditions
IL 1	1M DAP 48 hrs (single treatment)
IL 2	1M DAP 48 hrs (double treatment)
IL 3	1M DAP + 1mM $CaCl_2$ 48 hrs (single treatment)
IL 4	1M DAP + 1mM $CaCl_2$ 48 hrs (double treatment)
IL 5	1M DAP 48 hrs → Conservare® OH-100 12 hrs → EtOH-H_2O 24 hrs
IL 6	1M DAP 48 hrs → TEOS 12 hrs
IL 7	Conservare® OH-100 12 hrs (natural curing for seven weeks)
IL 8	Conservare® OH-100 12 hrs (natural curing for two weeks)

To study the kinetics of nucleation and growth, samples of marble were prepared with surfaces that were sawcut, roughened with sandpaper, or polished; these were then coated with HAP by immersion in solutions of 1 M DAP with or without addition of 1 mM $CaCl_2$. The phosphate phases were identified by grazing-incidence XRD, the roughness of the coating was

measured by laser profilometry, and the surface coverage was quantified using area maps of phosphorus obtained by EDX. Details are provided in Naidu and Scherer (2013).

Results and Discussion

Consolidation

It was previously demonstrated (Sassoni et al. 2011) that treatment with DAP results in a film of HAP that fully restores the dynamic modulus of damaged limestone. In the present work, we compared the performance of the phosphate treatment with that of Conservare OH-100®, and also investigated the sequential application of those two consolidants. As shown in Figure 1, the heat treatment reduces the dynamic elastic modulus, E_d, by almost 50%, and a single treatment with DAP restores it completely, while a double treatment raises E_d above its initial value.

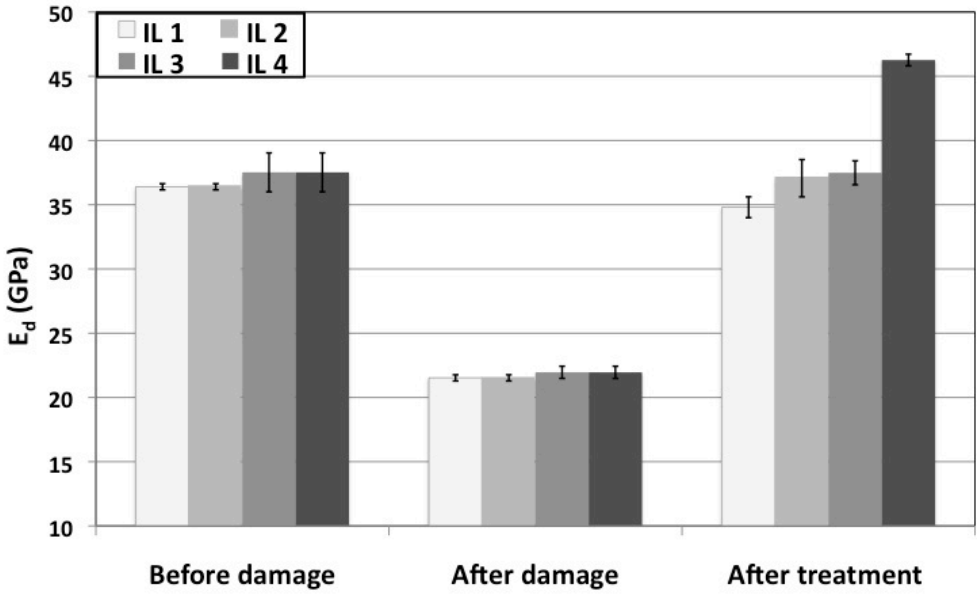

Figure 1. Dynamic modulus of DAP-treated IL samples. Error bars represent the values for the pairs of samples.

If the DAP treatment is followed by application of Conservare, there is very little improvement, as indicated in Figure 2. It was expected that HAP might act as a coupling agent

for the silicate to the carbonate, owing to the presence of OH groups in the crystal structure of HAP. However, spectroscopic analysis revealed no detectable OH groups on the surface of the HAP, possibly owing to carbonation of the surface. If a double treatment is to be applied, then it is much more effective to use DAP twice than to follow a single application of DAP with Conservare.

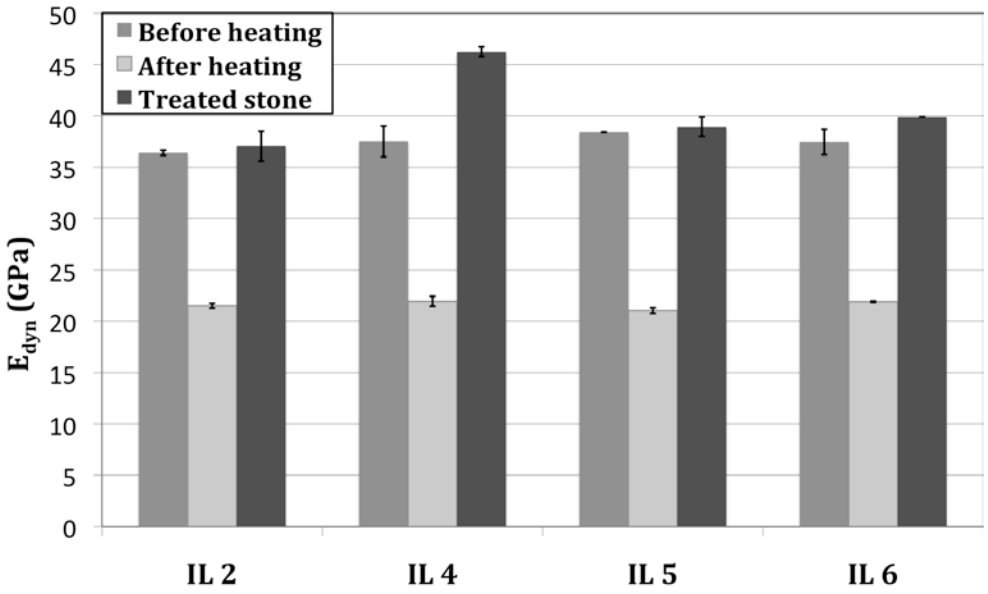

Figure 2. E_{dyn} comparison of different treatments. Error bars represent the values for the pairs of samples.

In the course of this work, we discovered that the hydrophobicity of the Conservare-treated stone could be drastically reduced by rinsing the stone with a solution of water and ethanol (EtOH). The alcohol solubilizes the water, so that the solution readily penetrates the hydrophobic consolidated stone, and the water accelerates hydration of the tetraethoxysilane. Only a small proportion of alcohol is required, so we used a 1:5 (v/v) EtOH:H_2O solution. The consolidated stone was immersed in the solution after 2 to 7 weeks of curing. As a result, the

sorptivity of the stone was dramatically increased, as indicated in Figure 3. This procedure will be very useful for conservators who need to retreat after application of a TEOS-based silicate consolidant.

These results are discussed in detail in Naidu et al. (2013b).

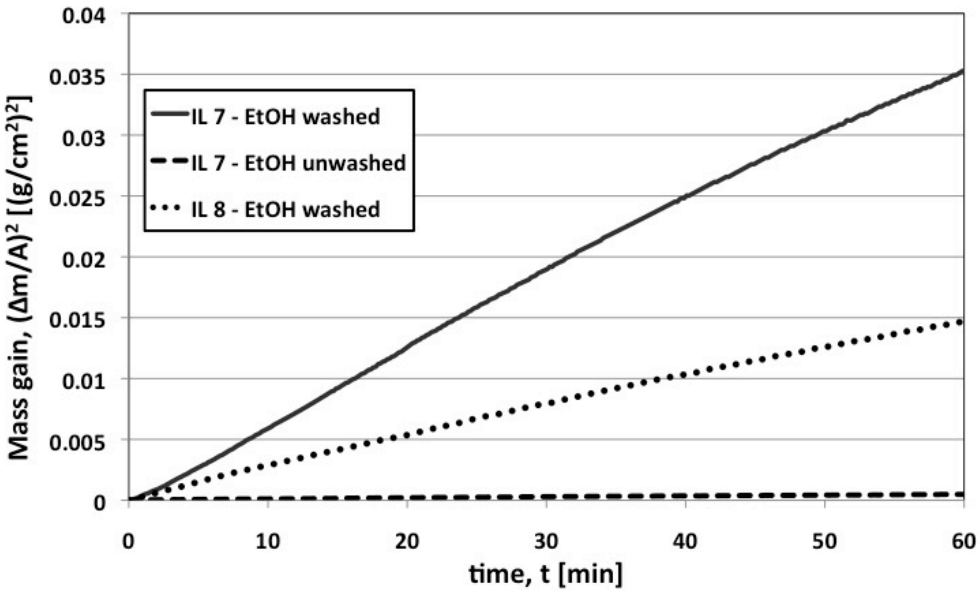

Figure 3. Initial water uptake of naturally cured Conservare-consolidated sample, pre- and post-rinsing with EtOH:H_2O = 1:5.

Acid Resistance

When marble is exposed to acid, the dissolution of calcium carbonate consumes protons in the solution, so the pH rises. The rate of change for bare marble is shown in Figure 4. When the stone is treated with DAP, the rate of attack is slowed, as indicated in Figure 5. Unfortunately, the benefit of the HAP coating is modest, in spite of the fact that the rate of dissolution of HAP is about 4 orders of magnitude slower than that of calcite. The problem is that the coating remains porous, so the acid can penetrate to the substrate.

Treatment of marble with HCT results in large scattered crystals of calcium tartrate that do not constitute a coating, and which dissolve quickly, so that no protection is provided to the marble. In contrast, exposure to ammonium oxalate results in a uniform coating of small crystals that do retard the dissolution of marble, as shown in Figure 6, in spite of the relatively high solubility of calcium oxalate.

The performance of the HAP coating would be greatly improved, if the porosity could be eliminated. This might be possible through the use of organic templates, but that possibility has not yet been explored. In biological systems, HAP typically grows in an organic matrix, such as collagen, but the crystals are acicular. It is not clear that there is a way to produce a smooth inorganic coating of HAP, but an organic/HAP composite coating might afford protection.

These results are discussed in detail in Naidu et al. (2013a).

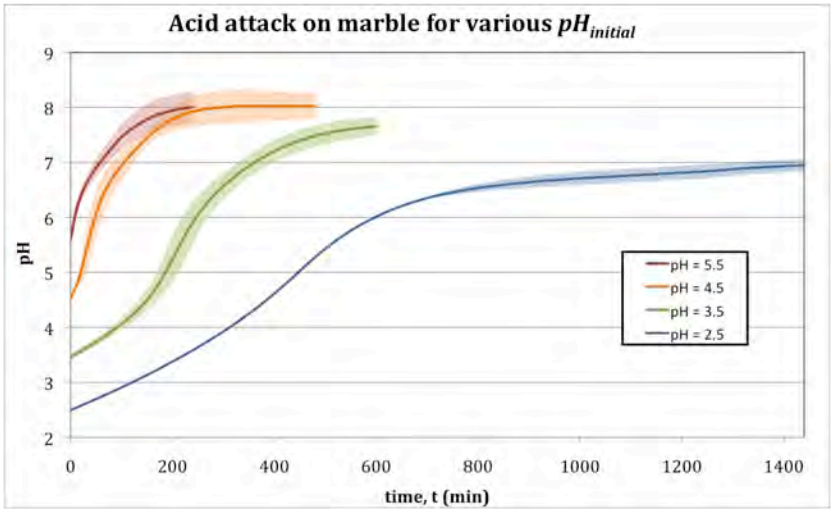

Figure 4. Acid attack profiles for uncoated marble at various initial pH values. Shading indicates the range of reproducibility of the results.

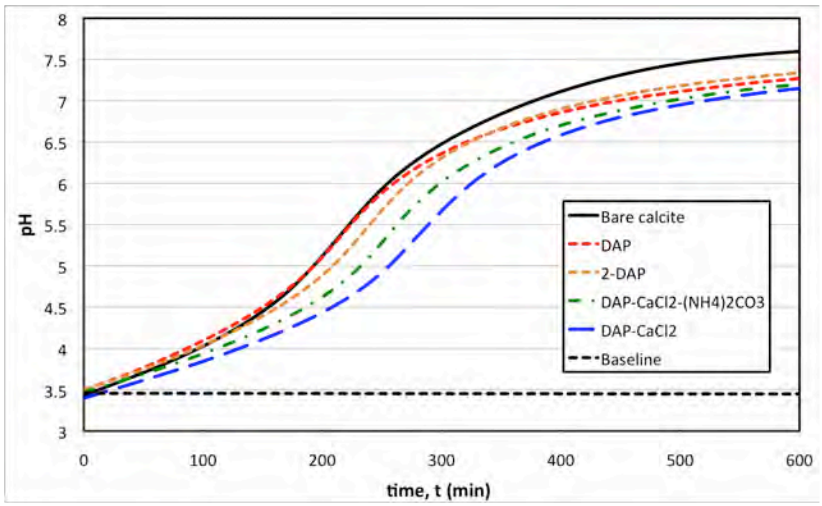

Figure 5. pH profiles for DAP-based treatments on marble: Bare calcite = uncoated marble; DAP = single treatment with 1 M DAP; 2-DAP = double treatment with 1 M DAP; DAP-CaCl2-(NH4)2CO3 = single treatment with 1M DAP solution containing 1 mM $CaCl_2$ and 150 µM $(NH_4)_2CO_3$; DAP-CaCl2 = single treatment with 1M DAP solution containing 1 mM $CaCl_2$; baseline shows the stability of the pH reading in the absence of a sample.

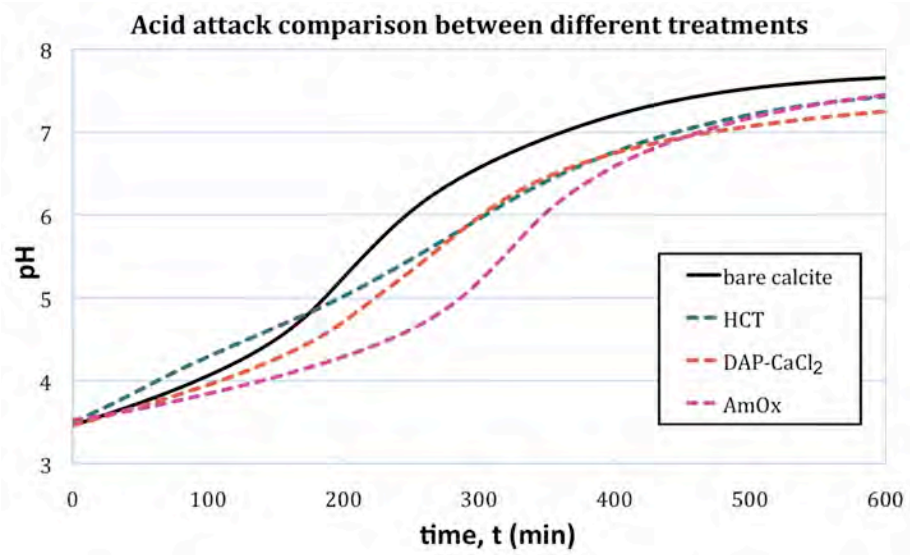

Figure 6. Comparison of the acid resistance of various coatings on marble: Bare calcite = uncoated marble; DAP-CaCl2 = single treatment with 1M DAP solution containing 1 mM $CaCl_2$; HCT = ammonium hydrogen tartrate; AmOx = ammonium oxalate

Nucleation and growth of HAP

The stages of nucleation and growth of the HAP film were observed in the SEM by interrupting growth at various intervals. The first phosphate phase to appear (as indicated by EDX) is in the form of small elongated grains shaped like grains of rice, as shown in Figure 7. It was not possible to identify the crystal phase using grazing incidence X-ray diffraction (GID), either because of the small amount present or because this material is non-crystalline.

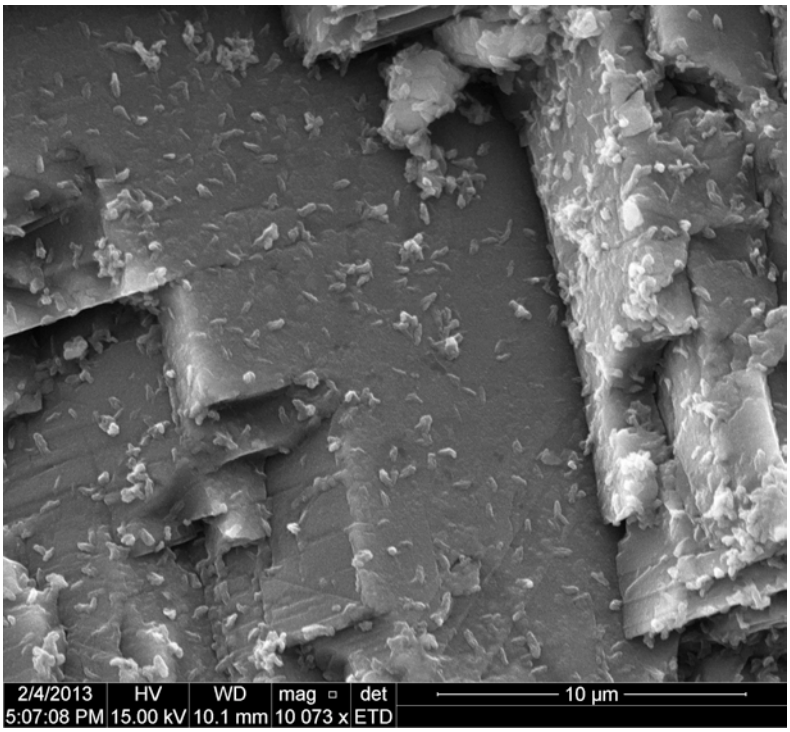

Figure 7. Surface of marble exposed to 1 M DAP + 1 mM $CaCl_2$ after ?? h. The small "rice grains" on the surface constitute the initial stage of growth of the phosphate film. This phase has not been identified, and may be non-crystalline.

As shown in Figure 8, the "rice grains" gradually spread over the surface and pile up in clusters, and then large flakes of octacalcium phosphate (OCP) appear. The identification of this phase is based on the fact that samples treated only with DAP show no large flakes, and the only

phase detected by XRD is HAP; however, samples (such as that in Figure 8) treated with DAP + $CaCl_2$ do produce large flakes and show both HAP and OCP in the XRD pattern.

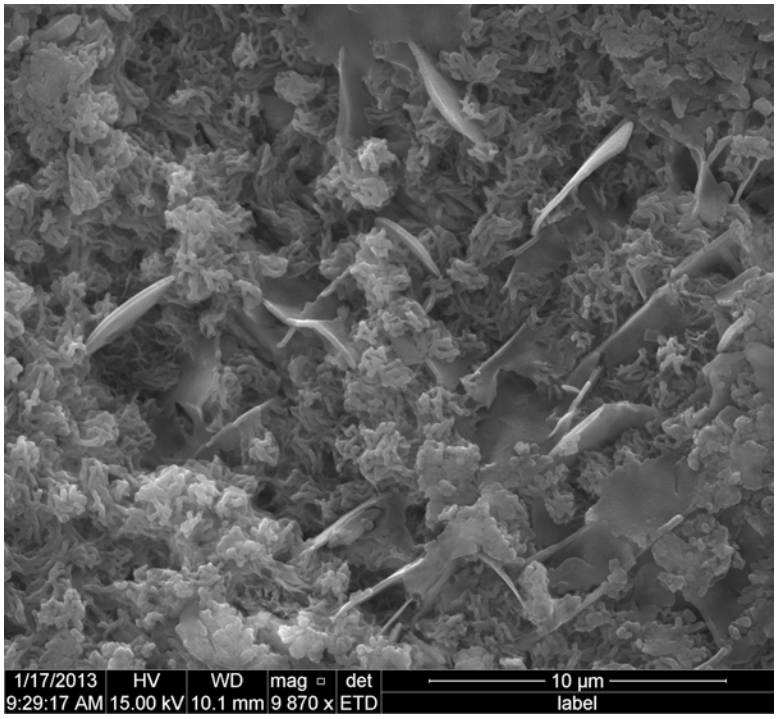

Figure 8. Surface of marble exposed to 1 M DAP + 1 mM $CaCl_2$ after ?? h. Flakes of octacalcium phosphate have begun to appear among clusters of the "rice grains".

Figure 9 shows the structure at the beginning of the final stage of deposition, when the "rice grain" phase has transformed into a flaky, flowery form of HAP that gradually covers the surface and buries (or transforms) the OCP. Eventually, the HAP will cover the surface entirely.

Figure 10 shows a cross-section prepared by cutting through a marble substrate after 24 h of exposure to a solution of 1 M DAP + 1 mM $CaCl_2$, then potting the sample in epoxy and polishing. From the phosphorus (P) EDX signal, the film is found to be about 8 microns thick. The calcium content steps down abruptly from its level in the $CaCO_3$ substrate to its level in the HAP layer. In contrast, the decay in the Ca and P signals at the outer surface is relatively gradual, reflecting the roughness of the surface, which allows the epoxy to penetrate a few microns into

the layer. These profiles must be interpreted with caution, because the width sampled by the electron beam is ~1-2 microns, so there would appear to be a gradual decline in concentration over that distance even if the concentration step were perfectly sharp. Nevertheless, the transition at the marble/film interface is clearly sharper than that at the film/epoxy interface, so the film is evidnetly porous, at least within a few microns of the outer surface. Near the substrate, it appears dense in the images, but the disappointing acid resistance indicates that the film is porous.

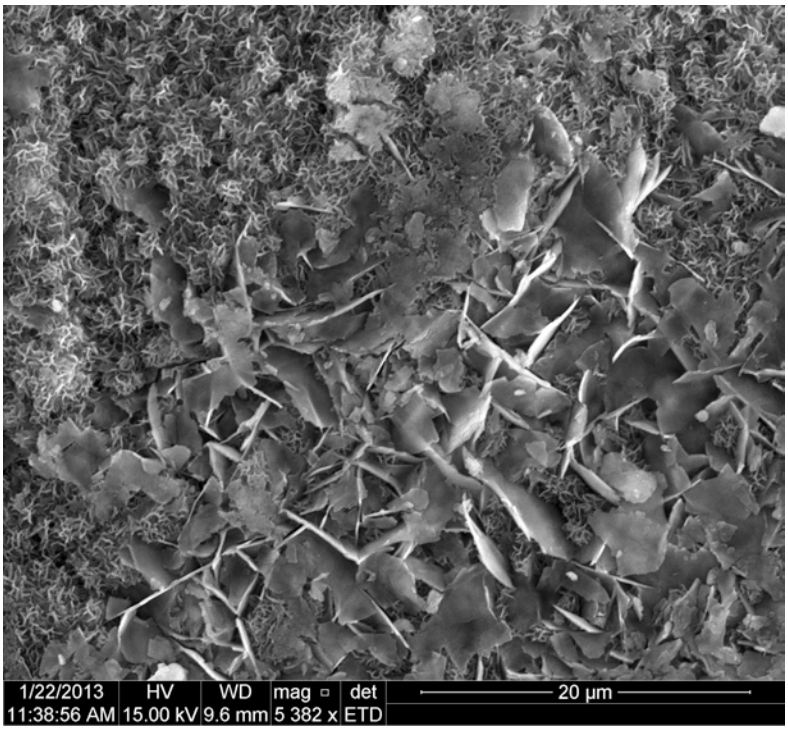

Figure 9. Surface of marble exposed to 1 M DAP + 1 mM $CaCl_2$ after ?? h. The "rice grain" structure has been replaced by flowery HAP crystals. The flakes of octacalcium phosphate will disappear (through burial in, or transformation to, HAP).

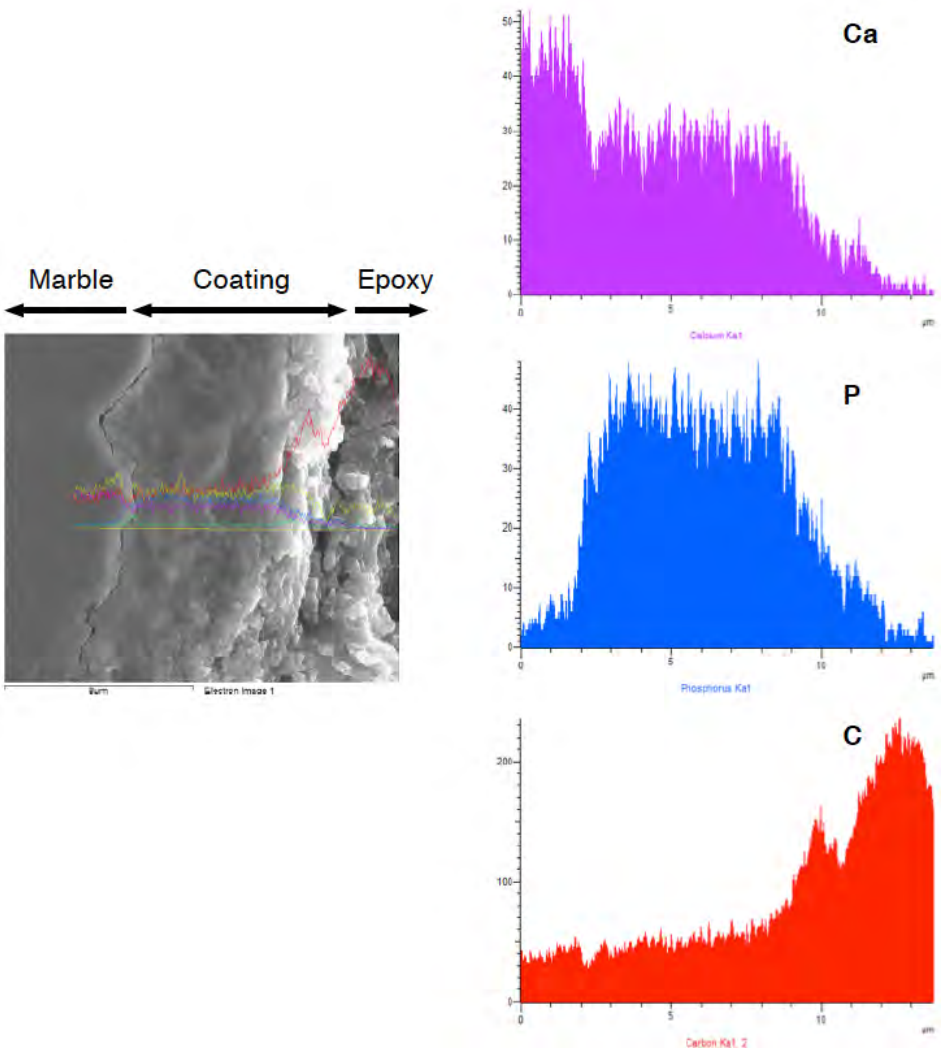

Figure 10. Cross-section of film deposited on marble from solution of 1 M DAP + 1 mM $CaCl_2$ for 24 h. The EDX profiles show the phosphorous (P) localized in the film, and the calcium (Ca) in the film and the substrate; to the right, the epoxy potting compound is the only phase present.

To evaluate the rate of nucleation and growth of HAP on marble, the amount of HAP on the substrate was measured using area scans of phosphorus by EDX; the results were normalized by the counts obtained on pure HAP. The rate of nucleation is strongly enhanced by roughening of the surface: compared to saw-cut marble, polishing strongly delays nucleation and roughening with sandpaper accelerates it.

To determine whether the orientation of the calcite grains has a significant influence on nucleation of the film, a sample of marble was highly polished, marked with a grid, and examined using EBSD so that the orientation of the grains under the grid could be identified, and then the stone was exposed to 1 M DAP + 1 mM $CaCl_2$. SEM examination of the resulting film showed no indication of preferential growth on certain grain orientations or on grain boundaries. Instead, the surface roughened by pitting, and then the phosphate film began to grow. If the grain orientation has any effect, it might be in the rate of pitting, but this would be a minor factor. Fortunately, it appears that natural marble surfaces, such as would be found in weathered or saw-cut stone, are rough enough to allow abundant nucleation after a few hours of exposure to the solution.

To investigate the influence of solution chemistry on the rate of growth, samples of saw-cut marble were exposed to solutions of 1 M DAP with or without additions of 1 mM $CaCl_2$ or 150 μM $(NH_4)_2CO_3$. The rationale for the latter additions is that we want to suppress dissolution of the substrate by raising the activity product of those ions above the equilibrium solubility of the calcite; the added calcium also feeds the growth of the HAP film. As shown in Figure 11, addition of calcium chloride accelerates nucleation and growth of the film, leading to much earlier coverage of the surface. Further addition of carbonate ions accelerates the early growth, but after 24 h the coverage is less than when carbonate is not added. This might be related to incorporation of carbonate ions into the HAP crystal, as such substitution is known to occur [Kamiya et al. 2004].

Addition of carbonate, or excessively long growth periods in the absence of carbonate additions, results in cracking of the film. This is thought to occur during drying of the porous film, rather than during growth. Unfortunately, it is not possible to see the surface of the film,

even with the ESEM, until the surface film of water evaporates, so it cannot be directly demonstrated that cracks are not present during growth. However, we know that the film is porous, and it is well known that porous films will crack if they are thicker than a critical threshold value [Brinker and Scherer, 1990]. Studies are in progress to try to observe cracking during growth or drying through the use of optical microscopy.

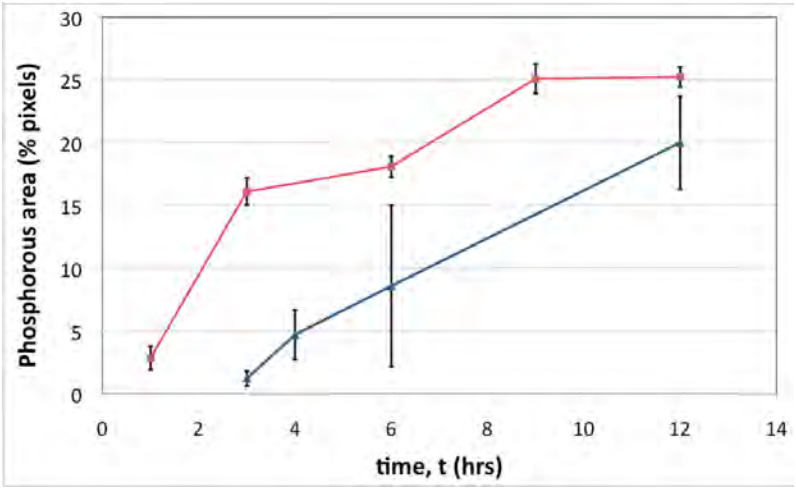

Figure 11. Effect of solution composition on the rate of HAP deposition, based on area scans by EDX. The area where P was detected was normalized by the count obtained on pure synthetic HAP. The lower (blue) curve is for growth from 1 M DAP, while the upper (red) curve is for 1 M DAP + 1 mM $CaCl_2$.

Conclusions

The use of coatings of HAP to protect marble from dissolution was unsuccessful, because the coatings remain porous, so the acid penetrates to the underlying stone. In spite of its higher solubility, the calcium oxalate coatings developed by Matteini et al. (2011) are more effective; nevertheless, the rate of attack is only reduced by about a factor of two. If the porosity could be eliminated from the HAP coatings, they would provide orders of magnitude better protection. In future work, we will investigate the use of organic templates to modify the structure of the HAP

film.

As a consolidant for limestone and marble, treatment with DAP has proven very effective. It restores the dynamic elastic modulus of damaged stone to values equal or superior to those of the virgin stone, while retaining hydrophilicity and sorptivity. It has been demonstrated that HAP is more effective than silicates for consolidation of carbonate stones. Although the HAP crystal contains OH groups, there is a negligible amount of them on the exposed surface, so HAP is not an effective coupling agent for silicates to carbonates. Consequently, there is no advantage to applying silicates on top of HAP; however, double treatments with DAP do enhance the consolidation of limestone.

Close examination of the nucleation and growth process of phosphates on marble shows that nucleation is faster on a roughened surface, and is strongly enhanced by millimolar additions of calcium salts. The first phase to nucleate is morphologically distinct from HAP, but it has not been possible to identify it. That phase is replaced flakes of octacalcium phosphate and then by flowery crystals of HAP before the surface is completely covered. The microstructure of the HAP film becomes more compact with time, but seems to retain significant porosity, so it does not provide significant acid resistance.

It was found that the hydrophilicity of stone consolidated with ethyl silicate could be restored by rinsing with a solution containing water:alcohol = 5:1 (~16 vol% ethanol). This will allow early retreatment of the consolidated surface with minimal VOC emissions.

Publications resulting from this grant

1. S. Naidu and G.W. Scherer (2012) "Development of hydroxyapatite films to reduce the dissolution rate of marble" in Proc. 12th Int. Cong. Deterioration and Conservation of Stone, New York, October, 2012

2. S. Naidu, C. Liu, G.W. Scherer (2013b) "New techniques in limestone consolidation: Hydroxyapatite-based consolidant and the acceleration of hydrolysis of silicate-based consolidants", submitted to J. Cultural Heritage
3. S. Naidu, G.W. Scherer (2013) "Nucleation and growth of hydroxyapatite on calcite", to be submitted to J. Am. Ceram. Soc.
4. S. Naidu, J. Blair, G.W. Scherer (2013a) "The mechanism of acid attack on Carrara marble and the efficacy of a hydroxyapatite-based treatment for reducing attack", to be submitted to J. Colloid Interface Sci.

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