Development of a surface-specific, anti-weathering stone preservative treatment

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Abstract

We are testing an anti-weathering preservation strategy that is specific to limestone surfaces. The strategy involves the application of a mineral-specific, bifunctional, passivating/coupling agent that binds to both the limestone surface and to the consolidating inorganic polymer matrix. The sol-gel based reactions form composite materials with desirable conservation and anti-weathering properties. We present the results of our efforts, the highlights of which are: 1) scanning probe microscopy of moisture-free calcite crystals treated with the trisilanol form of silylalkylaminocarboxylate (SAAC), reveals porous agglomerates that offer no significant resistance to the mild leaching action of deionized water. When the crystals are further consolidated with a silica-based consolidant (A2**), no dissolution is seen although the positive role of the passivant molecule is not yet delineated. 2) Modulus of rupture tests on limestone cores treated with an aminoalkylsilane (AEAPS) and A2** showed a 25-35% increase in strength compared to the untreated samples. 3) Environmental scanning electron microscopy of treated limestone subjected to a concentrated acid attack showed degradation of the surface except in areas where thick layers of the consolidant were deposited.

DISCLAIMER

1.0 Introduction

Historic stone structures such as monuments, sculptures and temples have immense aesthetic and cultural value and are a vital economic resource for many parts of the world. The design and development of preservative treatments is a technologically evolving process and plays an integral part in the conservation of these structures. The materials used so far to preserve stone include epoxies, polyesters, acrylics, urethanes, silicones, alkoxysilanes and other organic/inorganic polymers (Winkler [1]; Sleater [2]; Amoroso & Fassina [3]; Selwitz [4]; and Wheeler [5]). While many of these systems have been proven to work very well for selected problems, limestone preservation is still a challenge. This is due to the chemical composition and pore structure of the stone. The properties desired by the conservation community for a protective treatment are: chemical resistance against dissolution, strengthening or consolidation of the weathered stone, hydrophobicity yet permeability to water vapor, reversibility and, environmental friendliness. In addition, the main drawbacks of conventional treatments to be overcome are: weakness of the chemical bond between the stone and the protective treatment, oxidative degradation, discoloration, UV degradation and poor penetration (Winkler [1], Sleater [2], Wheeler [5,6]).

1.1 Design Strategy

Our strategy to protect limestone is a surface-specific treatment that is designed to retard any further chemical or physical weathering by first rendering the limestone surface passive toward hydrolysis and second by strengthening or consolidating the already weathered structure (Rao [7,8], Cygan [9], Nagy [10]). A mineral-specific passivant molecule energetically binds to the calcite surface and also acts as a coupling agent for the consolidant (see Figure 1). The coupling is achieved by a polymerizable "tail" on the passivant that enables sol-gel condensation reactions with the consolidant. The consolidant offers strength to the weathered stone by forming an inorganic framework within the pore system. The sol-gel based consolidation process is amenable to the introduction of strengthening metal oxides and water repelling agents.

The design of our protective treatment includes two phases: (a) computational modeling to predict and visualize the treatment process (Cygan [9], Nagy [10]), and (b) experimental testing. Experimental testing includes the following techniques: (1) scanning probe microscopy (SPM) of treated and untreated single crystal calcite, (2) leach tests on treated calcium carbonate powders and (3) modulus of rupture (MOR) strength tests on treated limestone cores and, 4) environmental scanning electron microscopy (ESEM) of calcite and limestone (Rao [11]). In this paper, we present the results from the SPM, MOR and ESEM work.

2.0 Materials & Methods

Three classes of silylated coupling passivants were tested based on the binding functional groups and the charge present on them: silylaminoalkylcarboxylates (SAAC), silylalkylphosphonates (SAP), and aminoalkylsilanes (AEAPS). For

the consolidant, partially hydrolyzed alkoxysilane solutions were tested (~50 % w/w silica designated as A2** stock) and a further catalyzed dilute form (15% w/w silica designated as A2** 1:2 sol) (Brinker [12]).
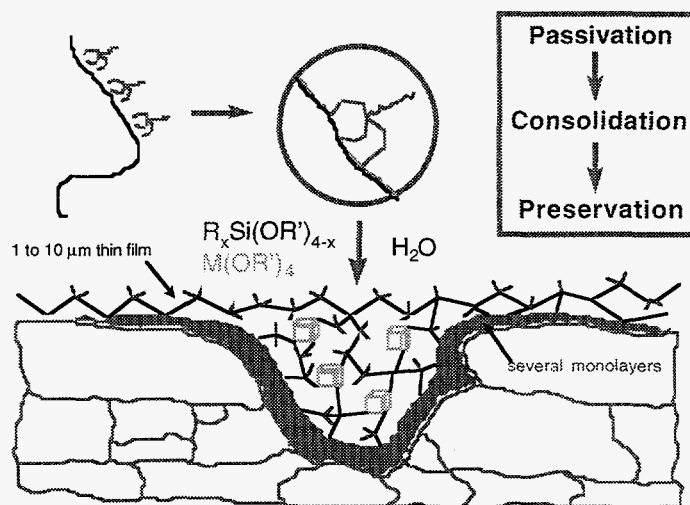

Figure 1. Schematic diagram of treatment for weathered limestone surface on a sculpted "nose". The gray area is the passivant that couples the limestone to the SiO_2-based consolidant above it. The R_x and M groups shown in the schematic can be tailored to increase the consolidant's hydrophobicity and strength respectively.

2.1 Scanning Probe Microscopy (SPM)

We use SPM to monitor the surface changes on single crystal calcite, the primary mineral in limestone and marble (Rao [8]). The samples are observed at high resolution, prior to, during, after the application of protective treatments, and finally while being subjected to simulated weathering. SPM is a technique by which an atomically sharp probe is raster-scanned across the surface being examined. The surface features are detected by deflections of a laser beam bounced off the probe. We utilize a fluid cell attachment to the microscope that facilitates the injection of preservatives and also acidic solutions to simulate weathering (Digital Instruments, Model-Nanoscope III [Ref# 13]).

Optically clear calcite samples from Chihuahua, Mexico were cleaved to expose the {104} surface. These were used directly to observe dissolution of calcite characterized by etch pit formation and step retreat on the surface, when exposed to corrosive solutions (see Figure 2). Samples to be treated were placed in the passivant solution for 30 min., rinsed with methanol and then placed in the consolidant for another 30 min. Following rinsing with ethanol they were dried in an oven at 60°C. We used a 12 μm SPM piezoelectric scanner (Model-E) and Si_3N_4 probes. The scan size was kept between 4-10 μm^2, the Z-range at less than 25 nm, and the scanning rate was 4-8 Hz which results in an image-acquisition time of less than 90 seconds. To simulate acid rain weathering we used freshly deionized water (18 MΩ) which was allowed

to equilibrate with atmospheric CO_2 for 15 minutes and filtered through a 0.2 μm nylon membrane filter (Acrodisc-13, Gelman Corp.). The pH of this water was approximately 5.5.

2.2 Strength Tests

Monks Park limestone cylinders of dimensions 75 mm length by 7.5 mm diameter were cut perpendicular to the bedding plane from stone quarried at Bath, England. The surface area of these limestone cores was 2-3 m^2/g (nitrogen gas adsorption). Mercury porosimetry yielded a porosity of 24%. Eight cores per treatment were dried at 60°C overnight before being treated. They were evacuated in a schlenk tube to a pressure of 80 kPa. The passivant was then injected into the tube until the cores were completely submerged for 2 hours. The passivant was then removed and the consolidant was added to the cores. They were exposed to the consolidant for 2 hours to propagate cross-polymerization between the passivant on the limestone surface and the consolidant. The unreacted consolidant was then removed and the cores were allowed to cure at ambient temperature for 12 hours after which they were dried at 60 °C for 24 hours. The modulus of rupture was determined from 3-point bend tests that approximated the ASTM method C674-88 [Ref#14]. A one KN load cell was used and the crosshead speed (loading rate) was 0.2 mm/min.

2.3 Environmental Scanning Electron Microscopy (ESEM)

The environmental SEM being used in our stone conservation research (ESEM Model E-3, Electroscan Corp. 66 Concord St., Wilmington, MA 01887, USA) facilitates the observation of materials in their natural and/or wet state without coating and drying. A microinjection system allows for the introduction of liquids such as acids onto the samples while they are examined at high magnification. Concentrated sulfuric acid (pH~0) was used to corrode the limestone surface to simulate aggressive attack on the stone. The microscope was operated at an accelerating voltage of 10-25 KeV with a lanthanum hexaboride electron emitter. Water vapor, the standard imaging gas was chosen for its simplicity and compatibility with the experiments. The untreated and treated samples were observed first at high magnification and then the acid was introduced on to the samples.

3.0 Results and Discussion

3.1 Scanning Probe Microscopy

Dissolution of untreated calcite was observed immediately upon addition of deionized water by the formation of etch pits approximately 200 nm along the diagonal and about 100 nm along the shorter diagonal (Figure 2a & b). The depth of the etch pits was about 0.5 nm which indicates that dissolution is occurring in monomolecular steps. The rate of surface loss was 4-7 nm^2/sec. Further dissolution resulted in the retreat of steps and merging of adjoining pits (Figure 2b). This dissolution of calcite in the presence of an acidic undersaturated solution continues until equilibrium is reached in the fluid cell volume of the microscope. The etching of the surface re-commences after

purging the cell with the leaching solution again. This simple reaction allows a comparison of the relative passivation of the surface.
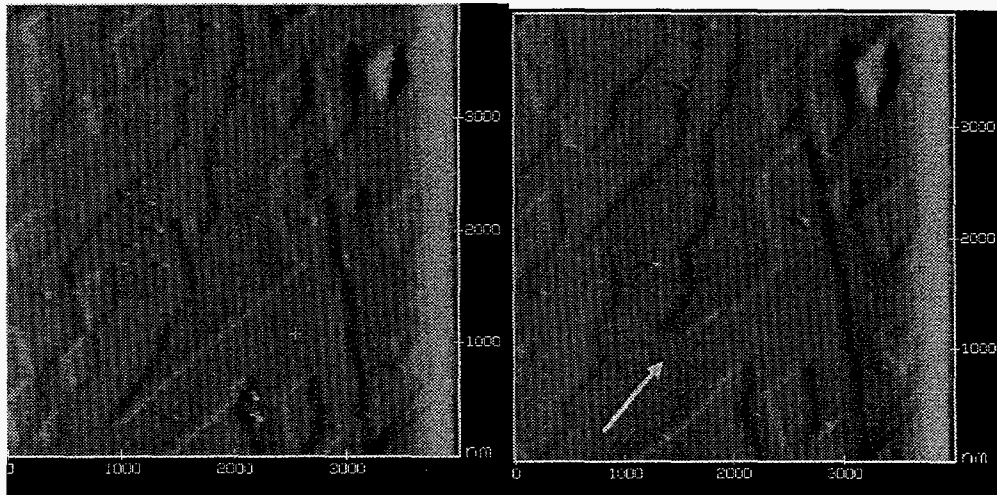

Figure 2a & b. SPM image (left) of single crystal calcite upon addition of simulated acid rain. The appearance of etch pits confirms rapid dissolution of calcite. The etch pits are diamond shaped (<1 nm deep). Figure 2b shows the same location after 3 more minutes of exposure to the weathering solution. Note the enlargement of the etch pits and retreat of steps (esp. peninsular region in the center of the images).

Calcite crystals treated with the 3% SAAC passivant and A2** consolidant (15% w/w) show no etch pit formation or step retreat upon addition of the weathering solution (Figure 3a & b). The steps are no longer visible and the surface appears rough. A triangular pattern of coating defects seen as bright circles with dark spots in them can also be identified in both the images. The increased contrast in Figure 3b is due to a deliberate decrease in the z-axis scale from 25 nm to 15 nm to highlight surface features. However, we note that calcite treated with just the 15% silica consolidant also showed no etch pits or step movement and the contrast between these two samples can be heightened, for example, by using a more corrosive solution. Thus the protection of the calcite may be due to the inorganic framework on the surface. Calcite treated similarly with a commercial consolidant, Wacker OH containing 75 % silica (not recommended for limestones), resulted in a film that cracked and peeled away.

3.2 Strength Tests

The effect of the different treatments on the modulus of rupture of the limestone cores as determined from the three-point bend tests is seen in Figure 4. Due to the heterogeneous nature of the stone, the standard deviations were large. The commercial consolidant Wacker-H with 75% silica gave the highest increase in flexural strength. The A2** consolidant alone (without a passivant) with 15% silica, strengthened the stone compared with the more concentrated A2** (50%). This counter-intuitive disparity is due to the processing conditions: the

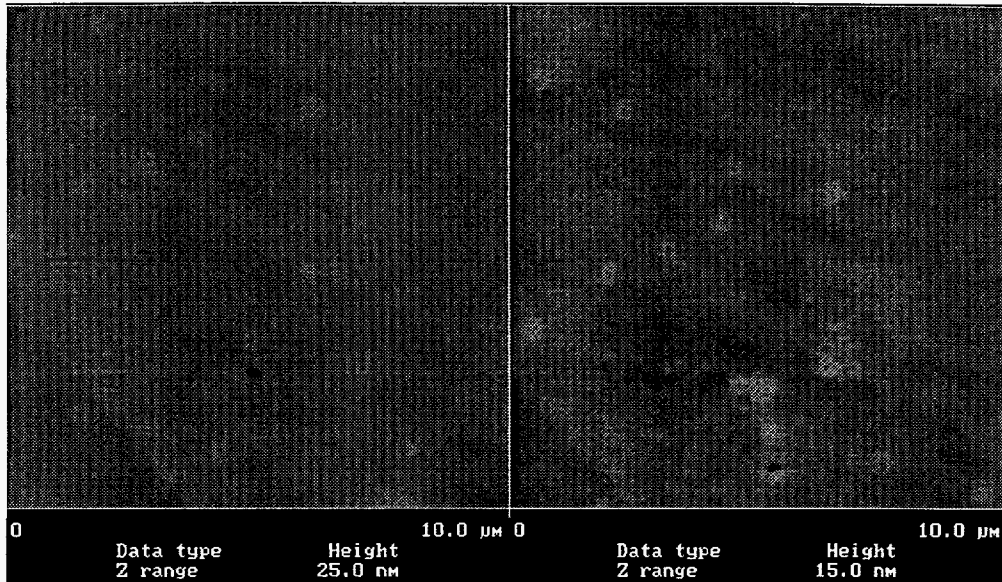| | | 10.0 μм | 0 | | | 10.0 μм |
| Data type | Height | | | Data type | Height | |
| Z range | 25.0 пм | | | Z range | 15.0 пм | |

Figure 3a & b. SPM images of single crystal calcite treated with the SAAC passivant and silica based A2** consolidant, before (left) and after (right) addition of simulated acid rain. Time elapsed between the two images is one hour. With the exception of increased contrast due to a change in the Z-axis scale, the surface remains unchanged. No etch pit formation or step retreat is seen.

A2** 15% sol is subjected to two acid-catalyzed steps, aged and then diluted while the 50% A2** sol is hydrolyzed by acid only once. The increased acid concentration and greater H_2O:Si ratio in the A2** 15% sol enhance the hydrolysis rate (Brinker [15]).
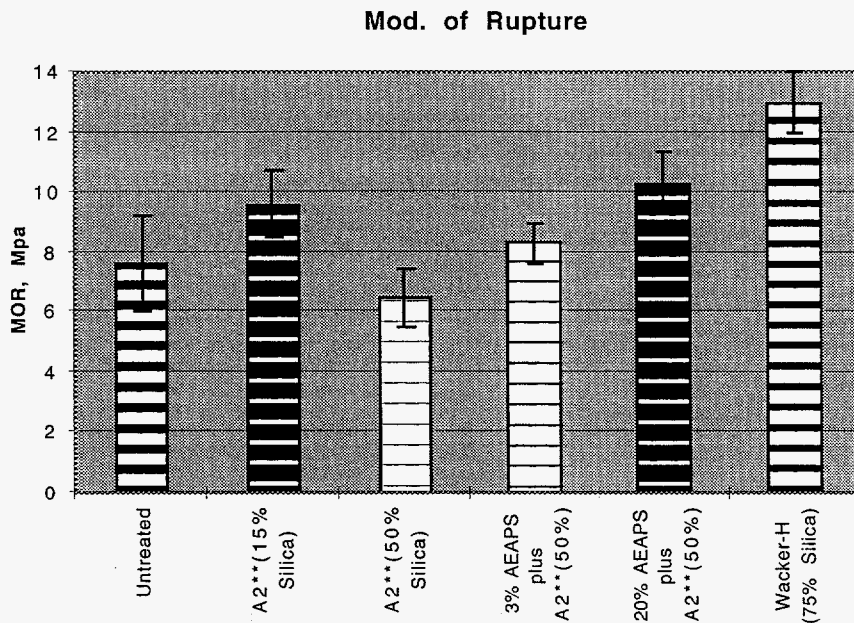

Figure 4. Plot of modulus of rupture for different treatments.

This combined with the aging of the sol ultimately forms a stronger gel. The increase in the concentration of the AEAPS passivant from 3 to 20% results in a 25% increase in strength and a 35% increase compared to the untreated stone. Other researchers have also observed that the incorporation of AEAPS into silica aerogels showed reductions in gel times and increases in the bulk density (from reductions in surface area) (Husing [16]). The amino group may be helping to catalyze the condensation reaction due to its basic nature. Cores treated with the 20% AEAPS sol and the 15% A2** sol were not tested due to the rapid gelation on the surface that prevents effective penetration and also leads to excess gelled material on the surface of the stone. The trisilanol form of the SAAC passivant was eliminated in preliminary experiments as it weakened the stone by binding too strongly to calcite and actually leached Ca^{2+} out of the samples.

3.3 Environmental Scanning Electron Microscopy (ESEM)

The untreated limestone is filled with ooids (concentric spherical structures) and consists of amorphous regions and polycrystalline phases of calcite (Figure 5a). Large voids amidst clusters of fine grained calcite in the limestone are seen. Figure 5b shows the same region after introduction of concentrated acid. Figure 6a shows limestone passivated with SAAC and consolidated with A2**. the composite coating has cracked and retracted exposing bare calcite. Upon exposure to acid, the bare areas exhibit corrosive attack, but the coated areas do not, suggesting that the protective treatment, if continuous, would retard acid-rain attack. We believe that cracking results because the SAAC passivation layer does not bind effectively to the calcite surface, allowing the biaxial tensile stress developed upon curing to cause cracking and delamination (Chapters 7, 8 in Brinker [15]). Improved coupling chemistry combined with a reduction in the coating thickness should remedy this behavior.
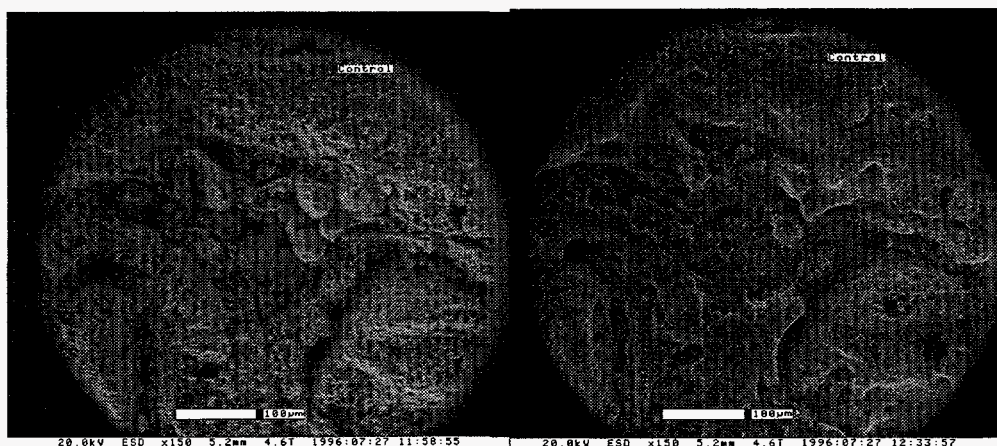

Figure 5a &b. Surface of untreated limestone shows ooids (concentric structures to the bottom left and right of Figure 5a) and polycrystalline regions (centre). Figure 5b shows the same region after addition of acid. Micron bar=100 μm.
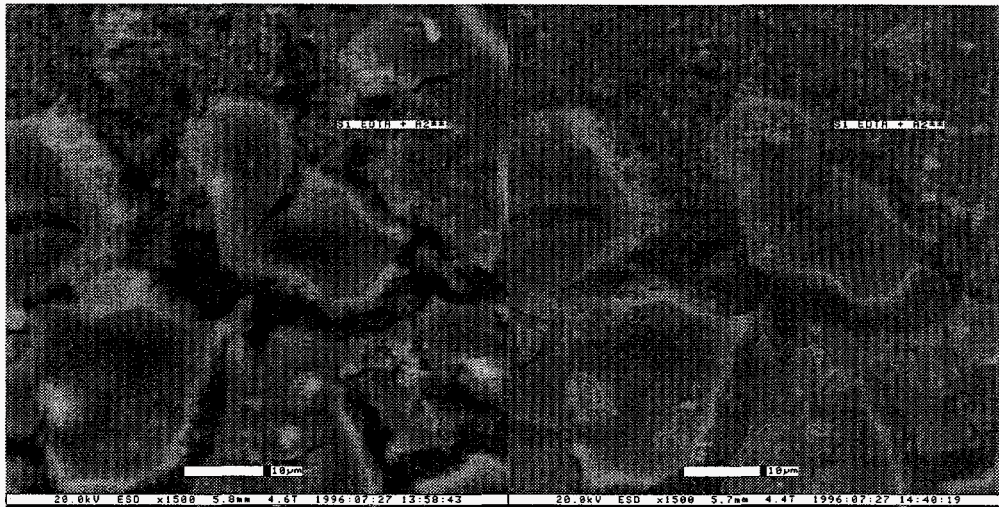
Figure 6a & b. Treated limestone before addition of concentrated sulfuric acid (Figure 6a). Inadequate coupling by the SAAC passivant led to shrinkage of the consolidant. Micron bar=10 μm. Figure 6b shows the same region after addition of acid. The consolidated areas remain unaffected although the layer is cracked. Better coupling passivants and thinner consolidating layers can prevent the cracking.

4.0 Conclusions

Our SPM study demonstrates the effectiveness of applying the sol-gel coatings to protect single crystal calcite. We have determined at a microscopic level, that calcite consolidated with the 15% A2** sol is resistant to corrosion by mildly acidic deionized water of pH 5.5. Environmental microscopy offers a means to subject limestone cores to in-situ corrosion tests and we find that to better protect limestone from sulfuric acid attack, we need good coupling with the surface and a thinner consolidating layer. The three-point bend tests show that the 15% silica A2** sol and the combination of 20% AEAPS plus the 50% A2** sol, strengthen limestone cylinders by as much as 25-35%.

Key words: Weathering, limestone preservation, acid rain, stone consolidation, sol-gels

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