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CHARACTERIZATION AND CONSOLIDATION
OF PENNSYLVANIA BLUE MARBLE,
WITH A CASE STUDY OF THE SECOND BANK OF THE UNITED STATES,
PHILADELPHIA, PA

Jocelyn Kimmel

A THESIS

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Supervisor
Frank G. Matero

Reader
Glenn Boornazian

Graduate Group Chair
Frank G. Matero

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Abstract

Pennsylvania Blue marble used at the Second Bank of the United States, Philadelphia, Pennsylvania, showed evidence of large-scale spalling, flaking, and sugaring. A program was designed to investigate the characterization of the Second Bank marble and the feasibility of consolidation as a treatment option for deteriorating Pennsylvania Blue marble. Characterization, which included thin section petrography, X-Ray diffraction, qualitative analysis of salts, and water absorption/bulk specific gravity analyses, resulted in the recognition of decay mechanisms which were related to inherent mineralogical composition. The experimental program assessed the performance of artificially weathered marble treated with ethyl silicate and Acryloid-B72 in methyltrimethoxysilane in relation to untreated marble through various standardized and non-standardized tests, namely depth of penetration, microstructural evaluation, accelerated weathering, water absorption, bulk specific gravity, evaporation rate, water vapor transmission rate, resistance to salt crystallization, and resistance to abrasion. The study suggests that ethyl silicate may be a better choice for the marble than B-72 in methyltrimethoxysilane.

Preface

For thousands of years, marble has been favored as a durable and aesthetic building material. From the Helenic Acropolis to Augustan Rome, from the Taj Mahal to Westminster Cathedral, marble has been chosen for the finest monuments. As dimensional stone and cladding, sills, thresholds, fireplaces, floors, and pavements, marble has provided a decorative, lavish appearance to countless buildings for centuries. In imitation of the Greek and Roman building traditions, and in evocation of their ideals, American architects conceived and executed marble banks and civic buildings well into the nineteenth century: every major city had its marble monuments. Philadelphia was no exception.

Among the marbles used in nineteenth-century Philadelphia, only Pennsylvania Blue marble was quarried in the immediate area. Its accessibility, appearance, and reputedly fine quality resulted in widespread use throughout Philadelphia and the surrounding mid-Atlantic region. It is not surprising that William Strickland, who worked extensively in Philadelphia, chose Pennsylvania Blue marble for the commission he "stole" from Benjamin Latrobe in 1818.

Strickland built the Second Bank from 1818-1824. Judging from the eighteen commissions Strickland received during these six years, which included the Philadelphia Custom House, St. Stephen's Episcopal Church, and additions to Wyck in Germantown,

it is clear that the Second Bank commission established him as an important Philadelphia architect.

In design, the bank exemplifies Strickland's manner of straddling old and new, of combining traditional form with utilitarian layout. When Strickland wrote that "the student of architecture need go no further than [Stuart and Revett's] *Antiquities of Athens* as a basis for design,"[1] he might have been speaking of the Second Bank. The exterior is Greek Revival in design, like many of Strickland's buildings, and augmented with late Georgian Neoclassical details. The Doric porticoes located on the front and rear facades are a direct copy of the Parthenon as illustrated by Stuart and Revett. A contemporary account lauded this portico as "an important landmark in the development of Greek Revival Style in this country."[2]

The same article pays only minimal attention to the building material. "The building is constructed of a pleasing Pennsylvania marble, white with blue veins, which weathers well. It is called Chestnut Hill marble." This stone, more commonly referred to as Pennsylvania Blue marble, is the focus of this thesis. As an easily accessible, fine quality marble, it was highly prized during the nineteenth century in Philadelphia. Girard College and the U.S. Customs House in Philadelphia, the Washington Sarcophagi at Mount Vernon, and the Pennsylvania marble blocks in the Washington Monument are all

[1] Strickland, William, quoted in Agnes Addison Gilchrist, *William Strickland: Architect and Engineer* (Philadelphia: University of Pennsylvania Press, 1950), 31.
[2] *Analectic Magazine* 13 no. 3 (March, 1819).

constructed of Pennsylvania Blue. The marble was quarried at Marble Hall, in Montgomery county, near Flourtown.

Though used for major buildings and monuments, Pennsylvania Blue marble has never been studied in depth. Now that serious deterioration has been observed at the Second Bank and the Merchant's Exchange, among others, it was vital that a thorough analysis be performed to assist in characterization of the marble as one component of an exterior building system, in understanding of its weathering patterns, and in development of treatment methods.

The thesis begins with a thorough petrographic and geo-technical characterization of the material and its intrinsic decay mechanism, followed by research on the chemistry and logistics of consolidation, and concludes with an experimental program designed to test for the compatibility of Pennsylvania Blue with the chosen consolidants. The thesis was intended to broaden technical knowledge of Pennsylvania Blue marble, and to utilize its information to address some of the possible major decay mechanisms present at the Second Bank of the United States, and in Pennsylvania Blue marble monuments throughout the mid-Atlantic states.

Consolidation was proposed as a potential conservation option based on the microstructural characterization and macroscopic decay patterns observed at the Second Bank. Two consolidant systems were examined in relation to each other and to the untreated stone in an attempt to evaluate the viability of this conservation procedure.

It is hoped that the information presented in this thesis will be utilized in two ways. First, the thesis has been written as a documentary tool, in which assessment and experiment are viewed as part of a larger conservation plan, composed of a monument, and in a larger sense, of a building's conservation history over time. In addition, the thesis has been written to provide introductory information about the performance of Pennsylvania Blue marble as a building material.

Throughout the following text and the appendices, samples will often be referred to in an abbreviated manner. The abbreviations are as follows: U refers to untreated Pennsylvania Blue marble, E refers to ethyl silicate-treated Pennsylvania Blue marble, and B refers to a Acryloid B-72 and methyltrimethoxysilane-treated marble

1.1 Overview

Chapter one focuses on characterization of Pennsylvania Blue marble at the Second Bank of the United States. A series of analyses and geo-physical tests were performed in order to ascertain the mineralogical composition, morphology, physical properties, and related decay mechanisms of Pennsylvania Blue. The following chapter will show that the degrad-ation of the Second Bank marble is largely due to the microstructure of Pennsylvania Blue. The interaction between moisture, calcite crystals, and accessory minerals can be related to both microscopic and macroscopic deterioration. Decay on primary and secondary building facades can be differentiated, and even predicted, by mineralogical composition.

The information gained in this chapter will provide baseline information for the Indepence National Historical Park division of the National Park Service regarding the current state of deterioration at the Second Bank of the United States, as well as archival information for future conservation campaigns. In addition, the characterization provided a basis for the selection of appropriate consolidants, and the formulation of an experimental program to test and refine those treatments.

Because composition, microstructure, physico-mechanical properties, and weathering patterns differ for every monument and its environment, characterization of the Pennsylvania Blue marble for this study was restricted to sampling from the Second

Bank, rather than expanded to include a range of Pennsylvania Blue marbles from various buildings over time.

1.2 Lithogenesis and General Characteristics of Marbles

Commercially, marbles are often confused with limestones. Though geologists classify metamorphic marbles as distinct from sedimentary limestone, builders' definitions are broader; any stone that will take a polish is termed a "marble." This disparate terminology represents a potential problem for the architectural conservator, as buildings called "marbles" may be assumed metamorphic marbles, and treated as such without proper understanding of the geo-chemical make-up of the stone. The subsequent use of incompatible cleaning and conservation techniques can irreparably damage the stone. This can be avoided if the conservator is familiar with the properties of metamorphic marble in general, and if a thorough analysis of each building stone is performed before any treatment is implemented.

Marbles, as metamorphic rocks, form due to intense heat and pressure exerted upon previously crystallized limestones in the earth's crust and upper mantle. During this process, they recrystallize and lose many characteristics of the parent limestone. Because the components are rearranged mechanically and/or chemically, the resultant stone is likely to attain entirely new structure and mineralogy.

Marble consists mainly of calcite ($CaCO_3$), or crystalline calcium carbonate. Where magnesium ions replace calcium ions to some extent, the result is dolomitic marble ((Mg, Ca)CO_3). During metamorphism, calcite and dolomite minerals alter and recrystallize to form a roughly interlocking network. The size of the constituent grains depends primarily upon the extent of metamorphism. Grain size generally increases with prolonged metamorphic exposure.

Non-calcareous minerals present in the parent stone metamorphose within the calcite matrix. These secondary or accessory minerals are often responsible for marble hue and banding, as well as for characteristic physical and mechanical properties exhibited by various marbles. Inclusions vary with location; quartz, iron, graphite, and various micas are common (Table 1).

1.3 History and Use of Pennsylvania Blue Marble

Throughout the nineteenth century, builders in the mid-Atlantic United States used Pennsylvania Blue marble extensively. Only the King of Prussia quarry and Marble Hall, both in Montgomery county, produced this prized marble. Three colors were available: white, gray, and white banded with gray-blue. The appearance of Pennsylvania Blue, combined with its reputedly fine quality and accessibility, made it a natural choice of Philadelphia architects. High-profile buildings such as Girard College, the Second Bank of the Unites States, and the United States Customs House in Philadelphia, the

Washington Sarcophagi at Mount Vernon, and the Pennsylvania marble blocks in the Washington Monument were all constructed of Pennsylvania Blue.

Contemporary geological literature characterized Pennsylvania Blue marble as a highly metamorphosed magnesian limestone. Its granular crystallinity was often noted, as was its gray-blue banding. The 1891 *Geological Survey of Pennsylvania* identifies the banding as graphite, and notes the presence of isolated iron sulfate crystals.[3]

Pennsylvania Blue is no longer quarried. By 1934, both the King of Prussia quarry and Marble Hall had been abandoned. The steep slope of the marble belt had made quarrying difficult and expensive, yet the stone remained highly desirable, and the limited quantity of fine-quality marble was quickly exhausted.

1.4 Macroscopic Deterioration of Pennsylvania Blue Marble

When Strickland chose Pennsylvania Blue marble for the Second Bank of the United States, it had a fine reputation. The *Analectic Magazine*, of March, 1819, described the stone as follows: "the building is constructed of a pleasing Pennsylvania marble, white with blue veins, which weathers well."[4] Judging from the performance of Pennsylvania Blue marble over the next sixty years, it appears that weathering "well" may actually have meant weathering "attractively." According to the geological literature, the first

[3] *Geological Survey of Pennsylvania* (Harrisburg, PA: Pennsylvania Geological Society, 1891), 469.
[4] *Analectic Magazine* 13 no. 3 (March 1819).

recorded incidence of damaged Pennsylvania Blue occurred in the last decade of the nineteenth century.

As early as 1891, geologists realized that Pennsylvania Blue buildings were spalling, and attributed this to bands of pyrite, which "subject[ed the buildings] to a slow decay" over time.[5] At the United States Customs House, frontal columns experienced serious loss less than sixty years after its construction. Philadelphiá's cold weather and winter storms were deemed responsible, decayed stone was ultimately replaced with new marble, and provisions were made for periodic replacement.[6]

The Second Bank of the United States, located on Fourth and Chestnut Streets in Philadelphia, displays decay mechanisms typical of Pennsylvania Blue. The first report of loss is dated to 1923, when the consulting architect noted the loss of the fluting was noted from the columns. Spalling of columns was reported twice in 1964. Similar cornice and column loss was reported in 1983, 1986, 1989, 1994, and 1995. It is probable that far more marble was lost than has been recorded; maintenance staff often re-adhered spalled marble without documentation.[7]

With continued spalling, potential hazards have increased. Because the Second Bank is a public museum, there is a constant flow of visitors below the cornice and columns. In addition, the aesthetic and structural integrity of the building may be compromised as

[5] *Geological Survey of Pennsylvania*, 467.
[6] Ibid., 468.

portions of the columns and cornice continue to spall. Before a conservation plan is undertaken, characterization of the building marble and its weathering patterns were deemed necessary to provide a basis for treatment. Samples of stone from the cornice, frontal blocks, and side blocks has been analyzed, utilizing petrography, x-ray diffraction, and microchemical analysis. The remainder of this chapter describes these results and attempts to relate the findings to macroscopic and microscopic deterioration patterns observed at the Second Bank, and, in a general sense, to all Pennsylvania Blue monuments.

[7] James Toner, "Literature Review and Conservation History for the Second Bank of the United States" (Independence National Historical Park, Philadelphia, PA), 22-23.

1.5 Characterization of Pennsylvania Blue Marble

1.5.1 Petrographic Analysis

Petrographic analysis was performed to ascertain the mineral geometries and relationships present in Pennsylvania Blue marble. Three samples of Pennsylvania Blue were selected from Independence National Historical Park's Second Bank collection of spalled marble. The samples, chosen by macroscopic visual examination, differed in mineralogical composition and building placement. One sample, from the cornice, appeared to be primarily calcite, with visible inclusions. A second sample, from an unspecified portion of the building (probably cornice or column), was white with fewer visible inclusions. The third sample, from a secondary facade, was markedly differentiated from the other two samples by its gray color. Thin sections were viewed in reflected light, plane polarized light, and with crossed polars. Sections were stained with Alizarin Red S to ascertain the extent of calcite, and with Trypan Blue to differentiate between quartz and dolomite.

1.5.1.1 Sample I

Hand Specimen

Location: primary facade[8]
Color: white
Grain size: fine-grained
Observable mineral content: calcite

Thin Section

Crystallinity: holocrystalline
Grain size: medium
Texture: crystalloblastic

Groundmass:

Calcite, 95 %, evidenced by rhombohedral cleavage traces, polysynthetic twinning. Lack of single focus for all grains points to extreme pitting on a granular level.

Accessory Minerals:

Foreign materials 5%.

- Infrequent granular porphyroblasts vary in size from small to large. White in plane polarized light, high order interference colors. Alteration due to metamorphism and weathering makes positive identification different. Quartz is suspected.
- Some platy, micaceous material, probably muscovite.

[8] Because the stone samples were obtained from an unlabeled building collection housed off-site, exact sample locations were impossible to obtain.

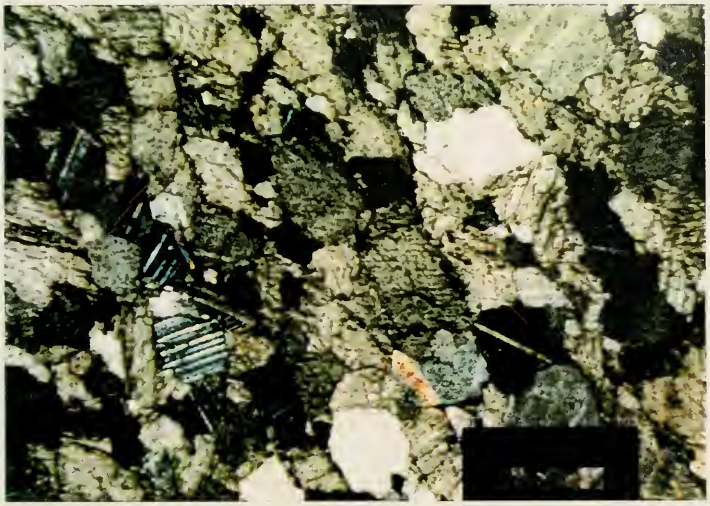

Figure 1. Thin Section of Sample I, crossed polars, 25X. Note twinning and tight interlocking of calcite grains.

Figure 2. Thin Section of Sample I, crossed polars, 100X. Micaceous inclusion, interlocking calcite grains.

1.5.1.2 Sample II

Hand Specimen

Location: cornice, primary facade
Color: white
Grain size: fine-grained
Observable mineral content: calcite, mica

Thin Section

Crystallinity: holocrystalline
Grain size: fine
Texture: crystalloblastic

Groundmass:

Calcite, 90 %, evidenced by rhombohedral cleavage traces, polysynthetic twinning. Some alteration visible.

Accessory Minerals:

Foreign materials 10 %.

- Isolated micaceous laths with single cleavage, high-order interference color, orientation in one direction. Probably muscovite.
- Angular to subrounded grains of quartz show heavy pitting. Same material forms veins. These grains are dark in reflected light, and fit well into the calcite matrix, implying that their formation was congruent with that of the calcite.
- Isolated subround crystals of orthoclase, evidenced by simple twinning.

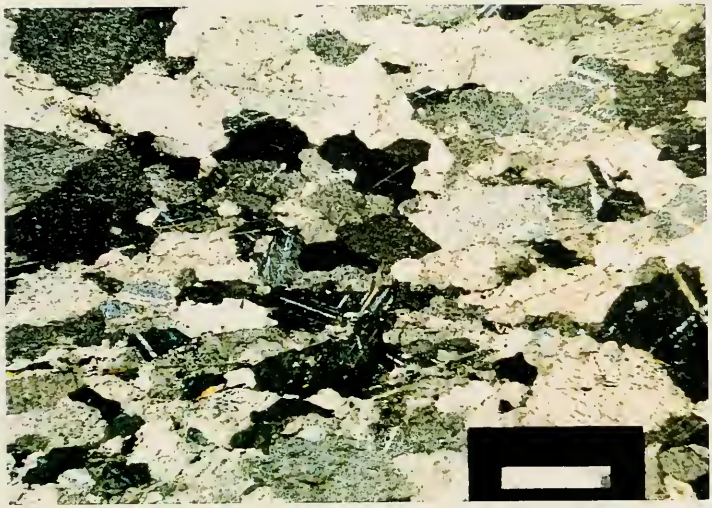

Figure 3. Thin Section of Sample II. Crossed Polars. 25X. Note interlocking calcite matrix, bright white quartz granules, and orthoclase, evidenced by simple twinning.

Figure 4. Thin Section of Sample II. Crossed Polars. 100X. Note mica inclusions and orthoclase.

1.5.1.3 Sample III

Hand Specimen

Location: secondary facade
Color: medium gray
Grain size: fine-grained
Observable mineral content: calcite, graphite

Note: tooling marks visible on surface of stone.

Thin Section

Crystallinity: holocrystalline
Grain size: fine
Texture: crystalloblastic

Groundmass:

Interlocking calcite grains, 99 %, evidenced by rhombohedral cleavage traces, polysynthetic twinning. Both white and gray calcite are visible. This may have to do with crystallographic orientation. White crystals have reflective surface; gray crystals do not.

Accessory Minerals:

foreign material 1 %.

- Black, opaque veins. In reflected light, reflective surface is visible, implying metallic component, appear to be graphite.
- Platy mica, evidenced by single cleavage trace, high-order interference color, orientation in one direction, probably muscovite.

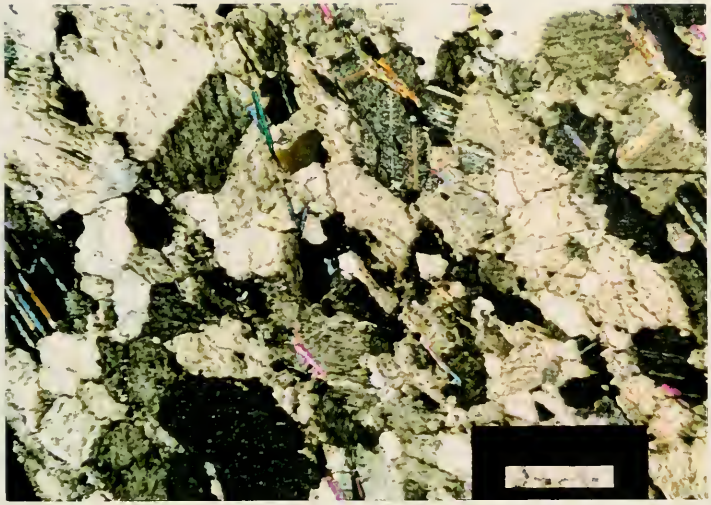

Figure 5. Thin Section of Sample III, plane polarized light, 25X. Note orthoclase, mica, replacement minerals at calcite centers.

Figure 6. Thin Section of Sample III, crossed polars, 100X, stained for calcite. Note graphite inclusion, replacement within calcite matrix.

1.5.2 Supplementary Analyses

1.5.2.1 X-Ray Diffraction

X-Ray diffraction was performed at the University of Pennsylvania's Laboratory for Research on the Structure of Matter, on a Rigaku Powder X-Ray Diffratometer set at 30 kilovolts and 20 milliamps, to ascertain mineralogical composition and to assist in petrographic analysis. Two samples from the Second Bank and one from the Study Collection at Independence National Historical Park were analyzed. Samples were chosen to provide mineralogical data for a range of compositions suspected to be present in Pennsylvania Blue marble.

The closest mineralogical match for all three samples was calcium magnesium carbonate ($CaMgCO_3$), or dolomite (Charts 1 and 2 present the information relevant to characterization of the Second Bank of the United States). None of the three samples, however, was an excellent match. Graphical information obtained using x-ray diffraction was used in conjunction with polarized light microscopy to explain this phenomenon.

In metamorphosed calcite, magnesium ions commonly replace calcium ions, resulting in crystals of $(Ca,Mg)CO_3$ rather than crystals of $CaCO_3$. The replacement factor, as well as isolated dolomite crystals present within the calcite matrix, account for the presence of magnesium. In short, x-ray diffraction provided conclusive evidence of magnesium,

which confirmed a century-old geological description of Pennsylvania Blue as a dolomitic marble.[9]

1.5.2.2 Soluble Salt Analysis

Purpose

To ascertain the presence and composition of soluble salts.

Relevance

Soluble salts may occur as intrinsic natural stone constituents, or result from associated building componenets, atmospheric pollution, rising damp, maritime environments, biological activity, or chemical treatment. Regardless of origin, salts are often seriously detrimental to porous building materials. Surface salt deposits are soluble in water, and can be easily carried into pores. When evaporation occurs, some salt remains within pore spaces and crystallizes. These salts can increase in size with repeated crystallization, eventually causing pore strain and resultant displacement, pitting, powdering, or flaking. Detection and analysis of these salts is necessary to complete characterization of stone; after documentation, a complementary conservation treatment can be prescribed, and protective measures instituted.

Methodology

[9] *Geological Survey of Pennsylvania* (Harrisburg, PA: Pennsylvania Geological Society, 1891), 469.

A chunk of representative Second Bank marble, consisting of surface crust, disaggregated stone, and sound stone, was chosen from the front facade. The sample was ground to a powder using a mortar and pestle. Representative samples were tested for the presence of carbonates, sulfates, chlorides, phosphates, and nitrates, using standard chemical reagent "spot tests."

Discussion and Conclusions

Qualitative analysis ascertained that three of the five salts tested for were present in Pennsylvania Blue marble (Table 3). Presence of carbonates and nitrates was immediately visible; phosphates and chlorides were not found. As the marble consists primarily of calcium carbonate, it was expected that its reaction with reagent sulfuric acid would be extreme. Nitrates can be attributed to biological activity, in this case, possibily pigeon excrement due to sample location.

Sulfates were detected in the surface crust and 0.5 cm below the surface after ground samples were soaked for 24 hours in distilled water. The sulfates can be attributed to the presence of atmospheric pollutants in an urban area.

1.5.2.3 Water Absorption and Bulk Specific Gravity

Purpose

To measure the water absorption and bulk specific gravity of weathered Pennsylvania Blue marble at the Second Bank of the United States.

Reference

ASTM C 97-83: "Standard Test Methods for Absorption and Bulk Specific Gravity of Dimension Stone"

Relevance

This test measures relative porosities of weathered Pennsylvania Blue marble. The information is critical to the conservator in regards to both stone durability and to the effectiveness of subsequent consolidation treatments. Bulk specific gravity provides a related measure of sample density versus porosity.

Methodology

Two representative samples were chosen, white marble from the cornice level of the primary facade and gray marble from the secondary facade. Both samples had naturally spalled from the building surface. The white marble had developed a surface crust and showed evidence of disaggregation. The gray marble was comparatively intact, and still showed evidence of tooling marks.

The samples were dried in the oven for 24 hours, placed in a dessicator for 24 hours, and weighed. They were then soaked in distilled water for 48 hours, and weighed again. Finally, the samples were hydrostatically weighed using a specific gravity balance. Percentages of water absorption and bulk specific gravity were calculated (Table 2).

Discussion and Conclusions

Both samples of Second Bank marble show less than one percent maximum water absorption. Bulk specific gravity shows the white marble to be denser that the gray. The amount of water absorbed by the white marble, however, is nearly triple that absorbed by the gray. This can be explained by the fact that the white marble is comparatively heterogeneous. Heterogeneity has resulted in enlarged pore space and disaggregation, which in turn has allowed for penetration of moisture and soluble salts.

1.6 General Conclusions

At least three varieties of Pennsylvania Blue marble appear to have been in the building of the Second Bank of the United States. All consist of at least 90 % calcite (with replacement magnesium, to some extent), and differ in the amount of accessory minerals and deterioration level. Marble used for the secondary facades (Petrographic Sample III) remains relatively intact. It is comparatively dark in color and nearly homogenous in texture, with 1 % or fewer accessory materials. Its interlocked structure is responsible for its lack of porosity. Medium-grained white marble was used to build the front and rear facades (Petrographic Sample I). This stone has a slightly higher proportion of foreign material and a higher porosity and permeability; hence it is often more deteriorated than the darker marble used for the side facades. Fine-grained, porous white marble was used at the cornice level, and presumably wherever sculptural details required a workable stone (Petrographic Sample II). This stone shows the highest proportion of accessory minerals, namely mica, quartz, and orthoclase. When this knowledge is combined with the stone's relatively high porosity and location, it is not surprising that high levels of salts, disaggregation, and spalling are present in this area.

Stone deterioration at the Second Bank stone is clearly related to the inherent geo-chemical and micro-fabric characteristics of Pennsylvania Blue marble in conjunction with varying exposure. Calcite crystals on the front and rear facades show extreme pitting in thin section. Micro-corrosion is visible along grain boundaries and cleavage traces, which act as weak micro-planes along which moisture and salts may enter porous stone.

On the darker secondary facades, where the stone is homogenous, it is relatively intact; 170-year old tooling marks are still visible. On the primary facades, where the stone is heterogeneous, and higher proportions of inclusions can be documented, the marble has disaggregated and spalled to a significant degree.

In conclusion, the presence of various shapes and sizes of accessory minerals weakens the interlocking calcite matrix of Pennsylvania Blue marble. Quartz and orthoclase, present as isolated crystals, tend to act as wedges, forcing the matrix apart and creating clumps of disaggregated grains. Mica, present in lamellar beds, is responsible for planar failure due to its phyllosilicate "sheet" structure. The weight of pollution-related surface crusts may aid in inducing surface flaking, causing additional areas of marble to spall.

2.1 Overview

This chapter addresses the chemistry, performance criteria, and application techniques of polymers, focusing on two stone consolidants: alkoxysilanes and alkoxysilane-acrylic resin mixtures. Because the project was begun knowing that consolidation was a viable consideration, the program has focused on the evaluation of two systems.

2.2 General Characteristics of Consolidants

All stone consolidants are natural or synthetic formulations intended to restore grain-to-grain contact of disaggregated stone and to slow the effects of deterioration. Typical stone consolidants include alkoxysilanes, acrylic polymers, epoxies, polyurethanes, waxes, barium hydroxide, and limewater.

A typical consolidant is applied as a liquid, reacts with its surroundings or other ingredients, and eventually solidifies to form a sound binding matrix. The cured consolidant alters physical and/or mechanical properties of weathered stone, effectively creating a more coherent stone. Numerous authors, including Horie, Amoroso and Fassina, Heaton, and Warren, have provided comprehensive guidelines for successful consolidants. The following is a general consensus of desirable properties for large-scale applications.

Before and during application

- The consolidant should penetrate to a sufficient depth during application, and remain there after it dries.
- It should not react with the substrate, nor should it form a continuous film on the surface.
- Application should not be harmful to the operator or environment
- The consolidant should be reasonably priced and easy to apply.

Compatibility with stone
- The product must have a thermal expansion coefficient which is compatible with the stone, and should adapt to the changing conditions of the stone, whether wet or dry, cold or warm.

Visual appearance
- After the consolidant cures, it should not alter the color, texture, or gloss of the stone.

Protection from external substances
- The product should protect the stone from exterior weathering agents, such as acid and alkaline pollutants, biological growth, wind, and moisture.

Strength and hardness
- By increasing grain to grain contact, the consolidant should strengthen the substrate to a reasonable degree.

Moisture passage
- The consolidant should not affect water vapor transmission.
- The consolidant should reduce accessibility of liquid moisture to the stone interior, while allowing sufficient moisture evaporation.

Durability
- The product should be durable and long-wearing.

reversibility
- The consolidant should allow for retreatment at any time.

Many properties, including clarity, strength, and stability, differ between consolidants. This is a result of such factors as the consolidant's chemical composition, the application procedure, its subsequent reaction, and the hardening process. The consolidant effect may differ between stone types. Ethyl silicates, for example, form a network similar to silica, which makes them particularly compatible with siliceous stones.

and are not soluble in solvents. Subsequently, cross-linked polymers are irreversible once they have solidified.[10]

The processes by which monomers become polymers are collectively called polymerization. Condensation, addition, and network polymers react to form stone consolidants. Addition polymerization may occur in any monomer with carbon atoms connected to a double bond (C=C; the monomer may use one of its bonds to join to another carbon. Condensation polymerization occurs when two dissimilar molecules react, forming a polymeric product and a by-product. Network polymerization occurs when long polymer chains are linked or interact with small molecules to form a branched network.[11] Relevant polymerization processes will be discussed later in this chapter.

Polymeric coatings show great variability in physical and mechanical properties. They range from flexible and strong to brittle and weak. They differ in refractive index, color, and gloss. Some mechanical properties of a polymer may be inferred through molecular size and weight and glass transition temperature. Molecular size and weight are responsible for the viscosity of a solution, because the large molecules show resistance to flow.[12] Glass transition temperature indicates the temperature at which a glassy substance loses its solid properties, and tends toward a semi-liquid state. When choosing a consolidant, the determination of glass transition temperature (gtt) is vital. A high gtt

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[10] C.V. Horie, *Materials for Conservation: Organic Consolidants, Adhesives and Coatings* (London: Butterworths, 1987), 11-12.

[11] Conservation Unit of the Museums & Galleries Commission, *Science For Conservators. Volume 3: Adhesives and Coatings* (London: Routledge, 1987), 32-36.

may be overly brittle, and crack under thermal or mechanical stress, while a low gtt may result in a malleable, tacky coating which attracts dirt and dust, and, once bound to the coating, is not removable without also removing the consolidant. An ideal polymer has a glass transition temperature near room temperature. It should be noted that cross-linked polymers cannot flow above the gtt (they may, however, become rubbery).

Polymers do not last forever. As the polymer ages, it may discolor, embrittle, weaken, attract dirt, migrate, or crack. Heat, ultraviolet light, oxidation, and pollution are natural enemies of polymers. However, polymeric consolidants used for architectural conservation must necessarily be exposed to some, if not all, of these mechanisms. Therefore polymeric consolidants should be applied and monitored with their formation and deterioration possibilities in mind to minimize the risk of inappropriate, improperly applied, or deficient polymeric materials.

2.4 Application of Polymers

Conservators have documented four successful methods of applying polymeric materials to stone. The methods include immersion in the consolidating solution at atmospheric pressure, immersion under vacuum, absorption by capillary rise (partial immersion), and surface application by brushing or spraying. Amoroso has reported good penetration of the consolidant (on sandstone) using all four methods. The percent of consolidant

[12] Ibid., 17.

absorbed by weight was similar.[13] However, porosity of the chosen material will affect the amount of consolidant retained, as will the chemical composition of the substrate itself (consolidants perform differently on siliceous stones, due to the compositional similarity of consolidant and stone, than they due on calcareous stones).

The following program examined application by two methods: absorption by capillary rise and surface application. Capillary rise was examined because it is easily performed in the laboratory and because it insures consolidation to the greatest depth possible. Surface application was also performed to simulate field application, as absorption by capillary rise is impossible when treating an entire building.

Regardless of technique, the stone must be clean and dry before application to insure adequate penetration. If the chosen consolidant gels through a hydrolysis reaction, the stone must not be completely without moisture, or the reaction cannot proceed. Dry, in this sense, refers to *excess* surface and substrate moisture. Stone moisture should be at equilibrium with room (or outdoor) temperature and humidity. In addition, all salts should be removed from the stone prior to the consolidation process where possible to avoid the possibility of consolidating foreign material within the stone substrate.

2.5 Ethyl Silicates

[13] Amoroso and Fassina

Ethyl silicates are possibly the most widely used consolidant for architectural stone conservation. As noted by geologists,[14] chemists,[15] and conservators,[16] their silicate structure gives them particular affinity to sandstone and other siliceous stones. Ethyl silicates have been successfully utilized in stone conservation for decades, "with good durability and no discoloring."[17] It should be noted that ethyl silicates alone do not have waterproofing properties. However, the minimization of pore size due to the application of consolidant may result in a slight decrease in moisture intake.

As mentioned in the previous section, ethyl silicates are cross-linking polymers, and within that group are alkoxysilanes. They may be chemically classified as silicic acid esters, and within this context, as monomeric silane derivatives. Conservators most commonly use tetraethoxysilane, a type of silicic acid ester, for stone conservation. The conservator should be aware that proprietary products or custom formulations entitled silicic acid ester, tetraethoxysilane, tetra ethyl silicate, and TEOS probably all refer to ethyl silicates. Wacker Chemie manufactures an ethyl silicate called Wacker OH in Germany, marketed by ProSoCo in the United States under the name of Conservare OH.

Ethyl silicates are widely appreciated for their dual nature as synthetic polymers with mineral structures. As stated by Amoroso and Fassina, ethyl silicates "possess both the

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[14] Erhard M. Winkler, *Stone in Architecture: Properties and Durability in Man's Environment* (New York: Springer Verlag, 1994), 270. (Hereafter Winkler.)
[15] A. Elena Charola, personal communication.
[16] Amoroso and Fassina, 245.
[17] Winkler, 270.

advantages of a synthetic polymer, when put in solution and applied to the stone, and the durability of a mineral product because of the formation of silicon dioxide."[18]

Once applied to the stone, polymerization occurs in the presence of traces of water. Through hydrolysis and condensation reactions, silica is deposited in a gel form within the pores of the stone. As the reaction proceeds, ethanol is given off as follows:

$$\underset{\text{pore water}}{Si(OC_2H_5)_4} + \underset{\text{silica gel}}{4H_20} \rightarrow \underset{\text{ethanol}}{4C_2H_5OH}$$

In the absence of sufficient humidity, the reaction will not proceed fully, as the pores will not retain sufficient water to impel the reaction. Completion of the reaction takes a number of weeks.

Tabasso's work with ethyl silicates on Lecce limestone allows for a projection of its performance on Pennsylvania Blue marble. The decrease in porosity should cause a slight decrease in water absorption. In addition, water vapor transmission and evaporation rate are expected to change slightly. In addition, performance over time is expected to show positive results.[19] It should be kept in mind, however, that as the ethyl silicate loses water, it may gradually shrink, causing matrix cracking over time.

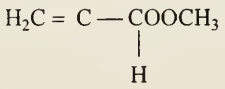
2.6 B-72 in Methyltrimethoxysilane

[18] Amoroso and Fassina, 245.

[19] M. Laurenzi Tabasso and U. Santamaria, "Consolidant and Protective Effects of Different Products on Lecce Limestone," 707, in *Fifth International Congress on the Deterioration and Conservation of Stone, 25 - 27 September 1985* (Lausanne, Switzerland: Presses Polytechniques Romandes, 1985). (Hereafter Tabasso and Santamaria.)

The second consolidant system to be tested is a combination of Acryloid B-72 in methyltrimethoxysilane (hereafter referred to as MTMOS), a system which has been proposed and studied in depth by George Wheeler, primarily on museum objects. In the past, the desirable aspects of MTMOS have been outweighed in the past by its extreme volatility and tendency to evaporate very quickly. The addition of B-72 to MTMOS stabilizes the system to some extent, and in addition provides an adhesive quality to the consolidant.[20] The adhesive quality is useful in providing the re-establishment of grain to grain contact of flaking stone, such as that found on the primary facade at the Second Bank of the United States. Furthermore, the addition of MTMOS to B-72 aids in larger polymeric chains, and eventually in even consolidant penetration. This prevents the formation of a surface film which may peel away.[21]

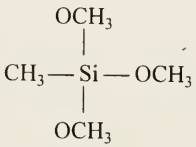
B-72 is an synthetic acrylic polymer, a one to one ratio of methylmethacrylate and ethyl acrylate. In the United States, it is distributed by Rohm and Haas in Philadelphia, Pennsylvania. As a synthetic resin, it consists of chains of monomers:



[20] George Segan Wheeler, G.L. Shearer, S. Fleming, L.W. Kelts, A. Vega, and R.J. Koestler, "Toward a Better Understanding of B-72 Acrylic Resin/Methyltrimethoxysilane Stone Consolidants: Materials Research Society Symposium Proceedings," 209, in *Materials Issues in Art and Archaeology II. San Francisco, 17 April 1990,* edited by Pamela B. Vandiver, James Druzik, and George Segan Wheeler. (Hereafter Wheeler, "Towards . . .")

[21] E. De Witte, "Resins in Conservation: Introduction to their Properties and Applications," in *Proceedings of the Symposium Resins in Conservation. University of Edinburgh, Edinburgh, United Kingdom, 21-22 May 1982*, edited by J.O. Tates, N.H. Tennent, and J.H. Townsend (Edinburgh: Scottish Society for Conservation and Restoration, 1983), 1-3. (Hereafter De Witte, "Resins in Conservation.")

As Amoroso states, a cross-linking, polymeric chain can be created by the addition of a cross-linking agent.[22] In the B-72/MTMOS system, MTMOS acts as such an agent. The B-72 structure above is alternated with the MTMOS structure:



The B-72/MTMOS system requires fresh dissolution of the B-72 in MTMOS before the consolidation procedure. During dissolution of B-72, the polymers' knotted solid state is dissolved as molecules of MTMOS penetrate the polymeric chain.[23] The use of a solvent "prevents the migration phenomenon, and therefore, movement of dissolved resin towards the evaporation surface."[24]

During polymerization, the B-72 copolymers react to become a single polymeric chain.[25] The reaction requires , moderate warmth, light, and air, in conjunction with a low reaction temperature, which allows macromolecules with high molecular weight to form, and proceeds through hydrolysis and condensation, as in the ethyl silicate reaction. B-72 counteracts the liquid MTMOS, resulting in a slowed reaction in which the methoxy

[22] Amoroso and Fassina, 335.
[23] De Witte, "Resins in Conservation."
[24] Amoroso and Fassina, 344.

groups of MTMOS hydrolyze, while the methyl groups do not. At this time, a low reaction temperature is desirable, as it allows the formation of large molecules.[26] As the liquid slowly gels, B-72 begins to promote condensation, and the reaction proceeds to completion over a number of weeks.[27]

The performance reports of B-72 underscore its variability. Tabasso's work with Lecce limestone projects that absorption and penetration depth are expected to be low. Water vapor transmission and evaporation rate will probably be reduced. Water repellency should be increased. B-72 may not perform well after artificial weathering.[28] However, Amoroso and Fassina's compilation reports more positive results; acrylics such as B-72 are UV- and heat-resistant, show strong water repellency, and low propensity to oxidize.[29] In addition, they note that "acrylics usually scratch fairly easily and can crack with time, although toughness and abrasion resistance are improved as molecular weight increases."[30]

As George Wheeler has suggested, the addition of MTMOS to B-72 may aid in the stability of the system. Horie notes that the polymer formed from MTMOS is tough, rigid, and resistant to solvents and photo-oxidation.[31] The combination of the two systems is expected to raise the overall results.

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[25] De Witte, Resins in Conservation.
[26] Amoroso and Fassina, 325-6.
[27] Wheeler. "Towards . . .," 225.
[28] Tabasso, 706.
[29] Amoroso and Fassina, 324.
[30] Ibid., 333.

3.1 Overview

This chapter details the program of the consolidation testing procedure based on characterization data and consolidant chemistry. Sample pretreatment, artificial weathering of samples, treatment of weathered samples, experimental program, conclusions, and recommendations for future research are addressed. Based on the experimental program designed for this research, an application of ethyl silicate or B-72/MTMOS to Pennsylvania Blue marble is likely to inhibit deterioration. Furthermore, this chapter provides an internal comparison of the properties and performance of B-72/MTMOS and ethyl silicate on Pennsylvania Blue marble.

The information gained in this chapter will provide baseline information for the National Park Service regarding the possible consolidants for use at the Second Bank of the United States, as well as archival information for future conservation campaigns. In addition, the program provides a basis for consolidation information on other Pennsylvania Blue marble monuments, as well as a theoretical comparison of consolidant properties and performance of two coatings commonly utilized in art and architectural conservation.

The procedures detailed in the following chapter provide only brief summaries of methodology, focusing instead on purpose, reference, rationale, discussion of results, and conclusions obtained. Full procedural documentation and program data (tables) can be

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[31] Horie, 156

3.1 Overview

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[31] Horie, 156

experiment simulates the weathering undergone by buildings and outdoor monuments as they are exposed to the environment over time.

Methodology

Samples may be variable in size; scrap samples with at least one crisp edge should be used to allow for evaluation of deterioration. Samples should be elevated in sulfuric acid solutions, by means of glass beads or rods, to insure penetration on all sides. Samples should be weathered in a fume hood. Protective goggles and acid-resistant gloves should be worn.

Discussion and Conclusions

Samples were weathered in sulfuric acid solutions of various molarity, based on a comparative review of relevant literature (Table 4). It was found that the relatively intact Pennsylvania Blue required a highly concentrated solution of acid to induce erosion. A solution of sulfuric acid with molarity of 3 was chosen for the weathering procedure, as an acid solution with high enough molarity to weather the stone, while remaining relatively safe to use.

3.3.2 Artificial Weathering of Pennsylvania Blue Marble Specimens

Concentrated sulfuric acid was diluted with distilled water to 3 molar in preparation for the acid bath. Two acid-resistant plastic tubs were filled with glass beads and glass rods

Samples were consolidated in a fume hood over a twelve-hour period following a pre-treatment weighing. The majority of the samples were treated using the partial immersion process, which promotes effective penetration through direct contact with the consolidant solution and through capillary rise of that solution. Samples were placed in a container filled with the consolidant to depth of 1-2 centimeters. When the capillary rise appeared complete, the samples were removed from the solutions (Figure 8).

Those samples to be tested for penetration depth were consolidated using one of the recommended field procedures, namely of a brush application procedure detailed by manufacturers and conservators as a simulation of field application. Samples to be treated with ethyl silicate has the consolidant applied in cycles of three applications to saturation, with five minutes between each application, and 20 minutes between cycles. Two cycles were performed on the Pennsylvania Blue laboratory samples, and three on the Second Bank Pennsylvania Blue samples. Samples to be treated with B-72/MTMOS were consolidated by brush application to the beading point, showing that no further consolidant was being absorbed.

Samples treated with B-72/MTMOS were tented with plastic wrap after the first half hour of drying to retard the volatility of the solvent (Figure 9). The samples were allowed to dry in a fume hood for 36 hours (Figure 10). Following the initial drying period, the consolidated samples were removed from the fume hood and allowed to dry at room temperature and relative humidity for two weeks.

Following the drying period, samples were reweighted to give an approximate weight percent increase (Table 5). Ethyl silicate-treated stones showed an increase of 0.22%, while B-72/MTMOS treated stones showed an increase of 0.19%. The result allows an accurate comparison of ethyl silicate-treated versus B-72/MTMOS-treated marble. Since the weight percent is comparatively minor, the properties of ethyl silicate and B-72 in MTMOS on the marble can be viewed as minimal, and can be expected to increase on more weathered marble, such as that at the Second Bank of the United States.

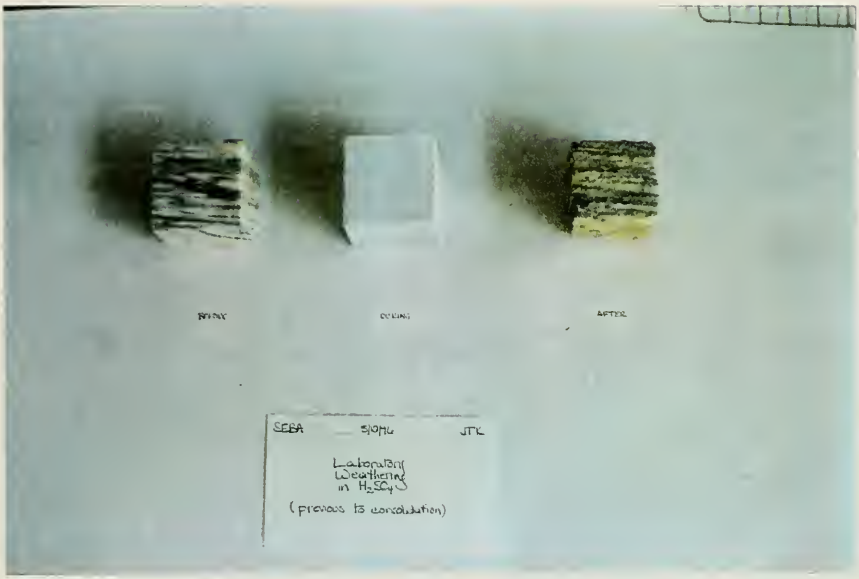


Figure 7. Pennsylvania Blue marble before, during, and after laboratory weathering.

Figure 8. Scrap sample during consolidation procedure, turned on its side to show capillary rise.

Figure 9. Samples treated with B-72/MTMOS, tented with plastic after consolidation.

Figure 10. Consolidated samples drying in fume hood.

3.5 Experimental Program

3.5.1 Depth of Penetration

Purpose

To measure the penetration depths of ethyl silicate and B-72 in Pennsylvania Blue samples and deteriorated Second Bank marble.

Reference

Rakesh Kumar and William S. Ginell(Getty Conservation Institute), "A New Technique for Determining the Depth of Penetration of Consolidants into Limestone Using Iodine Vapor"

Relevance

The depth of penetration of a consolidation treatment indicates the depth to which that stone will be protected. To perform effectively, the consolidant must penetrate through the deteriorated stone into the unaltered substrate. This test comparatively assesses the depths of penetration of the treatments in question.

Methodology

One 2 -inch cube treated with ethyl silicate and one with B-72/MTMOS were treated. In addition, irregular, disaggregating samples from the Second Bank, treated respectively with ethyl silicate and B-72/MTMOS were treated (Figure 11). The building samples

were tested to give a comparative penetration depth on actual deteriorated stone. For the purposes of this test, the consolidant was brush-applied to one side of each sample, as it would be on site. This allows an accurate look at initial consolidant performance in the field.

Discussion and Conclusions

Both samples of artificially weathered Pennsylvania Blue showed full surface coverage plus a penetration depth of 1 mm. Second Bank samples, however, showed a far greater penetration depth: B-72/ MTMOS absorbed to a depth five times that of the B-72/MTMOS treated laboratory sample, and ethyl silicate absorbed to a depth of 25 times. This shows that while relatively intact Pennsylvania Blue absorbs very little consolidant, weathered Pennsylvania Blue is receptive to the treatment. Ethyl silicate, in particular, appears to penetrate far into the stone.

Figure 11. Samples during testing of consolidant penetration depth.

3.5.2 Microstructure

Purpose

To ascertain the effect of consolidant treatment on the microstructure of a stone.

Reference

Ann Brackin, "A Comparative Study of the Effects of Applying Acrylics and Silanes in Sequence and in Mixture, with a Case Study of the Column in the Convento of Mission San Jose y San Miguel de Aguayo, Texas." (Master's thesis, University of Pennsylvania, 1994), and

A. Elena Charola , *et al.* "SEM Examination of Limestones Treated with Silane or Prepolymerized Silicone Resin in Solution." *Adhesives and Consolidants: Preprints of the Contributions to the Paris Congress, 2-8 September 1984,* edited by N.S. Bromelle, E.M. Pye, P. Smith, and G. Thompson, 184-192. London: Institute for the Conservation of Historic Works, 1984.

Relevance

To provide a microstructural comparison of consolidant performance based on assessment of penetration depth, pore coverage, and film characteristics.

Methodology

Six samples, two each of untreated, ethyl silicate- treated, and B-72/MTMOS treated were assessed. The samples were etched using 1M hydrochloric acid for approximately one minute. Because consolidant strands may be elusive under the scanning electron microscope, even at high magnification, two coating media were applied: one set was sputter-coated with carbon, and one with gold, to a thickness of 720 Angstroms. Samples were viewed using both coatings, under a JEOL 6300FV scanning microscope at 50 to 10,000 times.[32] The photographs shown here employ the carbon coating, which was surprisingly more effective in elucidating the consolidant film.

Discussion and Conclusions

The ethyl-silicate treated sample shows the ethyl silicate to lightly coat grains. Pitting and cracking of the surface are evident through the coating (Figure 12). At very high magnification, ropy strands of ethyl silicate link pore edges (Figure 14).

The sample treated with B-72 in MTMOS shows a smoother, heavier surface coating. Surfaces appear rounded and slightly thicker than the ethyl silicate-treated sample. Again, pitting and cracking are evident through the coating, showing that pores are not clogged by consolidant application (Figure 13).

[32] This experiment was supported by the National Science Foundation MRL Program, under Grant No. DMR91-20668, at the Laboratory for Research on the Structure of Matter at the University of Pennsylvania.

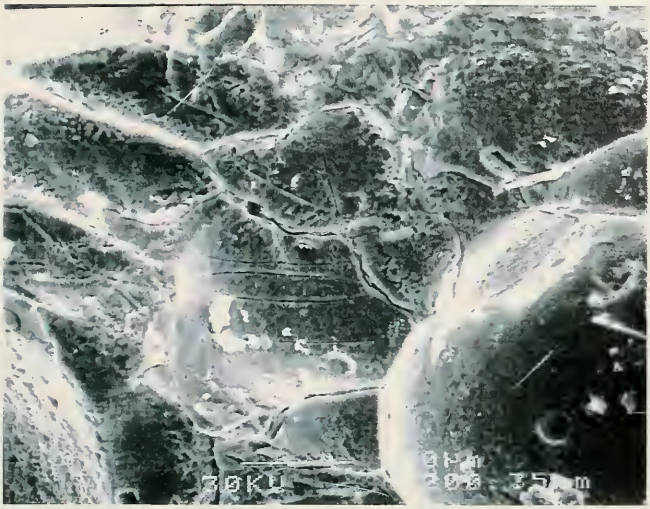


Figure 12. Scanning electron micrograph of sample treated with ethyl silicate, 200X.

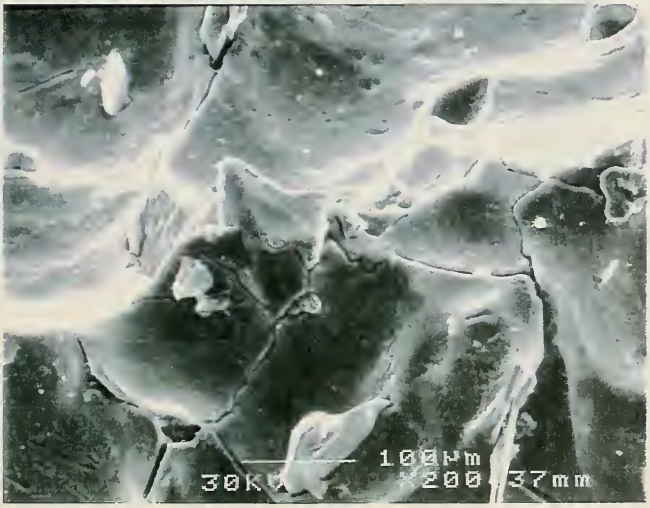


Figure 13. Scanning electron micrograph, samples treated with B-72/MTMOS, 200X.

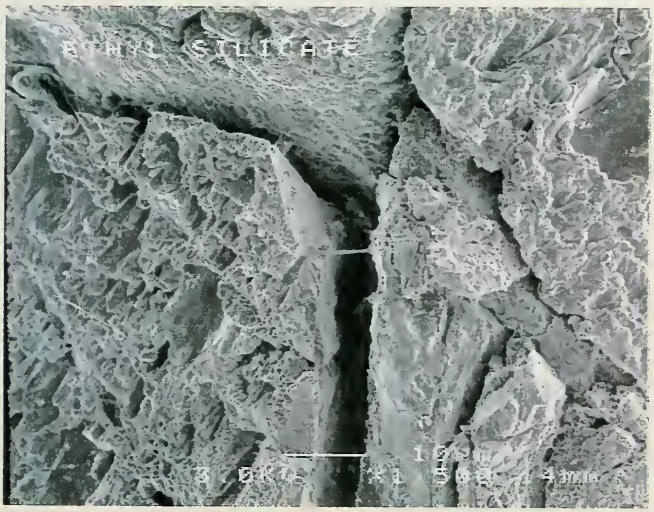


Figure 14. Scanning electron micrograph of ethyl silicate strands, 1500X.

3.5.3 Accelerated Weathering

Purpose

To simulate the combined cyclical effect of ultraviolet light, heat, and outdoor condensation over time.

References

- ASTM G-53-93: "Standard Practice for Operating Light- and Water-Exposure Apparatus for Exposure of Non-Metallic Minerals,"
- ASTM D-1535-89: "Standard Test Method for Specifying Color by the Munsell System,"
- Munsell Soil Color Book, and
- RILEM test VI.1: "External Aspects of Stones."

Relevance

This test measures the effect of ultraviolet light and wet-dry cycling, simulating multiple, long-term weathering patterns in a compressed period of time. Treated and untreated samples can be assessed for levels of change at the macroscopic and microscopic level, including ultraviolet-related degradation and consolidant performance.

Methodology

This test utilized a weatherometer in conjunction with color standards and visual analysis in order to assess performance of untreated stone in comparison with consolidated stone

II.

The samples were viewed under fluorescence microscopy to examine microstructural changes. Untreated samples showed evidence of shallow surface pitting. This was not apparent on either of the consolidated surfaces. Ethyl silicate-treated samples showed evidence of an extremely slight yellowing, not visible to the naked eye. B-72/MTMOS-treated samples showed evidence of intact consolidant at the surface level.

Both consolidants show some indications of change on a microscopic level after accelerated weathering. Ethyl silicate-treated samples should be further studied to assess the effect of weathering on consolidant stability, particularly in relation to color. If B-72/MTMOS is selected for monument consolidation, care should be taken to test an inconspicuous area for consolidant pooling at the surface level. It is believed, however, that this is not a concern, as the Pennsylvania Blue monuments requiring conservation are in general fairly porous as a result of disaggregation at the surface level, and hence consolidant is expected to be absorbed, rather than pool.

III.

Some color variability results in the artificial weathering of consolidated Pennsylvania Blue marble (Table 7). After exposure to ultraviolet radiation, untreated white

Pennsylvania Blue shows no change in color, while gray bands show a slightly more saturated value. Both white and gray Pennsylvania Blue treated with ethyl silicate shows an slightly increased value saturation level. Neither white nor gray bands of B-72/MTMOS treated stone, nor the charcoal gray band, show evidence of any change. Hue and chroma remained constant.

Both consolidants appear to be fairly stable in the presence of ultraviolet light. It should be noted that B-72/MTMOS produced no change in value, while ethyl silicate resulted in a slight value change. Value changes present in untreated and ethyl silicate-treated marble may be due in part to the gradual erosion of weathered surface material to a more pronounced appearance.

3.5.4 Water Absorption and Bulk Specific Gravity

Purpose

To measure the water absorption and bulk specific gravity of untreated samples as compared to samples consolidated with ethyl silicate and B-72 in MTMOS.

Reference

ASTM C 97-83: "Standard Test Methods for Absorption and Bulk Specific Gravity of Dimension Stone"

Relevance

Consolidation treatments may reduce water intake to the substrate, in effect imparting a degree of hydrophobicity, which can in turn limit deterioration. The water absorption test assesses this characteristic, measuring relative porosities of treated versus untreated samples. Bulk specific gravity provides a measure of the percentage of consolidant retained by the samples. In general, a higher percentage indicates a more effective treatment.

Methodology

Nine samples, three each of untreated, ethyl silicate, and B-72/MTMOS were tested following the standard ASTM procedure (Figure 15). Water absorption and bulk specific gravity were calculated for each sample (Table 8).

Discussion and Conclusions

I.

Water absorption, measured in weight percent, shows samples treated with B-72/MTMOS to absorb a similar percentage of water to the untreated stone. The samples treated with ethyl silicate absorb slightly less water.

II.

Bulk specific gravity appears to be similar for untreated and treated samples. This may be due in part to the relatively intact pore structure of the sample stone. The experiment should be repeated with decaying marble to assess consolidant retention.

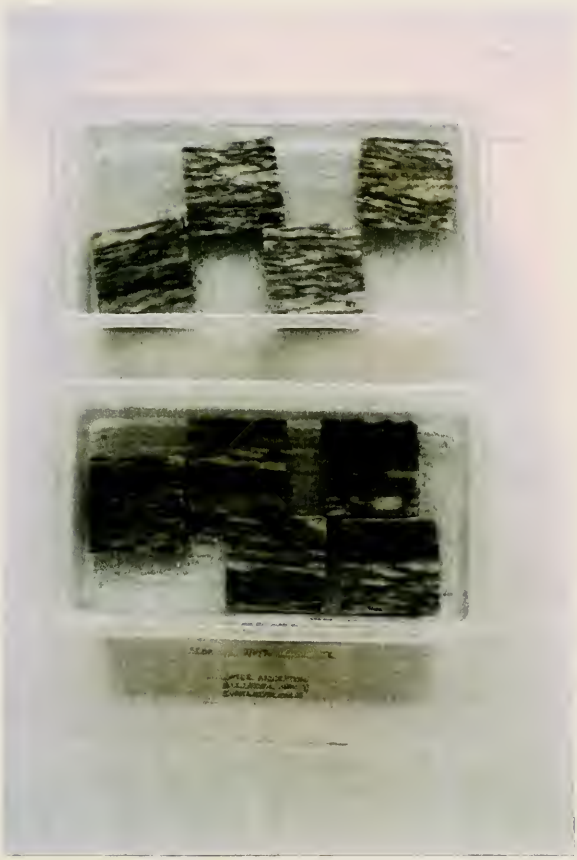


Figure 15. Samples soaking during water absorption/bulk specific gravity testing.

3.5.5 Evaporation Curve

Purpose

To measure the evaporation of standing water collected in pores over time within untreated samples untreated samples as compared to samples consolidated with ethyl silicate and B-72 in MTMOS.

Reference

RILEM test II.5: "Evaporation Curve."

Relevance

Moisture attacks all buildings through rain and snow, condensation, building cracks, and rising damp. Once the material has been wetted, drying occurs, and water within the pores will slowly evaporate. This test measures the hydrophobic effects of the consolidants compared with untreated stone, as well as the relative pore space per treated and untreated stone.

Methodology

One sample each of untreated, ethyl silicate-treated, and B-72/MTMOS-treated samples was tested for evaporation rate over time. The samples were placed in a water bath for 48 hours prior to testing to insure full saturation. Controlled evaporation was obtained using a dessicator and active desiccant.

Discussion and Conclusions

As expected, each of the samples lost the most moisture during the first 10 to 20 minutes of evaporation (Table 9, Chart 3). The sample treated with ethyl silicate lost more than 70% of its water content during the first 15 minutes of evaporation. The sample treated with B-72/MTMOS lost 68%, and the untreated sample lost 48%. After 25 minutes, the ethyl silicate had lost 85% of its water content, the B-72/MTMOS 83% and the untreated sample 66%.

It is clear from this information that consolidation is beneficial to Pennsylvania Blue in regards to evaporation rate. Both B-72 in MTMOS and ethyl silicate result in a significantly faster evaporation period, and hence less chance of decay due to moisture accumulation and generally wet conditions. The consolidants perform similarly, suggesting that either consolidant would be a good choice in terms of evaporation rate performance.

3.5.6 Water Vapor Transmission

Purpose

To measure the transmission rates of water vapor of untreated samples as compared to samples consolidated with ethyl silicate and B-72 in MTMOS.

Reference

ASTM E-96-80: "Water Vapor Transmission"

Relevance

This test measures the vapor permeability of treated versus untreated samples. A reduction in permeability is a distinctly negative characteristic; values are preferably similar, indicating that water vapor transmission is not affected by the consolidant. Differences in water vapor transmission indicate that treated samples are retaining moisture, which can impel deterioration.

Methodology

Three untreated samples, three ethyl silicate-treated samples, and three B-72/MTMOS-treated samples were utilized. The samples were in the shape of disks, approximately 33-34 mm in diameter (standard drill coring bit) and 0.75 inches thick. Each sample was attached to a 50 mL plastic beaker containing 30 mL of distilled water. Samples were placed in the chamber for 19 days (Figure 16).

Discussion and Conclusions

The samples show distinct variability in water vapor transmission rates (Table 10). The untreated samples showed an average water vapor transmission rate of 4.19 grams per hour per square meter. The ethyl silicate-treated samples showed an average water vapor transmission rate of 4.43 grams per hour per square meter. The B-72/MTMOS-treated samples showed an average water transmission rate of 2.97 grams per hour per square meter.

The fact that ethyl silicate consolidation has resulted in an improved water vapor transmission rate can be attributed to unavoidable relative humidity variations within the testing chamber. However, the difference between the untreated stone and the ethyl silicate is notably small particularly in comparison to the sample treated with B-72/MTMOS. Consolidation with B-72/MTMOS has resulted in a significantly lowered, and therefore undesirable, water vapor transmission rate.[33]

[33] The variations in the values obtained during this testing program, while comparable for the purposes of this project, suggest that further analysis may be required. Repetition of the test under strictly controlled weather and humidity conditions may corroborate the above findings without statistical variability.

Figure 16. Samples during water vapor transmission rate testing.

3.5.7 Sodium Sulfate Crystallization

Purpose

To observe durability by way of salt crystallization resistance of untreated samples as compared to samples consolidated with ethyl silicate and B-72 in MTMOS.

Reference

- Building Research Establishment Sodium Sulfate Crystallization Test,
- ASTM C 88-90, "Standard Test Method for Soundness of Aggregates by Use of Sodium Sulfate or Magnesium Sulfate," and
- RILEM Test V.1 "Crystallisation Test by Total Immersion," parts a and b.

Relevance

This test measures relative resistance to salt crystallization, as a measure of natural weathering over time. It should be kept in mind that many factors influence the deterioration of urban marble, and that this test is not meant to provide an accurate picture of deterioration, but to measure the protective effects of a consolidant when the marble is exposed to movement and stresses of salt.

Methodology

Samples were uniform in size and shape to reduce variability in testing conditions. Nine samples, three each of untreated, ethyl silicate-treated, and B-72/MTMOS treated

samples were submitted to the test procedure (Figure 17). The procedure utilizes aspects of the three standardized tests listed above.

Discussion and Conclusions

Untreated samples and those treated with ethyl silicate performed poorly in comparison to samples treated with B-72/MTMOS, losing 0.11% and 0.10% as compared to 0.03% respectively (Table 11).[34] It is clear that B-72/MTMOS inhibits salt deterioration on Pennsylvania Blue marble significantly more than ethyl silicate.

It should be kept in mind, however, that the loss of material was low for all samples, leading to the conclusion that this relatively intact Pennsylvania Blue is fairly sulfate resistant.. It is likely that Pennsylvania Blue with fewer inclusions and/or decaying Pennsylvania Blue will be more susceptible to sulfates. In this case, it is expected that the results of B-72/MTMOS treated stone versus the ethyl silicate and the untreated will be more dramatic.

[34] It should be noted that one corner of an untreated sample was blown off during the salt immersion process, causing some variability in final weight percents.

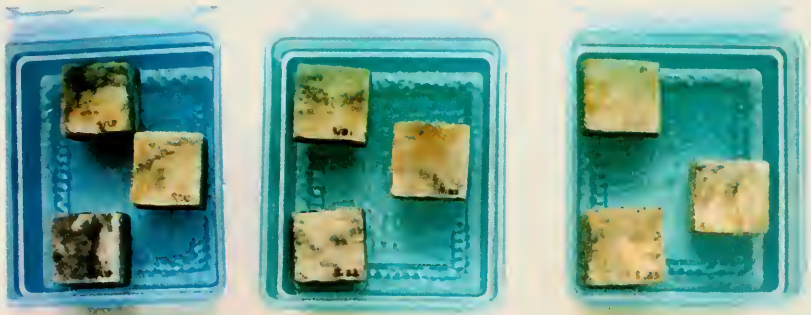


Figure 17. Samples during immersion in sodium sulfate solution.

3.5.8 Abrasion Resistance

Purpose

To determine the resistance to abrasion of untreated samples as compared to samples consolidated with ethyl silicate and B-72 in MTMOS.

Reference

Kumar, Rakesh, and Ginnell, "Evaluation of Consolidants . . ." in *Methods of Evaluating Products* (Rome: 1995), 163-178.

Relevance

This test measures relative cohesive strength as a function of the resistance of treated and untreated stones to external mechanical abrasion.

Methodology

Nine samples, three each of untreated, ethyl silicate-treated, and B-72/MTMOS-treated, were tested. The samples were exposed to 60 psi of alumina powder for four minutes at a distance of 10 cm. This was sufficient to create holes approximately the size of pencil erasers in each sample.

Discussion and Conclusions

The samples showed no appreciable difference in abrasion resistance (Table 12). We can conclude that the abrasion resistance of relatively intact Pennsylvania Blue does not

change when treated with either ethyl silicate or B-72/MTMOS. Further research should address the relative abrasion resistances of treated and untreated Second Bank marble to assess the affect of consolidants in regards to abrasion resistance on that particular building.

2.6 Conclusions

The consolidants chosen for study in this thesis showed varying effects on Pennsylvania Blue marble. Both consolidants showed weather resistance, a decrease in water absorption, and an improved evaporation curve. Ethyl silicate, in addition, shows good penetration depth and an excellent water vapor transmission rate. B-72/MTMOS outperforms ethyl silicate in regards to salt resistance and color stability. Neither consolidant affected abrasion resistance, probably due to the soundness of the samples tested.

B-72/MTMOS's questionable results during testing of water vapor transmission rate and penetration depth may result in an ineffectual, or even deleterious, consolidation campaign. The penetration depth is a particular issue as the consolidant must penetrate beyond the calcite-mica interfaces to provide effective cohesion. The volatility of the B-72/MTMOS system presents an additional challenge to exterior field consolidation.

The positive results obtained by ethyl silicate during testing of water vapor transmission rate, penetration depth, weathering resistance, water absorption, and evaporation rate outweigh the less positive results obtained for sulfate resistance and color stability, particularly since the color change was extremely minor. This study suggests that ethyl silicate is preferable to B-72/MTMOS for consolidation treatment of Pennsylvania Blue marble. However, ethyl silicate does not address the problem of flake reattachment.

Further assessment of the decay mechanisms of Pennsylvania Blue marble would be invaluable in treating decaying monuments. Evaluation of microstructural variances will

assist in further understanding, predicting, and possibly preventing, of decay. Expansion of the treatment program to include a detailed conditions survey at the Second Bank of the United States and other Pennsylvania Blue monuments would aid in understanding of the stone's macroscopic weathering patterns. The National Park Service may wish to address the largest scale spalling by mechanical pinning under the direction of an architectural stone conservator. Column integrity should be assesed by a structural engineer.

A consolidation program involving the use of naturally weathered Pennsylvania Blue marble would be useful in comparison to the data obtained during this project, particularly as it relates to seriously deteriorated Pennsylvania Blue monuments. A possible source for such marble is Laurel Hill Cemetery, where broken marble gravestone slabs have been stockpiled in the past. In addition, the Pennsylvania Blue marble quarries, while defunct, could be explored for remaining material.

In conclusion, it should be noted that before ethyl silicate (or any consolidant) is used to treat historic fabric, a comprehensive testing program should be carried out to asses its performance in relationship to that particular monument. This is particularly important for monuments of Pennsylvania Blue, as the stone shows mineralogical heterogeneity and an inherent tendency to disaggregate in extreme exposure. It is hoped that continued research and attention to this local building stone will result in further study, in documentation, and in conservation of the Second Bank of the United States, and in many other Pennsylvania Blue marble monuments.

Appendices

Manual Laboratory Weathering: What amount of deterioration is produced by various molarities of sulfuric acid solution over time?

sample size: variable
number of samples per type of treatment: variable
total number of samples: variable
duration of testing program: variable

Significance and Use
Qualitative and quantitative analysis of erosion, evidenced by degree of sugaring and erosion of crisp edges, allows for a quantification of artificial weathering. Quantitative results will allow a "percent lost" to be calculated for the weathered stone (in this case, Pennsylvania Blue), answering the question "How weathered is weathered?"

Specimens
Scrap samples with at least one crisp edge will be used.

Procedure

Three solutions of sulfuric acid, with molarity .02 M, .2 M, and .1M, are to prepared so that concentration as a function of time may be measured.

Samples must be brushed to remove marble dust that may clog surface pores, inhibiting the introduction of acid.

Samples shall be weighed before immersion in sulfuric acid.

Samples shall be placed in the various molarity solutions for 20 hours.

Samples shall be dried for 4 hours in 60° C oven.

Samples shall be brushed with stiff metal to remove sugared stone, and then weighed.

Process should be repeated to sufficient deterioration.

The data from this experiment (sufficient molarity of acid as well as amount of time in the acid) will be used in manual weathering of cut samples before beginning the tests, simulating the condition of the stone at the Second Bank.

Note: samples should be soaked in distilled water after acid bath and before beginning the testing program.

Depth of Penetration

sample size: 2 in cube
number of samples per type of treatment: 2
total number of samples: 4
duration of testing program: 1 day

Procedure

1. Expose the treated stone or its vertical section to iodine vapor in a closed glass chamber for about 5 - 10 minutes (It may take more time if the concentration of consolidants is below 1 - 2 %.)

2. Measure the colored (yellow or light brown) area or distance.

Parameters
Stone must be white or light-colored.
Silicates give comparatively faint color using this method.

Accelerated Weathering

sample size: variable
number of samples per type of treatment: 1
total number of samples: 3
duration of testing program: 14 days

Significance and Use
The use of the apparatus under this practice is intended to simulate the deterioration caused by water as rain or dew and the ultraviolet energy in sunlight. It is not intended to simulate the deterioration caused by localized weather phenomena, such as atmospheric pollution, biological attack, and salt water exposure.

Specimens
The samples must be approximately .25 cm thick, and no less than 7.5 x 5 cm. Specimens may vary in size and shape.

Procedure
1. Weigh samples. Samples should be at equilibrium with room temperature and relative humidity prior to testing.

2. Observe the samples in natural light. Use the Munsell system to record the value, chroma, and hue of each sample. Assess stones qualitatively on macroscopic level and record observations. Record the weather conditions and time of day.

3. Place the samples securely into the sample rocks, bending the metal clamps as necessary to secure a tight fit. Place the racks, sample side in, in the weatherometer.

4. Calibrate the UV exposure temperature and condensation exposure as desired.

5. Turn the weatherometer on. Monitor controls for 14 days.

6. Turn off weatherometer and remove samples.

7. Observe the samples in natural light. Use the Munsell system to record the value, chroma, and hue of each sample. Assess stones qualitatively on macroscopic level and record observations. Record the weather conditions and time of day.

Water Absorption and Bulk Specific Gravity

sample size: 3 x 3 x .75 in.
number of samples per type of treatment: 3
total number of samples: 9
duration of testing program: three days

Significance and Use
These test methods are useful in indicating the differences in absorption between the various dimension stones. These test methods also provide one element in comparing stones of the same type.

Specimens
The specimens may be cubes, prisms, cylinders, or any regular form with least dimension not under 2 inches and greatest dimensions not over three inches but the ratio of volume to surface area shall be not less than .3 inches nor greater than .5 inches.[35]

Procedure

1. Dry the specimens for 24 hours in a ventilated oven at a temperature of 105 ± 2 °C.[36]

2. After drying, cool the specimens in the room for 30 minutes and weigh. Determine the weights to the nearest 0.02 g.

3. Immerse the specimens completely in filtered or distilled water at 20 ° ± 5 °C for 48 hours. At the end of this period remove them from the water bath one at a time, surface dry with a damp cloth, and weigh to the nearest 0.02 g.

4. Weigh the saturated specimens suspended in distilled water at 20 ° ± 5 °C. Determine the suspended weights to the nearest 0.02 g. A satisfactory means of weighting specimens in water is to use a basket for suspending the specimens in a glass jar of water supported above the balance pan. Determine the weight of the basket when suspended in water to the same depth as when weighing specimens therein. Subtract the weight of the basket to the nearest 0.02 g from the combined weight of the specimen and basket. Carefully remove air bubbles clinging to the basket or specimen before recording the weight.

Calculation

1. Calculate the bulk specific gravity as follows:

$$\text{Bulk specific gravity} = A/(B-C)$$

[35] Due to amount of sample available, sample size is smaller than recommended test specimen size.
[36] Samples were dried at 60 °C to prevent possible damage of the consolidants.

The samples must be placed in a room of constant temperature and relative humidity. No artificial ventilation should take place.

Initial water content must be equal to maximum water content.

sample size: 34 mm in diameter x .75 in. thick
number of samples per type of treatment: 3
total number of samples: 9
duration of testing program: 21 days

Significance and Use

The purpose of these tests is to obtain, by means of simple apparatus, reliable values of water vapor transfer through permeable and semi-permeable materials, expressed in suitable units. These values are for use in design, manufacture, and marketing. A permeance value obtained under one set of test conditions may not indicate the value under a different set of conditions. For this reason, the test conditions should be selected that most closely approach the conditions of use.

Terminology

1. Water vapor permeability: the time rate of water vapor transmission through unit area of flat material of unit thickness induced by unit vapor pressure difference between two specific surfaces, under specified temperature and humidity conditions.

2. Water vapor transmission rate: the steady water vapor flow in unit time through unit area of a body, normal to specific parallel surfaces, under specific conditions of temperature and humidity at each surface.

Apparatus

1. The test dish shall be of any non-corroding material, impermeable to water or water vapor. it may be of any shape. Light weight is desirable. A large, shallow dish is preferred, but its size and weight are limited when an analytical balance is chosen to detect small weight changes. The mouth of the dish shall be as large as practical and at least 4.65 in.[37] The desiccant or water area shall not be less than the mouth area. An external flange or ledge around the mouth, to which the specimen may be attached, is useful when shrinking or warping occurs. When the specimen area is larger than the mouth area, this overlay upon the ledge is a source of error, particularly for thick specimens. This overlay material should be masked so that the mouth area defines the test area. If a rim is provided, it shall be not more than 6 mm higher than the specimen as attached.

2. The room or cabinet where the assembled test dishes are to be placed shall have a controlled temperature and relative humidity. The temperature chosen shall be between 21 and 32 °C and shall be maintained constant within 0.6 °C. The relative humidity shall

[37] Modifications to this size are warranted if amount of sample is limited.

be maintained at 50 ± 2 %. Both temperature and relative humidity should be measured frequently. Air shall be continuously circulated throughout the chamber, with a velocity sufficient to maintain uniform conditions at all test locations.

3. The balance shall be sensitive to a change smaller than 1 % of the weight change during the period when a steady state is considered to exist. The weights used shall be accurate to 1 % of the weight change during the steady-state period. The balance must have a sensitivity of .1 g and the weights must be accurate to .1 g.

Materials

1. Distilled water shall be used in the test dish.

2. Sealant used for attaching the specimen to the dish must be highly resistant to the passage of water vapor (and water). It must not lose weight to, or gain weight from, the atmosphere in an amount, over the required period of time, that would affect the test result by more than 2 %. It must not affect the vapor pressure in a water-filled dish.

Specimens

1. Specimens shall be representative of the material tested. When a product is designed for use in only one position, three specimens shall be tested by the same method with the vapor flow in the designated direction.

2. The tested overall thickness shall be at least five times the sum of the maximum pit depth in both its faces. The overall thickness of each specimen shall be measured at the center of each quadrant to the nearest 0.05 mm and the results averaged.

Preparation

Attach the specimen to the dish by sealing in such a manner that the dish mouth defines the area of the specimen exposed to the vapor pressure in the dish. If necessary, mask the specimen top surface, exposed to conditioned air so that its exposure duplicates the mouth shape and size and is directly above it. Thoroughly seal the edges of the specimen to prevent the passage of vapor into, or out of, or around the specimen edges or any portion thereof. The same assurance must apply to any part of the specimen faces outside there defined areas.

Procedure

1. Fill the test dish with distilled water to a level 19 ± 6 mm from the specimen. The air space thus allowed has a small vapor resistance, but it is necessary in order to reduce the risk of water touching the specimen when the dish is handled. The water depth shall be not less than 3 mm to ensure coverage of the dish bottom throughout the test.

2. Attach the specimen to the dish.

3. Weigh the dish assembly and place it in the controlled chamber on a true horizontal surface.

4. Continue to weight the dish assembly over time until a steady water vapor transmission rate is established.

Calculations

1. The results of the rate of water vapor transmission may be determined either graphically or numerically.

2. Plot the weight against elapsed time, and inscribe a curve which tends to become straight. Judgment here is required and numerous points are helpful. When a straight line adequately fits the plot of at least six properly spaced points, with due allowance for scale sensitivity, a nominally steady state exists, and the slope of the straight line is the rate of water vapor transmission.

3a. A mathematical least squares regression analysis of the weight as a function of time will give the rate of water vapor transmission. An uncertainty, or standard deviation of this rate, can also be calculated to define the confidence band. For very low permeability materials, this method can be used to determine the results after 30 to 60 days when using an analytical balance, with a sensitivity of $\pm$ 1 mg, even if the weight change does not meet the 100 times the sensitivity requirement. Specimens analyzed in this manner must be clearly identified in the report.

3b. Calculate the water vapor transmission, WVTR, as follows:

$$WVTR = G/tA = (G/t)/A$$

where, in metric units,

G = weight change (from the straight line) (g)

t = time (h)

G/t = slope of the straight line ($g \times h^{-1} \times m^{-2}$)

A = test area (cup mouth area) (m^2)

WVT = rate of water vapor transmission ($g \times h^{-1} \times m^{-2}$)

Resistance to Sodium Sulfate Crystallization

sample size: 2 in cube
number of samples per type of treatment: 3
total number of samples: 9
duration of testing program: 15 days

Significance and Use
The purpose of this test is to determine the resistance of stones to sodium sulfate crystallization. The test measure the weight change and deterioration rate of stone samples exposed to repeated cycles of sodium sulfate crystallization.

Specimens
Cubes of a standard size (50 mm is convenient) should be used.

Procedure
1. Prepare a stock salt solution using 10 % anhydrous sodium sulfate.

2. Dry samples in a 60±5° C oven for 24 hours. Cool to room temperature and weigh each sample.

3. Cover the bottom of a suitable container with glass beads or rods. Place the samples into the container. Cover with salt solution. Immerse samples in solution for 16 - 18 hours.

4. Remove the samples from the salt solution.

5. Dry samples in a 60±5° C oven for 4 hours. Remove from oven and cool to room temperature.

6. Immerse the samples in the salt solution as directed in step 3.

7. Repeat steps 3 through 6 for 14 days.

8. On day 15, after oven-drying samples, cool to room temperature and weigh each sample. Calculate the weight change.

Abrasion Resistance

sample size: variable
number of samples per type of treatment: 3
total number of samples: 9
duration of testing program: one day

Significance and Use
This test method is useful in indicating the differences in abrasion resistance between the various building stones. This test method also provides one element in comparing stones of the same type.

Specimens
At least three specimens 2 inches square and preferably 1 inch in thickness shall be sawed from the sample. The sharp edges shall be rounded by grinding.

Procedure

1. Insure that abrasive canister is filled with desired abrasive. Turn on micro-abrasive unit and set to desired psi.

2. Place one specimen into the testing chamber. Stabilize with wooden blocks. Set the powder gun the desired distance from the sample. Measure the distance to insure that the gun-sample distance remains constant throughout the experiment. Place a metal plate in front of the sample.

3. Turn on powder flow. Allow to stabilize for 10 seconds. Remove metal plate. Allow the sample to be abraded until the desired hole size has been created. Be sure to keep close track of the time.

4. Turn off powder flow. Remove sample from testing chamber. Remove powder residue from hole in sample.

5. Place a small amount of fine sand into a weighing boat. Weigh the boat. Using a disposable pipette, remove sufficient sand from the boat to fill the sample hole. Reweigh the weighing boat. Subtract the final amount of sand from the initial amount to determine relative weight lost during abrasion.

4. Perform steps 2 through 5 for each sample. Compare data to determine relative resistance to micro-abrasion.

Appendix A.2 Tables

Table I. Physical Properties, Crystallography, and Composition of Calcite ($CaCO_3$)

Crystallography
System: hexagonal
Form: prismatic, rhombohedral, scalenohedral. Anhedral or aggregated grains.
Cleavage: perfect rhombohedral cleavage (74 °55')
Twinning: lamellar twinning common, often pastel pink and green
Birefringence: creamy high-order interference colors
Relief: variable with rotation. moderately negative to high positive relief.

Physical Properties
Specific gravity: 2.71
Hardness: 3 on cleavage planes, 2 1/2 on base
Optical properties: uniaxial negative
Refractive index: 1.66
Luster: vitreous to earthy
Color: white or colorless (gray, red, green, blue, yellow, brown, and black less common)
Color in thin section: colorless

Composition
Composition: CaO 56.0 %, CO_2 44.0 %.
Replacement: manganese, iron, zinc, opal, and particularly magnesium are common[38]
Alteration: magnesium often replaces calcium (dolomitic marble)

[38] Because magnesium and calcium ions have the same ionic charge of 2+, as well as a similar atomic radius in 8-coordination, replacement of calcium with magnesium within the calcite matrix is likely. It follows that differentiation between calcite and dolomite in thin section can be difficult. Many properties of dolomite, including rhombohedral cleavage, lamellar twinning, variable relief, and creamy interference colors, are comparable to those of calcite. Though dolomite is minimally harder than calcite (3.5-4), with a higher specific gravity (2.86-2.93), it may be difficult to distinguish between calcite and dolomite in thin section. Where practical, dolomite can be distinguished from calcite by its lack of effervescence in cold hydrochloric acid. Moreover, dolomite may be cloudy, colorless, or iron-stained in thin section, with commonly euhedral grains. Refractive indices tend to be higher than those of calcite. Calcite has a stronger tendency to twin, and its lamellae are never parallel to the short diagonal of the calcite rhomb.

Table 2. Water Absorption and Bulk Specific Gravity of Weathered Pennsylvania Blue Marble at the Second Bank of the United States

Location and Color of Marble	Water Absorption (%)	Bulk Specific Gravity (%)
Primary Facade (White)	.93	2.54
Secondary Facade (Gray)	.36	2.12

Table 3. Qualitative Analysis of Soluble Salts Present in Pennsylvania Blue Marble

Type of Salt	Reagent	Observation	Presence Detected
Carbonate	sulfuric acid	extreme evolution of carbon dioxide, evidence by fizzing	x
Sulfate	hydrochloric acid, barium nitrate solution	white precipitate after 24 hours in distilled water	x
Chloride	nitric acid, silver nitrate solution	no reaction	
Phosphate	ammonium molybdate in dilute nitric acid	no reaction	
Nitrate	sulfuric acid, diphenylamiine solution	formation of deep blue color	x

Table 4. Manual Laboratory Weathering of Pennsylvania Blue Marble

Molarity of Sulfuric Acid

	0.02		0.20		0 10		1.00		2.00		3.00	
Cycle	Wt (g)	% Lost	Wt (g)	% Lost	Wt (g)	% Lost	Wt (g)	% Lost	Wt (g)	% Lost	Wt (g)	% Lost
1	358.20		353.80		373.90		371.50		65.09		359.63	
2	358.20	0.00	353.90	-0.03	374.10	-0.05	371.60	-0.03	64.64	0.70	343.62	4.66
3	357.80	0.11	353.80	0.03	373.90	0.05	371.40	0.05	63.99	1.02	326.30	5.31
4	357.90	-0.03	353.40	0.11	373.20	0.19	371.93	-0.14			302.94	7.71
5	357.50	0.11	353.40	0.00	373.30	-0.03	371.05	0.24				
6	356.80	0.20	353.00	0.11	373.00	0.08	371 14	-0.02				
7	357.00	-0.06	352.40	0.17	373.20	-0.05						
8	356.80	0.06	353.00	-0.17	373.00	0.05						
av. % lost		**0.06**		**0.03**		**0.03**		**0.02**		**0.86**		**5.89**
% lost after three cycles		**0.11**		**0.00**		**0.00**		**0.03**		**1.71**		**9.97**
cum. % lost		**0.39**		**0.23**		**0.24**		**0.10**		**1.71**		**17.68**

Note not all molarities were tested for the same amount of time
due to time constraints and clear evidence in favor of higher molarity sulfuric acid.

Table 5. Sample Weights, Pre- and Post-Consolidation				
sample	wt before treatment (g)	wt after treatment (g)	wt increase (g)	% of total weight
WA/E1	219.8	220.02	0.22	0.10
WA/E2	213.68	214.11	0.43	0.20
WA/E3	252.45	252.88	0.43	0.17
SEBA D/E1	118.3	118.78	0.48	0.40
R/E	2910.1	2913.6	3.50	0.12
M/E1	509.1	509.9	0.80	0.16
M/E2	498.6	499.5	0.90	0.18
M/E3	529.1	530.4	1.30	0.25
S/E1	285.6	286.08	0.48	0.17
S/E2	264.43	264.96	0.53	0.20
S/E3	287.62	288.08	0.46	0.16
WV/E1	55.05	55.22	0.17	0.31
WV/E2	60.06	60.28	0.22	0.36
WV/E3	56.85	57.09	0.24	0.42
WE/E1	243.49	244.06	0.57	0.23
WE/E2	472.1	472.89	0.79	0.17
average				**0.22**
WA/B1	214.54	214.57	0.03	0.01
WA/B2	225.99	226	0.01	0.00
WA/B3	252.44	254.63	2.19	0.86
SEBA D/B1	62.4	62.4	0.00	0.00
R/B	2893.1	2895.5	2.40	0.08
M/B1	490.5	490.8	0.30	0.06
M/B2	497	497.2	0.20	0.04
M/B3	425	425.1	0.10	0.02
S/B1	272.25	272.24	-0.01	0.00
S/B2	300.07	305.06	4.99	1.64
S/B3	290.63	290.61	-0.02	-0.01
WV/B1	60.52	60.53	0.01	0.02
WV/B2	52.92	52.94	0.02	0.04
WV/B3	59.08	59.12	0.04	0.07
WE/B1	381.3	381.5	0.20	0.05
average				**0.19**

Table 8. Water Absorption and Bulk Specific Gravity of Untreated and Consolidated Pennsylvania Blue Marble					
Treatment Type	**dry weight (g)**	**saturated weight (g)**	**weight in water (g)**	**water absorption (%)**	**bulk specific gravity (%)**
Untreated	273.63	274.99	173.15	0.50	2.69
Ethyl silicate	285.95	286.55	180.75	0.21	2.70
B-72 in MTMOS	300.15	300.74	189.55	0.197	2.70

Table 9. Evaporation Curve			
Minutes	Sample Weight (g)		
	U	E	B
0	274.61	286.34	301.09
1	274.51	286.25	300.99
2	274.41	286.17	300.87
3	274.37	286.14	300.83
4	274.31	286.08	300.74
5	274.26	286.04	300.7
10	274.13	285.9	300.54
15	274.02	285.76	300.42
21	273.89	285.59	300.32
25	273.8	285.59	300.26
30	273.72	285.56	300.21
35	273.61	285.55	300.18
45	273.49	285.55	300.14
55	273.44	285.55	300.13
65	273.42	285.54	300.13
75	273.4	285.52	300.13
85	273.4	285.52	300.12
95	273.38	285.52	300.12
105	273.38	285.51	300.1

Table 10. Water Vapor Transmission

Date (month/day/year)	U1			U2			U3			avg	adj. avg	R H (%)	int temp (C)
	Wt (g)	Water Vapor Loss over 1 day	WVTR ($g/h/m^2$)	Wt (g)	Water Vapor Loss over 1 day	WVTR ($g/h/m^2$)	wt (g)	Water Vapor Loss over 1 day	WVTR ($g/h/m^2$)				
5/9/96	84.99			84.46			84.60					49%	20
5/10/96	84.86	0.13	6.58	84.42	0.04	2.02	84.57	0.03	1.52	0.07		42%	22
5/11/96	84.86	0.00	0.00	84.44	-0.02	-1.01	84.56	0.01	0.51	0.00		52%	24
5/12/96	84.83	0.03	1.30	84.42	0.02	0.87	84.54	0.02	0.87	0.02	0.01	60%	24
5/13/96	84.76	0.08	4.25	84.34	0.10	4.86	84.45	0.11	5.46	0.10	0.04	40%	23
5/14/96	84.75	0.01	0.51	84.33	0.01	0.51	84.43	0.02	1.01	0.01	0.03	40%	21
5/15/96	84.72	0.03	1.52	84.33	0.00	0.00	84.41	0.02	1.01	0.02	0.03	44%	23.5
5/16/96	84.58	0.14	7.08	84.2	0.13	6.58	84.28	0.13	6.58	0.13	0.05	49%	20
5/17/96	84.61	-0.03	-1.52	83.95	0.25	12.65	84.31	-0.03	-1.52	0.06	0.05	42%	22
5/18/96	84.46	0.15	7.59	83.78	0.17	8.60	84.17	0.14	7.08	0.15	0.06	48%	22
5/19/96	84.31	0.15	7.59	83.66	0.12	6.07	83.94	0.23	11.64	0.17	0.07	70%	29
5/20/96	84.22	0.09	4.55	83.23	0.43	21.76	83.74	0.20	10.12	0.24	0.09	56%	29
5/21/96	84.15	0.07	3.54	83.17	0.06	3.04	83.66	0.08	4.05	0.07	0.09	35%	29
5/22/96	84.06	0.09	4.55	83.09	0.08	4.05	83.51	0.15	7.59	0.11	0.09	34%	27
5/23/96	84.11	0.08	4.22	83.12	-0.03	-1.52	83.56	-0.05	-2.53	0.00	0.08	40%	27
5/24/96	83.93	0.18	9.11	82.98	0.14	7.08	83.41	0.15	7.59	0.16	0.12	44%	24
5/25/96	84.01	-0.08	-4.05	83.05	-0.07	-3.54	83.41	0.00	0.00	n/a	0.12	56%	21
5/26/96	83.93	0.08	4.05	82.96	0.09	4.55	83.31	0.10	5.06	0.09	0.12	54%	20
5/27/96	83.85	0.08	4.05	82.88	0.08	4.05	82.92	0.39	19.73	0.18	0.12	55%	21
5/28/96	83.76	0.09	4.55	82.78	0.10	5.06	82.67	0.25	12.65	0.15	0.13	59%	20
5/29/96	83.84	-0.08	-4.05	82.88	-0.10	-5.06	82.74	-0.07	-3.54	n/a	0.13	52%	19
avg WVTR (g/hr/m2)			**3.48**			**5.11**			**3.99**	**0.08**	**0.08**		
median WVTR			**4.13**			**4.05**			**4.55**				
std. dev.			**3.61**			**5.79**			**5.68**				
avg WVTR U1-3 (g/hr/m2)										**4.19**			

note: n/a refers to a negative and hence indivisible denominator. n/a cells do not effect the final calculations.

Water Vapor Transmission

	E1			E2			E3						
Date (month/day/year)	Wt (g)	Water Vapor Loss over 1 day	WVTR ($g/h/m^2$)	Wt (g)	Water Vapor Loss over 1 day	WVTR ($g/h/m^2$)	wt (g)	Water Vapor Loss over 1 day	WVTR ($g/h/m^2$)	avg	adj. avg	R.H (%)	int temp (C)
5/9/96	85.18			89.03			84.16					49%	20
5/10/96	85.15	0.03	1.52	89.01	0.02	1.01	84.14	0.02	1.01	0.02		42%	22
5/11/96	85.13	0.02	0.87	89.03	-0.02	-0.87	84.16	-0.02	-0.87	n/a		52%	24
5/12/96	85.14	-0.01	-0.51	89.02	0.01	0.51	84.15	0.01	0.51	0.00	0.00	60%	24
5/13/96	85.05	0.11	5.46	88.71	0.37	18.82	83.99	0.19	9.72	0.22	0.11	40%	23
5/14/96	85.03	0.02	1.01	88.54	0.17	8.60	83.58	0.41	20.75	0.20	0.14	40%	21
5/15/96	85	0.03	1.52	88.53	0.01	0.51	83.54	0.04	2.02	0.03	0.11	44%	23.5
5/16/96	84.89	0.11	5.57	88.42	0.11	5.57	83.42	0.12	6.07	0.11	0.11	49%	20
5/17/96	84.92	-0.03	-1.52	88.45	-0.03	-1.52	83.45	-0.03	-1.52	n/a	0.11	42%	22
5/18/96	84.79	0.13	6.58	88.29	0.16	8.10	83.34	0.11	5.57	0.13	0.12	48%	22
5/19/96	84.65	0.14	7.08	88.15	0.14	7.08	83.00	0.34	17.20	0.21	0.13	70%	29
5/20/96	84.53	0.12	6.07	88.03	0.12	6.07	82.85	0.15	7.59	0.13	0.13	56%	29
5/21/96	84.46	0.07	3.54	87.98	0.05	2.53	82.78	0.07	3.54	0.06	0.12	35%	29
5/22/96	84.32	0.14	7.08	87.89	0.09	4.55	82.70	0.08	4.05	0.10	0.12	34%	27
5/23/96	84.32	0.00	0.00	87.93	-0.04	-2.02	82.75	-0.05	-2.53	n/a	0.12	40%	27
5/24/96	84.17	0.15	7.59	87.79	0.14	7.08	82.61	0.14	7.08	0.14	0.13	44%	24
5/25/96	84.19	-0.02	-1.01	87.79	0.00	0.00	82.65	-0.04	-2.02	n/a	0.13	56%	21
5/26/96	84.11	0.08	4.05	87.74	0.05	2.53	82.58	0.07	3.54	0.07	0.12	54%	20
5/27/96	84.04	0.07	3.54	87.67	0.07	3.54	82.44	0.14	7.08	0.09	0.12	55%	21
5/28/96	83.93	0.11	5.57	87.59	0.08	4.05	82.25	0.19	9.61	0.13	0.12	59%	20
5/29/96	83.98	-0.05	-2.53	87.65	-0.06	-3.04	82.25	0.00	0.00	n/a	0.12	52%	19
avg WVTR (g/hr/m2)			**3.29**			**4.46**			**5.55**	**0.12**	**0.12**		
median WVTR			**3.54**			**3.04**			**3.79**				
std. dev.			**3.15**			**4.87**			**5.98**				
avg WVTR E1-3 (g/hr/m2)										**4.43**			

note: n/a refers to a negative and hence indivisible denominator. n/a cells do not effect the final calculations.

Water Vapor Transmission

Date (month/day/year)	B1 Wt (g)	B1 Water Vapor Loss over 1 day	B1 WVTR ($g/h/m^2$)	B2 Wt (g)	B2 Water Vapor Loss over 1 day	B2 WVTR ($g/h/m^2$)	B3 wt (g)	B3 Water Vapor Loss over 1 day	B3 WVTR ($g/h/m^2$)	avg	adj. avg	R.H (%)	int temp (C)
5/9/96	82.81			90.21			87.98					30%	80°
5/10/96	82.77	0.04	2.02	90.18	0.03	1.52	87.96	0.01	0.50	0.03		29%	77°
5/11/96	82.76	0.01	0.43	90.2	-0.02	-0.87	87.98	0.01	0.64	0.00		30%	78°
5/12/96	82.81	-0.05	-2.53	90.21	-0.01	-0.51	88.01	0.01	0.51	n/a	n/a	30%	78°
5/13/96	82.68	0.16	7.89	90.13	0.10	4.86	87.89	0.01	0.58	0.13	0.06	31%	78°
5/14/96	82.66	0.02	1.01	90.1	0.03	1.52	87.87	0.00	-0.15	0.03	0.05	32%	78°
5/15/96	82.64	0.02	1.06	90.09	0.01	0.51	87.83	0.79	40.00	0.02	0.04	30%	79°
5/16/96	82.53	0.11	5.52	89.99	0.10	5.06	87.75	0.02	0.91	0.10	0.05	28%	80°
5/17/96	82.53	0.00	0.00	90.01	-0.02	-1.01	87.76	0.00	0.09	n/a	0.05	29%	81°
5/18/96	82.43	0.10	5.06	89.91	0.10	5.06	87.65	0.02	1.10	0.10	0.06	29%	79°
5/19/96	82.29	0.14	7.08	89.82	0.09	4.55	87.55	0.05	2.50	0.12	0.07	29%	80°
5/20/96	82.19	0.10	5.06	89.71	0.11	5.57	87.49	-0.03	-1.50	0.11	0.07	28%	80°
5/21/96	82.11	0.08	4.05	89.68	0.03	1.52	87.40	-0.09	-4.50	0.05	0.07	30%	81°
5/22/96	82	0.11	5.57	89.61	0.07	3.54	87.34	0.04	2.00	0.09	0.07	31%	79°
5/23/96	82	0.09	4.47	89.65	-0.04	-2.02	87.37	0.03	1.38	0.02	0.07	31%	79°
5/24/96	81.87	0.13	6.58	89.54	0.11	5.57	87.24	0.13	6.58	0.12	0.09	44%	24
5/25/96	81.92	-0.05	-2.53	89.6	-0.06	-3.04	87.31	-0.07	-3.54	n/a	0.09	56%	21
5/26/96	81.76	0.16	8.10	89.54	0.06	3.04	87.26	0.05	2.53	0.09	0.09	54%	20
5/27/96	81.46	0.30	15.18	89.48	0.06	3.04	87.19	0.07	3.54	0.14	0.10	55%	21
5/28/96	80.96	0.50	25.30	89.39	0.09	4.55	87.11	0.08	4.05	0.22	0.11	59%	20
5/29/96	80.9	0.06	3.04	89.46	-0.07	-3.54	87.18	-0.07	-3.54	n/a	0.11	52%	19
avg WVTR (g/hr/m2)			**3.44**			**2.14**			**3.35**	**0.07**	**0.07**		
median WVTR			**4.76**			**2.28**			**0.77**				
std. dev.			**6.10**			**2.90**			**8.94**				
avg WVTR B1-3 (g/hr/m2)										**2.97**			

note n/a refers to a negative and hence indivisible denominator. n/a cells do not effect the final calculations.

Table 11. Resistance to Sodium Sulfate Crystallization					
Sample	**Initial Weight of Dried Sample (g)**	**Final Weight (g)**	**Weight Change (g)**	**% Change**	**% of Total Weight**
U1	272.42	271.74	0.68	0.25	0.25
U2	277.49	277.37	0.12	0.04	0.04
U3	286.96	286.82	0.14	0.05	0.05
average			**0.31**	**0.11**	**0.11**
E1	285.68	285.4	0.28	0.10	0.10
E2	287.67	287.39	0.28	0.10	0.10
E3	264.58	264.32	0.26	0.10	0.10
average			**0.27**	**0.10**	**0.10**
B1	304.85	304.72	0.13	0.04	0.04
B2	272.04	271.97	0.07	0.03	0.03
B3	290.38	290.29	0.09	0.03	0.03
average			**0.10**	**0.03**	**0.03**

Table 12. Abrasion Resistance			
Sample	initial weight (g)	final weight (g)	difference (g)
U1	11.72	11.63	0.09
U2	11.56	11.49	0.07
U3	11.59	11.49	0.10
average			**0.09**
E1	11.59	11.5	0.09
E2	11.57	11.48	0.09
E3	11.6	11.52	0.08
average			**0.09**
B1	11.57	11.49	0.08
B2	11.59	11.48	0.11
B3	11.77	11.71	0.06
average			**0.08**

Appendix A.3 Charts

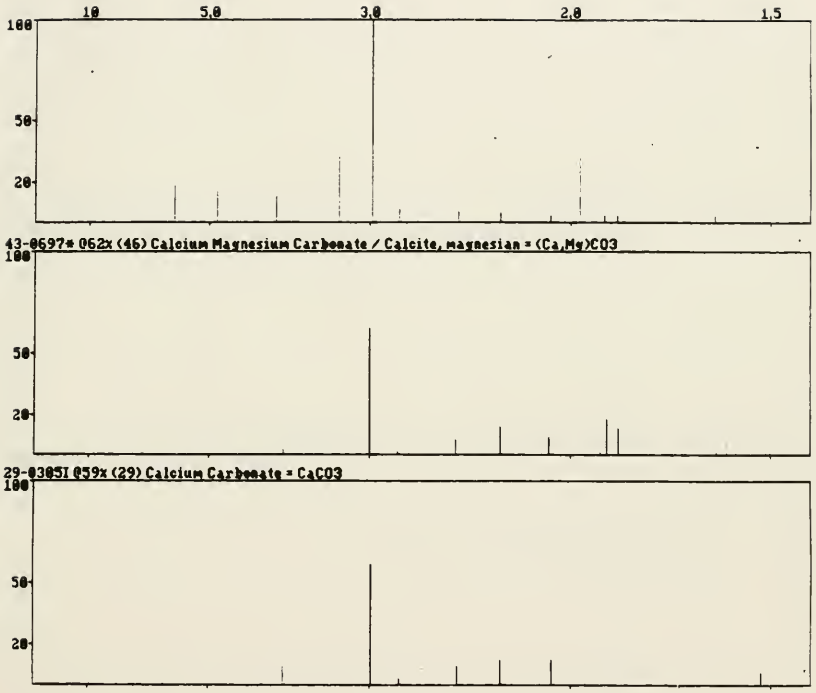


Chart 1. X-Ray Diffraction Pattern Comparison of Sample I to LRSM library.

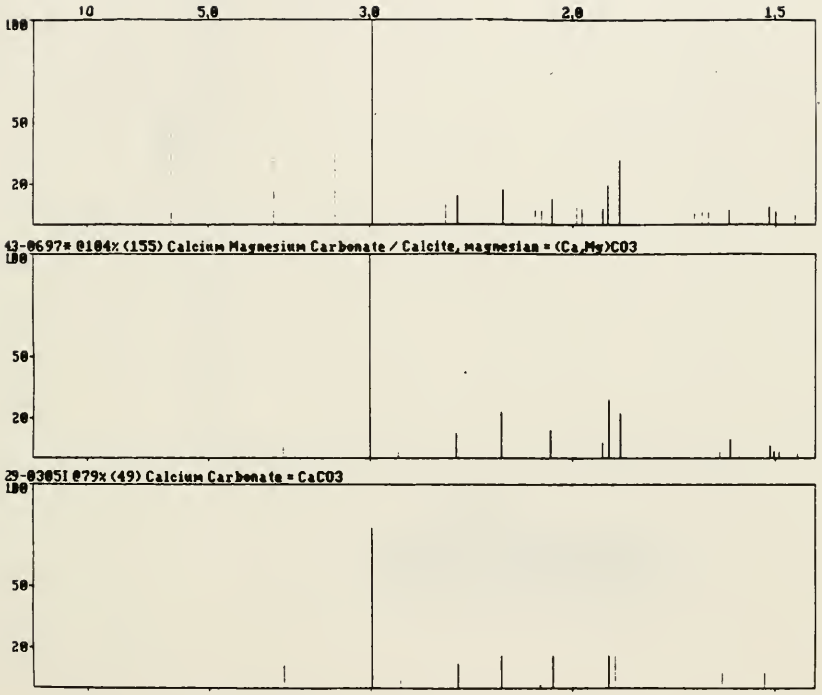
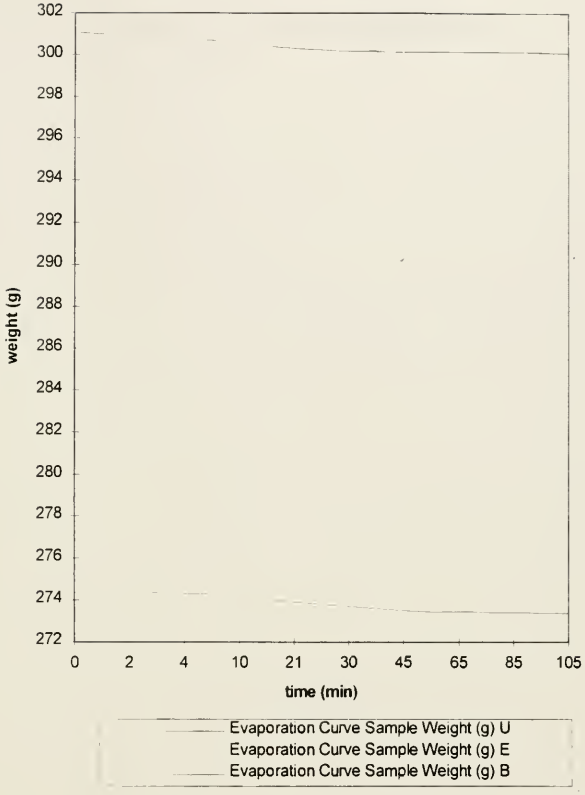


Chart 2. X-Ray Diffraction Pattern Comparison of Sample II to LRSM library.

Chart 3. Evaporation Curve



Appendix B Technical Data for Ethyl Silicate, B-72, and MTMOS

Product name: **ProSoCo Conservare OH Stone Strengthener**
batch number: not listed on package
date of supply: April 1996
address of supplier/manufacturer: 111 Snyder Road, South Plainfield, NJ 07080 (908)754-4410
properties of product as supplied:
solution,
viscosity: (2mm in DIN cup) 42S
method of setting:
how activated:
hydrolysis
proportions of components: 75% tetraethylorthosilicate, 25% by weight MEK and acetone
setting time two (-three) weeks @ 68°F and 50% R.H.
modification of product by conservator: none
special requirements:
shelf life: 12 months in sealed container
pretreatment of objects: control of surface conditions during application. Area to be treated should
be clean and dry. No direct sunlight for several hours prior to application to insure cool surface. Surface and air temperature should be 50 - 80°F during application. Screen against direct sun, wind,
and rain.
hazards:
toxicity: liquid and vapor highly irritating to eyes, moderately to skin, nose, and throat. serious ill effects by ingestion.
flash point: 2°C
precautions necessary: protective clothing, solvent resistant gloves, boots, headgear. splash goggles.
physical properties from manufacturer's literature:
specific gravity @ 25°C: .94
boiling point: 56°C
ignition temperature: 505°C
% volatile by volume: 75
solubility in water: negligible
optical properties:
color: colorless
refractive index: 1..38
reversibility of treatments: none

Product name: **Acryloid B-72 100% Resin**
batch number: 709235
date of supply: not listed on package
address of supplier/manufacturer: Rohm and Haas Company, Independence Mall West, Philadelphia, PA 19105; (215)428-4044
properties of product as supplied:
solid
how activated:
mixing,
proportions of components: 98% by weight acrylic copolymer, .15% residual monomer, 1.0% residual toluene
modification of product by conservator: dissolution in MTMOS
hazards:
toxicity: vapor can irritate nose throat, lungs, eyes, skin.
flammability: combustible
precautions necessary: wear respirator, cotton or canvas gloves, safety glasses.
physical properties from manufacturer's literature:
hardness: Tukon hardness 10-11
glass transition temperature: 40 °C
solubility in water: negligible
% volatile by weight: 1.15
specific gravity: 1.15
solubility parameter: 9.3
bulk density @ 25°C: 9.6 lbs/gal
optical properties:
color: clear granules

Product name: **Dow Corning Z 6070 Silane**
batch number: BK 12383
address of supplier/manufacturer: Midland, MI 48686-0994; (800)252-9899
properties of product as supplied:
solution,
viscosity .5 Nsm^{-2} x 10^{-3} at 20 °C
physical properties:
boiling point: 215F/102C
specific gravity (at 77°F/25°C): .95
vapor pressure (at 77°F/25°C): 20 mmHg
% volatiles: not determined
evaporation rate: less than one
solubility in water: reacts
method of setting: hydrolysis and condensation
how activated:
water activated
setting time 15 min - 24 hrs
modification of product by conservator: mixed with B-72
special requirements:
shelf life: 12 months from shipment date
pretreatment of objects: clean
hazards:
toxicity: high. may be fatal or cause blindness if ingested. vapor may irritate eyes. vapor overexposure may cause drowsiness.
flash point: 47F/8C
precautions necessary: safety glasses, respiratory protection.
optical properties:
color: clear
contents:
methyl alcohol/67561 2%
dimethyldimethoxysilane/1112396 1%
methyltrimethoxysilane/1185553 97% by weight

Appendix C.1 Annotated Bibliography of Related Non-Carbonate Manual Laboratory Weathering

Emery, J.A. "A Laboratory Weathering Method for Evaluating Finish Durability on Plywood Sidings and Composite Panels." In *Permanence of Organic Coatings*, 86-125. Philadelphia: American Society for Testing and Materials, 1982.

⇒ Describes accelerated weathering of plywood, incorporating Weatherometer wet-dry cycling and laboratory freeze-thaw testing, over a period of 12 weeks.

Sasse, H.R., and D. Honsinger. "A New Chemical and Engineering Approach for Development and Optimization of Stone Protecting Materials." In *Science, Technology, and European Cultural Heritage*, 648-652. Bologna, 1991.

⇒ Mentions accelerated weathering, but with little elaboration.

Suga, Shigeru, and Shigeo Suga. "Development of Simulated Acid Rain Test Using CCT Method." In *Accelerated and Outdoor Durability Testing of Organic Materials*, 247-262. Philadelphia: American Society for Testing and Materials, 1994.

⇒ This article focuses on the effects of salt spray and acid rain on automotive metals, including steel, zinc, copper, and aluminum. 45 cycles were performed, in which one eight-hour cycle consisted of two hours acid mist (5 ± 1% NaCl + HNO3 + H2SO4 (pH 3.5)) at temperature 35 ± 1° C, four hours dry period at temperature 60 ° ± 1° C at R.H. less than 30 %, and two hours wet period at temperature 50 ° ± 1° C and R.H. greater than 95 %. Test method follows JASO M 609 test by the Society of Automotive Engineers in Japan.

Suits, L. David. "Accelerated Weathering of Geosynthetics." In *Accelerated and Outdoor Durability Testing of Organic Materials*, 183-198. Philadelphia: American Society for Testing and Materials, 1994.

⇒ Though the article deals with polymer weathering, the method of laboratory may be applicable to carbonates treated with polymeric coatings. ASTM tests D4355 and G26 were modified and synthesized to create a test for wet-dry cycling and UV light exposure. Samples were placed in a borosilicate glass box and submitted to the following: each cycle consisted of 102 minutes of exposure at 150 ° ± 10 ° C and R.H. of 30% ±5%, followed by 18 minutes of light plus water spray. Samples were cycled for 500 hours.

Appendix C.2 Working List of Artificial Laboratory Weathering Methods

accelerated weathering code and author	description of cycle, including use of standardized tests	# of cycles	sample size	carbonate stone type	remarks
S Accardo	24h immersion in saturated sodium sulfate soln, 24h oven drying at 60° C (forced ventilation)	30	5 cm cube	Carrara marble (Bianco)	results in irregular surfaces. Increase in pore size and water absorption.
C Bortz	chemical exposure: 1/8" deep .01 molar sulphurous acid soln and .01 molar salt soln.	up to 300 cycles where 12-16 = 1 yr	less than 2 in	Vermont marble Georgia marble Alabama marble Tennessee marble New York marble Missouri marble Carrara marble	
C, L Charola	4 h .02 M H_2SO_4 soln, 20 h UV exposure at 50 ° C and 70% R.H.	21	5 cm cube	Indiana limestone Vincenza limestone	dissolution of some surface grains
C Eastes	0.6-0.06 M H_2SO_4 sprayed on samples using handheld atomizer attached to container of compressed gas.		3 cm x 5 cm x 2 mm	Salem (IN) limestone, Shelborne (VT) marble	used to produce surface deposits of gypsum with a range of concentrations
L, SS Fassina	I. 9 days UV lamps (300 lux) at 30 ± 1° C and R.H. of 90 ± 5%, 30 days .05 M NaCl spray + H_2SO_4 added to pH 5 (spray 5 min/h) with temp 25 ± 2 ° C, repeat 9 days UV. II. 5 h salt spray as above, 19 h UV lamps (300 lux) at 30 ± 1° C and R.H. of 20 ± 5%	I. one cycle II. 15 cycles	5x5x1 cm	Carrara marble Proconnesian marble	part I produced little weathering; part II was more successful. Samples showed evenly strongly etched surface, as well as deeper cleavage lines and diffused corrosion pits.
C Gauri (1973)	dynamic SO_2 system: reaction chamber containing 900 cc SO_2 per minute of air flow. Unspecified amount of water added to achieve high humidity.	to sulfation	4 x 2.5 x 1 cm	Carrara marble	possible to produce thick gypsum crusts through this manner of sulfation.

	description of cycle, including use of standardized tests	# of cycles	sample size	carbonate stone type	remarks
C Jain	samples submerged in .1 M oxalic, succinic, malic, citric, lactic, and ketoglutaric acid solns.	7 days	5 cm cube	marble	succinic, malic, citric, lactic, and ketoglutaric acids increased surface roughness through dissolution of calcium content. Citric, lactic, and ketoglutaric acid increased deterioration.
C Sleater	DIN 50 018. 2 L sulfur dioxide gas + 2L d. H_2O in closed cabinet. 8h heating + 16h cooling	49	2x2x1 cm	Indiana Limestone	weathering produced surface deposits with a small amount of blistering and color change.
C, S, F, L Sleater	Chamber: 3 IR + 6 UV lights, water spray, inlet for acid soln, revolving specimen holder. 16h: -40° C, 1.5h: rotation + lamps to surface t= 50° C, 1/2 h: water spray + rotation, 1/2h: lamps + rotation, 5h: rotation + lamps + soln of 3% NaCl/ .01 M sulfurous acid soln	10-20 cycles	10 cm cubes	Indiana limestone	
C, Sabbioni	chamber with temp 25° C + introduction of 3 ppm SO_2, 100% R.H.	90 days		Carrara marble Travertine Trani limestone	performed to enhance sulfate and sulfite production
C, SS Laurenzi Tabasso	salt spray chamber: (soln = 2 % NaCl, 5% $Na_2SO_4 \cdot 10H_2O$, 0.2% $CaSO_4 \cdot 2H_2O$) sprayed at 60 ml/h, H2SO4 added to bring pH to 5 (total SO4=11.5g/L), climatic chamber: 30±1° C, R.H.=35 ± 5%. half of climatic cycles included UV radiation with intensity of 320 lux.	14 days salt, 21 days clim.	5 cm cube	Lecce limestone	Heavy deterioration due to environmental factors, water soluble salts, and morphology
L Sleater	ASTM G 27, method A. 6000 W xenon lamp, with black panel temp 62° C.	1100 h	10x10x 2.5cm	Indiana limestone	weathering yellowed some methacrylates, acrylic polymers, linseed oil, & inorganics

accelerated weathering code and author	description of cycle, including use of standardized tests	# of cycles	sample size	carbonate stone type	remarks
S De Casa	24 h immersion in artificial sea water solution, 24 h at 60 ° C, 24 h immersion in saturated sodium sulfate solution, 24 h at 60° C	45	5 cm cube	Proconnesian marble	frequent thermal stresses and polluted atmospheres result in intercrystalline deterioration. Marked structural anistropy due to size and shape of minerals as well as thin micaceous layers
S Sleater	ASTM C88. 16-18 h immersion in saturated sodium sulfate soln at 22-24 ° C, 4h at 105° C	10	10.5x 2.5x 2.5 cm	Indiana Limestone	spalling observed after 2 cycles
SS Sleater	ASTM B 117-64. Samples placed in 1m cube plastic chamber containing fine spray of saturated water vapor blown through 5% sodium chloride soln. Temp kept at 35° C.	180 days	2x2x1 cm	Indiana limestone	
T Bortz	thermal expansion: (-10° C - 170° C)	up to 300 cycles where 12-16 = 1 yr	less than 2 in	Vermont marble Georgia marble Alabama marble Tennessee marble New York marble Missouri marble Carrara marble	
W Sleater	ASTM D 2247. 90 min condensing: samples mounted over water bath kept at 38°C, 30 min evaporating: warm air blown through water bath.	2400 cycles(5 mos.)	5x2.5x 2.5cm	Indiana limestone	surface deposits; condensation reported as alkaline.

Types of Weathering, Column 1:[39]

C	Chemical
F	Freeze-thaw
L	Light
S	Salt
SS	Salt Spray
T	Thermal
W	Water Only

[39] Note: All available information has been recorded for each article. Articles conveyed selected information depending upon the problem focus.

Appendix D. Working List of Documents Citing B-72 Used as a Consolidant

Author (Year Published)	Percent B-72 in Solvent	Application Time (where mentioned)	Type of Stone Consolidated	Monument Consolidated (where specified)
Accardo (1981)	most successful: 10% in 1,1,1-trichloroethane	28 days	Montagnola senese marble, Carrara marble	
Berry (1994)	20 % in toluene	-	oolitic limestone	-
Charola (1986)	15 % v/v of 30 % w/v in 1:1 toluene/xylene mixture	18 hours of continuous contact	Indiana limestone, Vicenza limestone	-
Charola (1990)	10% in 1,1,1,-trichloroethane	28 days	Indiana limestone, Vicenza limestone, Lecce limestone	-
De Witte (1977)	10 % in toluene	-	Maastricht limestone	-
Fassina (1987)	**See Nonfarmale (1974)**	-	Carrara marble, Proconnesian marble	Arconi di San Marco, Venice
Nonfarmale				
Rubio (1994)	5 % in 1,1,1, trichloroethane	immersion for 10 minutes (sufficient for total impregnation)	dolomitic limestone (Almeria quarry), calcitic sandstone (Puerto de Santa Maria quarry)	Almeria Cathedral, Spain
Tabasso (1985)	10 % in 1,1,1, trichloroethane	applied for 20 days by capillarity	Lecce limestone	-
Verges-Belmin (1991)	50 % in toluene, followed by 9 vol. % in trichloroethane 50 % vol. in acetone	one application	Carrara marble	lion sculptures, Ecole Des Beaux Arts, Paris
Villegas (1994)	10 % in 1,1,1, trichloroethane	immersion for 10 minutes (sufficient for total impregnation)	calcitic sand-stones (p. to de S. Maria, Ubeda), dolomitic sand-stones (Almeria), limestones (Sevilla, Granada)	Cathedral of Seville, Cathedral of Granada, and Cathedral of Vaeza, Spain

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