Final Report

Improved Sol-Gel Consolidants for Stone

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Executive Summary

The purpose of this project was to develop improved consolidants for restoration of stone damaged by weathering. Conventional consolidants are organic polymers or silica gels, which are simple materials that do not permit matching of a range of properties of the stone. To provide consolidants with a wider range of properties, we prepared composite materials consisting of colloidal oxide particles suspended in a silicate matrix. Initially, we succeeded in preparing satisfactory suspensions by adsorbing a layer of nanosilica (silica particles with a diameter of 10-20 nm) onto titania pigment particles. The silica layer prevents the titania particles from agglomerating, allowing them to penetrate deeply into the stone. Later improvement of the suspension procedure resulted in consolidants that are much more stable and fluid. Stone treated with the particle-modified consolidant (PMC) increases dramatically in stiffness and strength. Most impressively, in a sodium sulfate test, the PMC provided better protection than a commercial silicate consolidant. The results of this research were reported at the Fall Meeting of the Materials Research Society in a symposium entitled, *Materials Issues in Art & Archaeology VI*. Continuing research is directed toward use of other colloidal particles, which will permit preparation of consolidants with a wider range of colors and properties.

1. Introduction

Silicate consolidants, such as Conservare OH® [1], are effective at increasing the modulus and strength of weathered stones. However, the physical properties of the consolidants, such as modulus and thermal expansion, generally do not match those of the stone. Moreover, the effectiveness of the consolidants can be reduced following wetting/drying cycles, particularly when the stone contains inclusions of swelling clay [2]. By incorporating colloidal oxide particles into a silicate consolidant, we have previously shown that the drying shrinkage of the consolidant is reduced [3,4] and the consolidated stone preserves more of its rigidity after wetting and drying [5]. However, those results were obtained with a limestone, so that a limiting factor in the development of strength is the ability of the ethyl silicate to bind to the surface [6]. Furthermore the limestones used [5] were very porous (~ 30 v%) which contributed to making particle ingress easier.

The general objectives in the preparation of the PMC used in this study were:

1. dispersion viscosity comparable to that of commercial ethyl silicate consolidants
2. volume fraction of solids of 10%. (Increasing volume fraction makes it increasingly difficult to obtain a good dispersion; however, a sufficient amount of particles is necessary to obtain a meaningful modification of the consolidant properties as shown in previous studies.)
3. binder content as high as possible without sacrificing dispersion quality
4. dispersions that are stable over time and require minimal preparation on site

With these objectives in mind, several variations to the basic composition were investigated using viscosity as the primary factor in the screening process. Most tests were performed with TiO_2 as the major particle. This pigment is commercially available as a high quality powder with a relatively narrow size distribution.

2. Methods and Materials

The consolidants consist of a silicate binder, which is either tetraethoxysilane (TEOS) or Conservare OH-100 (Prosoco), plus colloidal particles and a solvent. Titania particles (0.2 μm, DuPont R-101) were combined with nano-silica particles (30 wt% dispersion of 10-20 nm

particles in isopropanol, Nissan IAP-ST); the latter form a monolayer coating on the titania [5] that provides steric stabilization. The pigment + nanosilica constitute 10 vol% of the consolidants and the binder is 29 or 39 vol%.

Initial preparation of PMCs had been done by adding liquids successively to the particles in a container and sonicating for 15 minutes. Though these mixes appeared to be well dispersed, they often failed to fully impregnate samples and tended to segregate over time at a rate faster than expected from the size of the primary particles involved. The following mixing procedure resolved this problem. The nano-silica dispersion and about a third of the solvent were mixed together. The pigment particles were added to this solution in three steps under magnetic stirring and followed by an ultrasonic treatment (600W pulses of 1.5 s every 5 s, for a total pulse duration of 15 minutes). During ultrasonic treatment, the mix had to be placed in an ice bath to prevent excessive heating leading to solvent loss. The mix so prepared did not segregate over a time lapse of days. The preparation was completed by adding the remaining solvent and binder without further need for sonication.

Samples were placed in individual containers with 8 ml dispersion and left to impregnate for several hours. The impregnation did not require pre-wetting with ethanol as had been the case in earlier formulations, indicating that the particles are now better dispersed. This is very important for the mechanical testing because the alcohol used for prewetting is driven to the top of the sample, preventing complete impregnation by the consolidant within reasonable time. In such cases, the fractures in the splitting test initiated in that poorly consolidated region, so the tensile strength results were questionable. To insure the best possible impregnation, consolidated samples were inverted and allowed to imbibe consolidant from the other direction, so that the splitting test would truly reflect the strengthening potential of the consolidants.

Most rheology tests were done using capillary viscometers (Cannon 100, 150, 200). This method determines a viscosity based on the time a known volume of liquid takes to flow through a capillary of known length and diameter, while assuming the liquid is Newtonian. The advantage of this simple measurement in the case of PMC is that the flow through the capillary should be very sensitive to the presence of agglomerates. For a limited series of mixes, flow curves were determined using a cup and bob geometry mounted on a Rheometrics RFS II (Rheosource series). Shear rates were decreased from 300 s^{-1} to 0.02 s^{-1}, in 25 logarithmically

spaced steps. At each step, the sample was given 10 s to equilibrate before a 15 s measurement. At each step this was done twice, once for each direction of rotation.

The stone used was an Ohio Massilian sandstone obtained from Pasvalco (Closter, NJ). Its porosity was determined by vacuum impregnation to be 22.6%. Sandstone was chosen so that improvements in mechanical properties would not be limited by the poor binding of ethyl silicates to the pore wall, as may be the case in limestone. The final objective being to study the effect of particles on consolidant performance, this appeared a reasonable choice. The samples used were core drilled (2 cm diameter) from two 5 cm thick plates. They were distributed in groups of ten so that each group would be representative of both plates. This assures that the average properties of the groups are all the same and comparing treatments of different groups is truly reflective of the treatment effect rather than of questionable sampling.

The pulse velocity was measured using a commercial instrument (PUNDIT) with 54 kHz transducers. Dynamic elastic modulus, E, was calculated from density, d, and pulse velocity, V, according to the formula

$$E = dV^2 \tag{1}$$

Tensile strength was measured by performing the Brazil test on the core-drilled samples.

Cycles of impregnation (with a 16 wt% solution of sodium sulfate) and drying (at 60°C, as higher temperatures may damage consolidants) were done to determine the resistance to salt crystallization. The procedure, which is described in detail elsewhere [7], included measurements of the stone at each stage of wetting and drying, and measurement of all debris. The pulse delay of each sample was measured at the end of each drying cycle.

3. Results and Discussion

a. Optimal composition

With TEOS, it was not possible to increase the fraction of binder beyond about 5 vol%. It was concluded that the problem came from a hydrophilic flocculation of the nano-silica in an increasingly hydrophobic liquid. To remedy this, silicate oligomers were found to be successful (Silbond 40, Silbond 50). The experiments reported here used a commercially available ethyl silicate consolidant (Conservare OH-100 by Prosoco) that contains a tin dibutyldilaurate catalyst in addition to oligomers. The ratio of TiO_2 to nano-silica has to be no greater than 9:1, or the

viscosity increases drastically; below this threshold, little effect is seen. This observation is compatible with the nano-silica having a strong affinity for the TiO_2 surface and acting as a steric dispersant once it is adsorbed. Figure 1, from ref. 5, is an electron micrograph showing a monolayer of silica nanospheres adsorbed onto a titania particle. The gray mottling in the background is from silica particles that are not adsorbed.

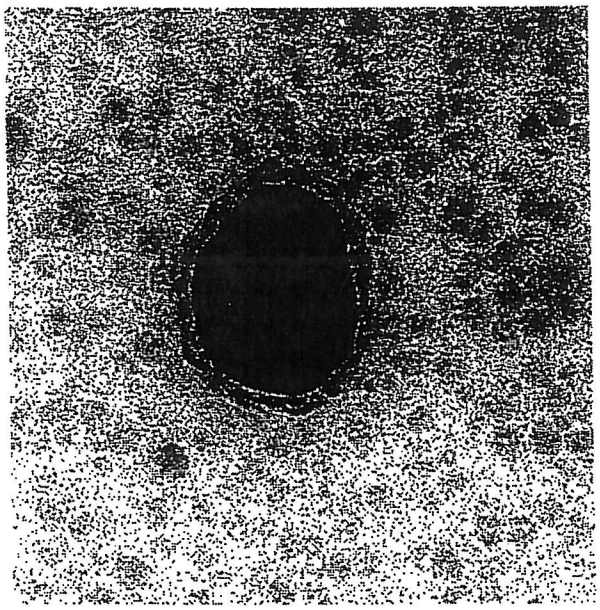

Figure 1. Transmission electron micrograph of titania pigment particle (diameter ~100 nm) coated with silica particles.

As shown in Table I, lower viscosities were obtained with ethanol provided it was of high purity; in earlier tests, water contamination of the ethanol led to poor impregnation, attributed to silicate condensation.

Table I. Viscosity of PMC (mPa•s)

High binder (39 vol%)	Ethanol	Isopropanol
80% Titania	2.61	3.93
60% Titania	2.96	3.69
Low binder (29 vol%)		
80% Titania	2.99	3.59
60% Titania	3.92	3.63

On the basis of these results, a PMC composition was chosen that contained 39 vol% binder (with respect to liquid), 80 vol % TiO_2 (with respect to particles) and 200 proof ethanol as solvent. All the properties of the treated samples given in this paper are for this mix. The density of the consolidants was measured after stirring, taking samples from the top and bottom of the beaker; the measurements were repeated after 2 and 24 hours of standing without stirring. The density values ranged from 1.17 to 1.19 g/cm^3, which is within the error of the measurement, so there was no evidence of settling over the course of a day.

b. Consolidation

Figure 2 is a micrograph of a fracture surface of a consolidated sample, which reveals that the consolidants penetrated the entire body. The titania particles are clearly visible. The silicate binder is not visually evident, but its presence is revealed by EDX analysis.

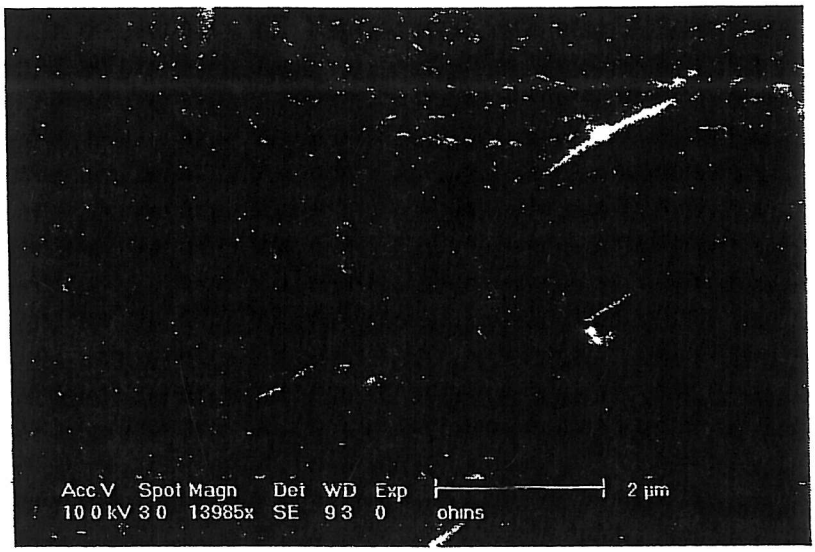

Figure 2. PMC in Ohio sandstone. Small spheroidal particles are titania pigment.

The effects of the PMC on modulus and tensile strength of the sandstone are shown in Figures 3 and 4; the error bars represent 90% confidence intervals. Each consolidant provides about a three-fold increase in modulus and 60% increase in tensile strength, compared to the original stone.

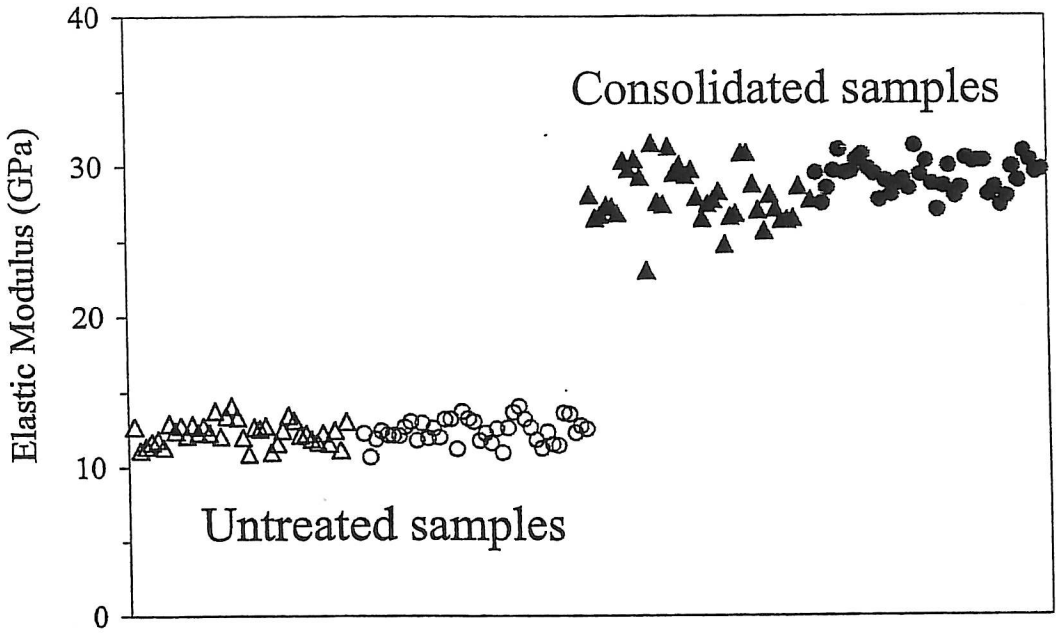

Figure 3. Dynamic elastic modulus of Ohio Masillian sandstone before and after consolidation with PMC (●,o) and Conservare OH-100 (▲,Δ).

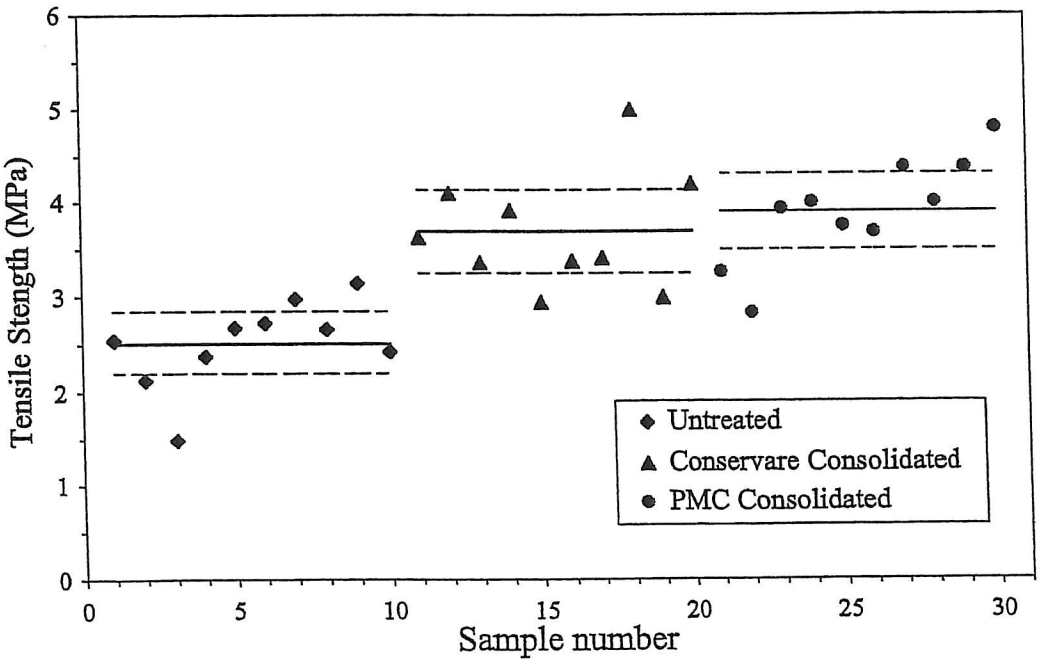

Figure 4. Tensile strength of Ohio Masillian sandstone before and after consolidation with PMC and Conservare OH-100.

The effect of the consolidant on the salt resistance of the stone is shown in Figures 5 and 6. The damage is most rapid for the bare stone, but the PMC gives more protection than Conservare OH-100 alone.

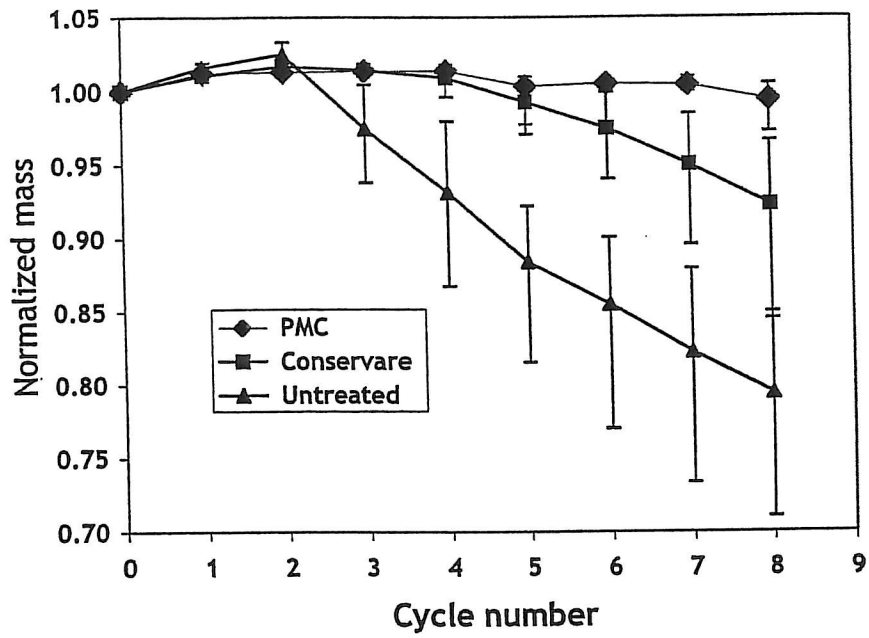

Figure 5. Normalized mass of stone versus number of cycles in sodium sulfate test.

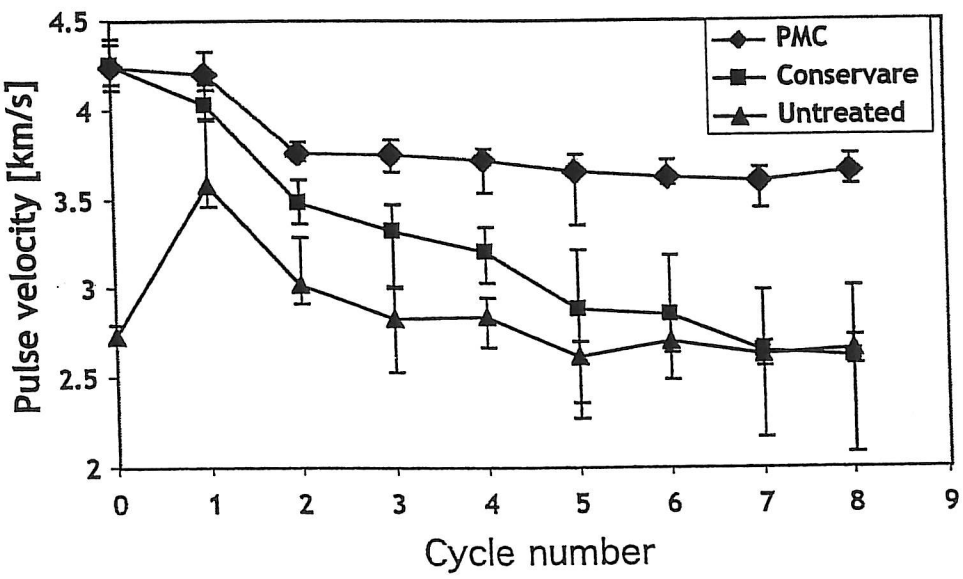

Figure 6. Pulse velocity in stone versus number of cycles in sodium sulfate test.

4. Conclusions

Titania pigment particles can be stabilized by a monolayer nano-silica particles within a silicate binder, such as Conservare-OH. The resulting consolidants preserves a low viscosity and the particles do not show any settling over 24 hours. The PMC provides better salt resistance than Conservare alone. We now plan to examine the effect of added particles on thermal expansion and wetting and drying cycles. In this process we will begin to integrate more systematically other particles, also looking at the possibility of matching the consolidant color to that of the stone.

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Rheology optimization of Particle Modified Consolidants

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ABSTRACT

Ethyl silicate-based consolidants are used to restore strength to degraded stones. One of the limitations of strength development using these products is their reported cracking behavior during drying. Particle Modified Consolidants (PMC) consist of a silicate matrix plus colloidal oxide particles. The presence of particles physically limits the silicate network from shrinking under capillary pressures, and thereby reduces strength loss during drying. In addition, the network maintains a higher permeability, because the dried consolidants remains porous. When the particles used are pigments, it is also conceivable to adjust the consolidant color. Moreover, a careful choice of particles should allow matching the thermal dilatation of the consolidant to that of the stone. An important limitation to further development of PMC has been the ability to avoid particle agglomeration in the dispersion. When agglomerates are present, not only do they increase the viscosity but they also can block pore entrances, preventing consolidant from entering the stone. In this work we demonstrate the feasibility of adsorbing nano-silica particles onto pigment particles to create a layer of low dielectric constant that acts as a steric barrier to agglomeration. Rheology and density measurements confirm that the resulting dispersion is fluid and stable against settling. The consolidants readily penetrates Indiana limestone, providing improved strength, stiffness, and salt resistance, compared to a commercial silicate consolidants.

INTRODUCTION

Silicate consolidants, such as Conservare OH® [1], are effective at increasing the modulus and strength of weathered stones. However, the physical properties of the consolidants, such as modulus and thermal expansion, generally do not match those of the stone. Moreover, the effectiveness of the consolidants can be reduced following wetting/drying cycles, particularly when the stone contains inclusions of swelling clay[2]. By incorporating colloidal oxide particles into a silicate consolidants, we have previously shown that the drying shrinkage of the consolidant is reduced[3],[4] and the consolidated stone preserves more of its rigidity after wetting and drying[5]. However, those results were obtained with a limestone, so that a limiting factor in the development of strength is the ability of the ethyl silicate to bind to the surface[6]. Furthermore the limestones used[5] were very porous (~ 30 v%) which contributed to making particle ingress easier.

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necessary to obtain a meaningful modification of the consolidant properties as shown in previous studies.)

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With these objectives in mind, several variations to the basic composition were investigated using viscosity as the primary factor in the screening process. Most tests were performed with TiO_2 as major particle. This pigment is commercially available as a high quality powder with a relatively narrow size distribution.

EXPERIMENTAL PROCEDURE

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RESULTS

Optimal composition

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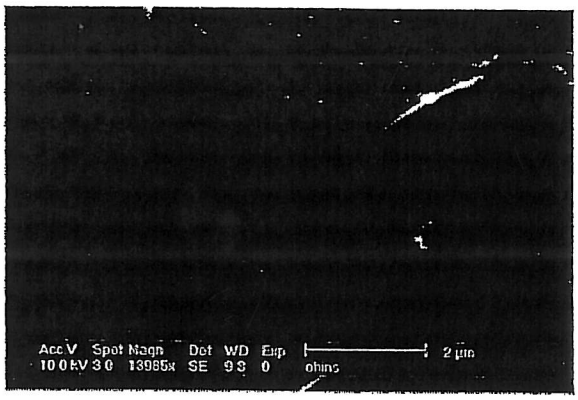

Figure 1. PMC in limestone. Small spheroidal particles are titania pigment.

The effects of the PMC on modulus and tensile strength of the sandstone are shown in Figures 2 and 3. Each consolidant provides about a three-fold increase in modulus and 60% increase in tensile strength, compared to the original stone.

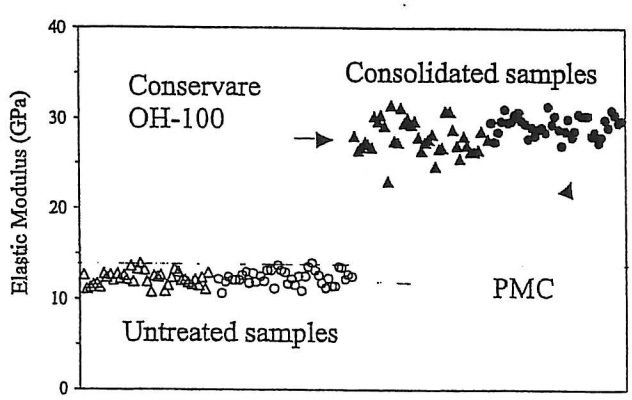

Figure 2. Dynamic elastic modulus of Ohio Masillian sandstone before and after consolidation with PMC and Conservare OH-100.

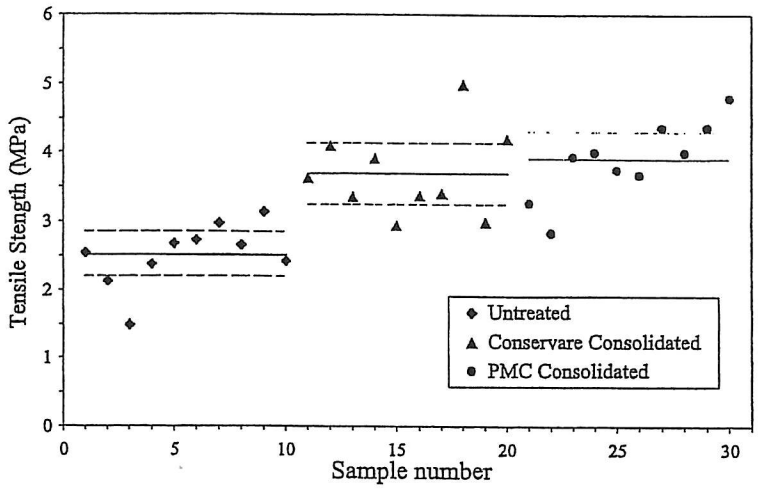

Figure 3. Tensile strength of Ohio Masillian sandstone before and after consolidation with PMC and Conservare OH-100.

The effect of the consolidant on the salt resistance of the stone is shown in Figures 4 and 5. The damage is most rapid for the bare stone, but the PMC gives more protection than Conservare OH-100 alone.

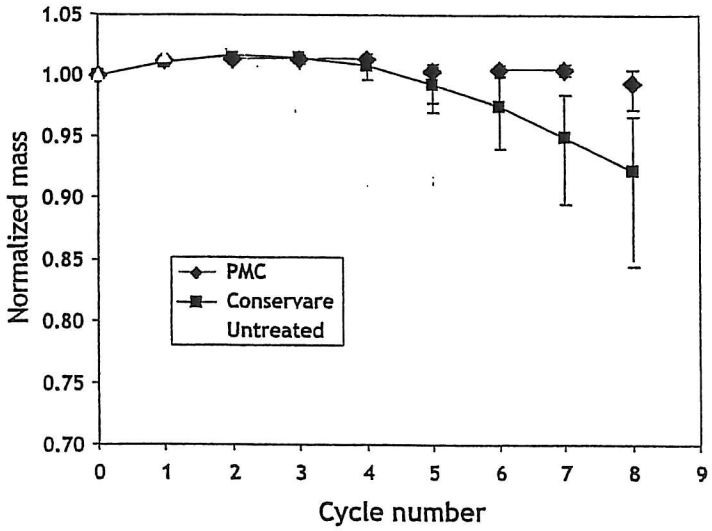

Figure 4. Normalized mass of stone versus number of cycles in sodium sulfate test.

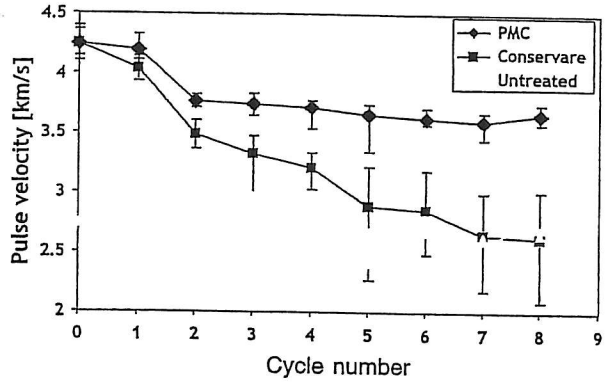

Figure 5. Pulse velocity in stone versus number of cycles in sodium sulfate test.

CONCLUSIONS

Titania pigment particles can be stabilized by a monolayer nano-silica particles within a silicate binder, such as Conservare-OH. The resulting consolidants preserves a low viscosity and the particles do not show any settling over 24 hours. The PMC provides better salt resistance than Conservare alone. We now plan to examine the effect of added particles on thermal expansion and wetting and drying cycles. In this process we will begin to integrate more systematically other particles, also looking at the possibility of matching the consolidant color to that of the stone.

ACKNOWLEDGMENTS

This work was supported by NCPTT Award No. MT-2210-9-NC-21. We thank Dr. William Farneth (DuPont Co.) for the titania pigment and Dr. David Boyer (PROSOCO) for the Conservare.

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