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CALCIUM TARTRATE TETRAHYDRATE PRECONSOLIDATION OF SALT-CONTAMINATED LIMESTONE AT MISSION SAN JOSÉ Y SAN MIGUEL DE AGUAYO

JENNIFER CORREIA AND FRANK MATERO

ABSTRACT—The highly carved limestone of the mission church of San José y San Miguel de Aguayo in San Antonio, Texas is considered to be the zenith of artistic expression of eighteenth century Spanish baroque architecture in the continental United States. Salt contamination, leading to flaking and delamination of the basal stone of the celebrated sacristy window, has caused accelerated disfigurement and instability of the carved surface. Physical and chemical analyses were performed on original and newly quarried stone to assess the performance of various consolidation treatments in the presence and absence of salts. Petrographic and chemical analyses identified the stone as a dense, impure micritic limestone and the salts as extrinsic gypsum and nitrates. Subsequent testing examined the effects of a tartrate-based preconsolidant followed by an ethyl silicate consolidant on salt-impregnated and non-salt-impregnated stone. Results from the analysis and testing, together with observations during field treatment, suggest that the application of a tartrate-based preconsolidant (ProSoCo Hydroxylating Conversion Treatment/HCT), followed by ethyl silicate (ProSoCo Conservare OH 100 Stone Strengthener/OH100) consolidation, was successful in stabilizing the fragile stone surface, even in the presence of salts, and did not negatively reduce the water absorption and water vapor permeability of the stone. After consolidation, the stone was grouted with a moderately hydraulic lime grout (St. Astier 3.5), fractured and delaminated stones were micro-pinned with alumina ceramic pins and Paraloid B-72 adhesive, and losses were filled with a hydraulic lime mortar. In addition, the entire surface was cleaned with a commercial, low-pressure/low-volume, micro-abrasive system (Sensi-Clean) utilizing precipitated chalk.

TITRE—La pré-consolidation à l'aide de tartrate de calcium tétrahydraté de la pierre calcaire contaminée par des sels de la Mission San Jose Y San Miguel de Aguayo. **RÉSUMÉ**—Le décor élaboré en pierre calcaire de l'église de mission de San Jose y San Miguel de Aguayo, à San Antonio au Texas, est con-

sidéré comme le summum de l'expression artistique de l'architecture baroque espagnole de la portion continentale des États-Unis. Une contamination par des sels a provoqué l'écaillage et la délamination de la pierre d'assise de la fenêtre de la sacristie, ce qui a causé une perte de lisibilité et l'instabilité de la surface sculptée. Des analyses physiques et chimiques ont été effectuées sur des pierres d'origine et d'autres fraîchement taillées dans le but d'évaluer le comportement de plusieurs consolidants, en présence et en l'absence de sels. Des analyses chimiques et pétrographiques ont permis d'identifier la pierre comme un calcaire micritique, impur et dense, et les sels comme des contaminants naturels de gypse et de nitrate. Des tests subséquents ont examiné les effets d'un pré-consolidant à base de tartrate, suivi d'un consolidant à base d'éthyl silicate sur des échantillons de pierre imprégnés ou non de sels. Les résultats d'analyse et des tests suggèrent que l'application d'un pré-consolidant (traitement de conversion par hydroxylation ProSoCo) suivi d'une consolidation à l'éthyl silicate (consolidant pour la pierre ProSoCo Conservare OH/100) parvient à stabiliser la surface fragile de la pierre, même en présence des sels, sans réduire la capacité d'absorption de la pierre à l'eau, ni sa perméabilité à la vapeur d'eau. Après consolidation, la pierre a été enduite d'un coulis de chaux moyennement hydraulique (St-Astier 3,5), les pierres brisées et délaminées réunies à l'aide de micro tiges de céramique et d'Paraloid B-72, et les pertes furent comblées avec un mortier de chaux hydraulique. De plus, toute la surface fut nettoyée avec un appareil commercial à faible pression/faible volume (Sensi-Clean) à l'aide de carbonate de calcium.

TITULO—La utilización de tetrahidrato de tartrato de calcio en la pre-consolidación de piedra caliza contaminada con sal en la Misión de San José y San Miguel de Aguayo. **RESUMEN**—La piedra caliza elaboradamente tallada de la iglesia de la Misión de San José y San Miguel de Aguayo en San Antonio de Tejas, es considerada como el ejemplo mas importante de la expresion artística de la arquitectura barroca del

Siglo XVIII en el área continental de los Estados Unidos. La contaminación salina que llevo al descaramiento y delaminación de la piedra fundamental de la famosa ventana de la sacristía, ha causado una desfiguración acelerada e inestabilidad de la superficie tallada. Análisis físicos y químicos se llevaron a cabo en piedra original y piedra recientemente sacada de la cantera para evaluar el comportamiento de varios tratamientos consolidantes en presencia y ausencia de sales. Análisis petrográficos y químicos identificaron la piedra como piedra caliza micrítica, densa e impura, y las sales como yeso extrínseco y nitratos. En pruebas posteriores se examinaron los efectos de un pre-consolidante con base de tartrato, seguido por un consolidante de silicato etílico sobre piedra impregnada de sal y no impregnada de sal. Los resultados de los análisis y las pruebas, tanto como las observaciones hechas durante los tratamientos en el sitio sugieren que la aplicación de el pre-consolidante con base en tartrato (ProSoCo Hydroxylating Conversion Treatment/HCT), seguido de una aplicación del consolidante de silicato etílico (ProSoCo Conservare OH 100 Stone Stenther/OH100), fue exitoso en la estabilización de la superficie frágil de la piedra aún en presencia de sales, y no redujo negativamente la absorción de agua ni la permeabilidad de la piedra al vapor de agua. Después de la consolidación la piedra se relleno con lechada caliza moderadamente hidráulica (St. Astier 3.5), las piedras fracturadas y delaminadas fueron adheridas con micro barritas de aluminio y cerámica y adhesivo Paraloid B-72, las perdidas fueron rellenadas con un mortero de caliza hidráulico. Adicionalmente, toda la superficie fue limpiada con un sistema comercial de baja presión y bajo volumen micro abrasivo (Sensi-Clean) utilizando tiza precipitada.

TÍTULO—Preconsolidação com tetrahidrato tartrato de cálcio e calcário contaminado por sais na Missão de São José e São Miguel de Aguayo (*Mission of San Jose and San Miguel of Aguayo*) RESUMO—A muito esculpida pedra calcária da igreja da Missão de São José e São Miguel de Aguayo (*Mission of San Jose and San Miguel of Aguayo*) de Santo Antônio, Texas é considerada o zênite da expressão artística da arquitetura barroca espanhola do século XVIII no continente dos Estados Unidos da América. A contaminação pelo sal levando à descamação e delaminação da pedra base da conhecida Janela da Sacristia, causou acelerada desfiguração e instabilidade da superfície esculpida. Análises físico-químicas foram executadas em pedras originais e recém escavadas para avaliar o de-

sempenho de vários tratamentos de consolidação na presença ou ausência de sais. Análises petrográficas e químicas identificaram a pedra como sendo uma densa e micrítica pedra calcária e os sais como gesso e nitratos extrínsecos.

Testes subseqüentes examinaram o efeito de um pré-consolidante à base de tartrato seguido de um consolidante de silicato de etil em pedra impregnada em sais e em pedra não impregnada com sal. Resultados das análises e dos testes juntamente com observações durante o tratamento sugerem que a aplicação de um pré-consolidante à base de tartrato (*ProSoCo Hydroxylating Conversion Treatment/HCT*) seguido pela consolidação com silicato de etilo (*ProSoCo Conservare OH 100 Stone Strengthener/OH100*) foi bem sucedida na estabilização da frágil superfície pétre, mesmo na presença de sais, e não reduziu negativamente a absorção da água e a permeabilidade da pedra ao vapor de água. Após a consolidação, a pedra foi então rebocada com um reboco calcário moderadamente hidráulico (*St. Astier 3.5*), as pedras delaminadas e fracionadas foram presas com micro pinos de cerâmicas de alumina e com adesivo Paraloid B-72; e as lacunas foram preenchidas com cimento calcário hidráulico.

Além disto, toda a superfície foi limpa com um sistema comercial de baixa pressão/baixo volume micro-abrasivo (*Sensi-Clean*) utilizando giz precipitado.

1. OVERVIEW

Current conservation practice advocates an integrated approach whereby any remedial interventions are to be considered in the larger context of past and present condition evaluation, treatment testing, field monitoring, and preventive maintenance. In reality, there are few projects for which conservators have the baseline data and the possibility for long-term oversight required to satisfy such a program. The recent conservation of the ornately carved limestone sacristy window at Mission San José y San Miguel de Aguayo in San Antonio, Texas, provides an opportunity to study the interrelationship of traditional and new techniques for stone conservation, set within a 75-year context of repairs and restoration. A century of documentation, together with more recent study over the past 10 years, have revealed unstable and accelerating deterioration that now threatens the integrity of the structure's celebrated carved stonework.

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2. SITE DESCRIPTION

Mission San José y San Miguel de Aguayo is one of four Spanish frontier missions that comprise San Antonio Missions National Historical Park. Established in 1778, the park covers approximately 800 acres outside the city of San Antonio, Texas, and includes Nuestra Señora de la Purísima Concepción de Acuña, San Juan Capistrano, and San Francisco de la Espada. The sculptural and architectural stonework of San José is considered by North American scholars to be the zenith of artistic expression of 18th century Spanish Baroque in the continental United States. The sacristy window is a personal and sophisticated design, executed in the florid 17th-century style known as Churrigueresque. Mission San José is one of the few sites in North America outside Mexico where this elaborately distinctive style was employed (Pierson 1976). The carving of the window has been dated to 1782, after the church and sacristy were finished, and is probably the work of the church's master mason Antonio Salazar and master carver Pedro Huizar (Ivey 1997) (fig. 1).¹ A large elongated quatrefoil design 5-1/2 ft. wide and 16 ft. high (1.68 × 4.87 m), the "window" is actually an elaborate proscenium from which the clergy delivered orations and possibly religious services to the mission's indigenous native population. The elaborate enframing is carved directly from the load-bearing stone blocks that make up the arched window opening.

The stone is a soft impure micritic limestone most likely quarried nearby from the Austin Chalk Group formation. It is predominantly calcite (88–95%) with accessory minerals of limonite and glauconite in the lower stonework (McDowell 1997) (fig. 2). Fossil clasts present in the stone are responsible for differential surface erosion that is especially prevalent in the face-bedded lower basal stonework of the enframing. The weathering of the limonite, especially beneath the sill, has caused the original light buff-colored stone to turn a darker yellow color.

3. CONDITION ASSESSMENT

A comparison of stone conditions based on graphic surveys from 1997 and 2004 using Geographic Information System software (ArcView 9.1) revealed an alarming increase in the extent of deterioration in the lower stonework. (Blocks 18–26, fig. 3). Flaking and delamination were selected for reexamination



Fig. 1. The Sacristy Window before excavation of the base, Mission San Jose y San Miguel de Aguayo, San Antonio, Texas, Wister Collection, 1893, Texas State Library, copy from NPS Archives.

over the seven-year period as they appeared to be active and are obvious weathering forms that can lead to loss and disfigurement of the carved surfaces. A comparative analysis revealed a two-fold increase in

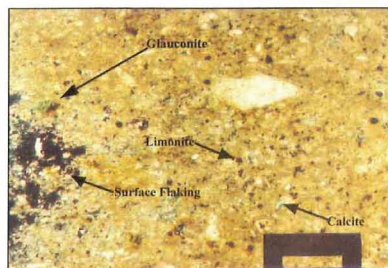


Fig. 2. Petrographic thin section of Sacristy window basal limestone. Note fine micritic texture and the presence of accessory minerals limonite and glauconite. Surface decay is evident on the left, mag. 100×, cross polarized light (McDowell 1997).

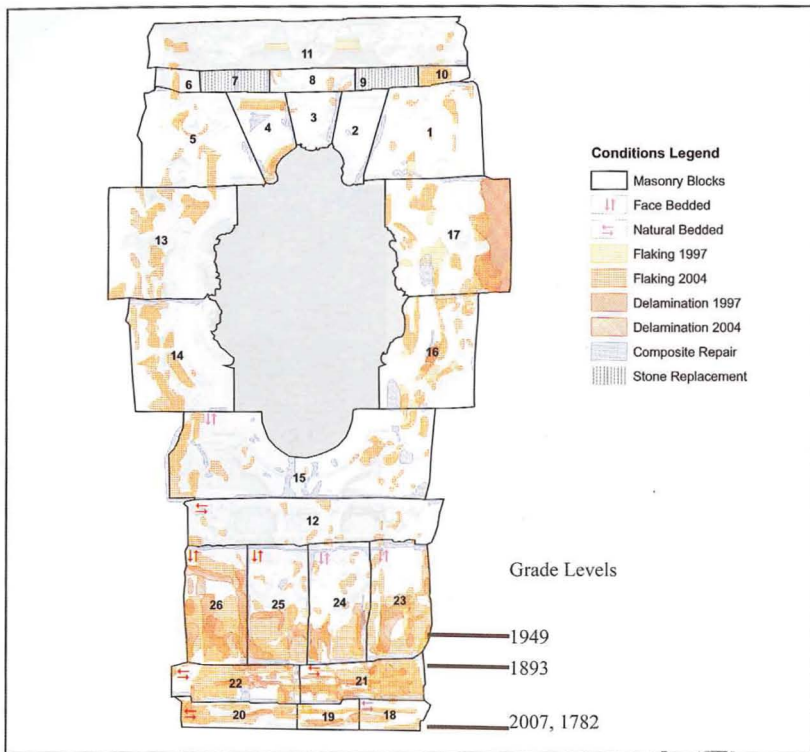


Fig. 3. 1997 and 2004 condition surveys for flaking and delamination of the Sacristy Window limestone.

the total percent area of flaking with 10% in 1997 and 20% in 2004 (Correia 2005). Delamination, a more serious form of detachment than flaking, was less extensive but also showed a significant increase. Total percent area of delamination in 1997 was 2% and increased to 6% in the 2004 assessment (Correia 2005). Historical photographs from the late 19th century reveal that a significant rise in the grade level had occurred, resulting in burial of the lower stonework for at least 50 years (see figs. 1, 3). This condition has led to salt contamination from groundwater and later wet-dry cycling after the base was exposed for display in 1950 (McDowell 1997). The resulting flaking and delamination caused by salt crystallization, disso-

lution, and recrystallization, in an open environment, have clearly accelerated over the past decade since condition recording began (1997–2007) and can be attributed to the excessive precipitation recorded for southern Texas from the late 1990s to 2004 (Correia 2005).

Analysis by x-ray diffraction (XRD) identified calcium sulfate dihydrate (gypsum) in the lower buried stonework. (XRD analysis was performed on a Rigaku D-Max/B powder diffractometer with a Cu-target sealed tube; the x-ray source set at 40 kV/30 mA.) This was supplemented with semi-quantitative ion strip (EM Quant) analysis of salt samples which also revealed sulfates and nitrates,

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thus confirming and extending information from the XRD analysis. This test was particularly important because some salts may be masked by the calcite peaks in XRD. The presence of sulfates can be traced to the naturally high concentrations of gypsum deposits in the area, and the nitrates from organic sources such as landscape fertilizers and nearby ancient burials. The concentration of gypsum was highest at the base of the window (9% calcium sulfate dihydrate) and lessened significantly in samples taken higher up, thus confirming their ground source and role in the basal deterioration.

Examination of the same samples with scanning electron microscopy-energy dispersive spectroscopy (SEM/EDX) revealed sulfur and calcium (the former attributed to the gypsum salts and the latter to the gypsum and limestone) and silicon, possibly related to the previous application of a water repellent and colored cement wash that was suggested in past treatment documentation. (SEM/EDX analysis was run on a JEOL JSM 6400 Scanning Electron Microscope with tungsten filament, with an Oxford INCA EDS system.) The colored wash is visible in situ under low magnification.

4. TESTING PROTOCOL

Given the fragile nature of the unstable carved surfaces of the basal stone, emergency stabilization was considered a first priority before cleaning or consolidation. Traditional methods of preconsolidation based on the application of solvent resin solutions (e.g., Paraloid B-72) were rejected, as the researchers were interested in studying the effects of a tartrate-based compound (ProSoCo Hydroxylating Treatment/HCT) as a preconsolidant for subsequent ethyl silicate treatment. The formation of calcium tartrate tetrahydrate (CTT) on carbonate materials, as a pre-treatment for the use of ethyl silicate consolidants, is a relatively new procedure that has had limited field testing or reporting (Weiss et al. 2000, Wheeler 2000, Hansen et al. 2003). This treatment requires the calcite grains to be free of coatings or contaminants which would hinder chemical reaction with the tartrate-based compound to form CTT. HCT was therefore studied as a preconsolidant for suitability for emergency stabilization, as well as for its reported ability to improve the performance of ethyl silicate (ProSoCo OH 100/OH100) consolidation.

4.1 ANALYSIS AND SAMPLE SELECTION

Petrographic analysis was used to characterize the original and new quarry stone, while physical tests were performed on the quarry stone only to assess the performance of various consolidation methods in the presence and absence of salts. Physical tests included capillary absorption (NORMAL 11/85, 1986) and drying curve (NORMAL 21/85, 1985 and NORMAL 29/88, 1991), both important indicators in confirming effective impregnation of consolidants and any potential adverse effects from pore size reduction. The test stone was provided by a local quarry from a source believed to be both similar to the source of the original stone and the same source of the stone used for the restoration efforts in the 1940s (McDowell 1997). These samples displayed an average water absorption of 15.7% and an average drying rate of 0.03 g/hr.

4.2 TREATMENT TESTING

Treatment testing addressed the effects of preconsolidation with HCT and ethyl silicate (OH100) consolidation in two separate phases of testing. Site conditions were replicated for both phases by impregnating sample groups H and L with salts. This allowed the authors to observe the difference in efficacy of the HCT and OH100 on both uncontaminated and salt-contaminated quarry stone. Samples were made in triplicate and organized in the following groups: Group G, uncontaminated stone treated with OH100; Group H, prepolycrystallized salt-contaminated stone treated with HCT and OH100; Group K, uncontaminated stone treated with HCT and OH100; Group L, salt-contaminated stone treated with HCT and OH100; Group M, uncontaminated untreated stone (control).

4.2.1 Preconsolidation Treatment Testing

A modified combination of two tests (ASTM C 88 (2000) and RILEM Test V. 1a. (1980)) was used to introduce salts into the quarry stone samples. Saturated solutions of calcium sulfate dihydrate and sodium nitrate were prepared and allowed to sit for 3 days, then combined. Stone samples from groups H and L were saturated by a combination of capillary rise followed by immersion. The stones were immersed for

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24 hours and allowed to air-dry for 24 hours before being placed in an oven at 60°C until their weight was stabilized (a mass difference of no more than 0.01 g between consecutive weighings). The stone was allowed to air-dry before being placed in the oven to prevent micro-cracks. The salt-impregnated dry weight was compared with the initial dry weight to determine the amount of salt uptake. Sodium nitrate is more soluble than gypsum and was the principal salt that ultimately impregnated the stone samples. A poultice was made with rag paper pulp soaked in deionized water. Gravimetric analysis was used to determine the amount of soluble salts that could be removed from the stone samples in various stages of the testing process (before HCT, after HCT, and after OH100). The poultice removed a maximum of 3% of the mass (presumably salts) from the Group H samples before preconsolidation treatment with HCT. The quantitative results of salt analyses are recorded in Table 1.

HCT is a relatively new pretreatment developed for use in combination with ethyl silicate consolidation of carbonate rocks. HCT is a water-borne compound based on tartaric acid that is applied before an ethyl silicate consolidant (Weiss et al. 2000). Successfully applied HCT forms a crystalline layer of CTT on the calcite grains of the substrate, a hydroxyl-functional layer that facilitates a better bond with the silicate groups of an ethyl silicate. The CTT layer itself may also impart a consolidating effect and increase resistance to acid attack, thus making it a good candidate for use in preconsolidation (Hansen et al. 2003). At the time of this study, most previous research of HCT had been conducted in laboratory settings, and had not considered its efficacy on salt-contaminated stone.

Although HCT was applied by low-pressure spray in the field, laboratory samples were impregnated by capillary rise to ensure good and even penetration.

Table 1. Salt Analysis Results of OH100 and HCT Treated Laboratory Samples for all Phases of Testing

Conductivity of Solutions from Poultice Extracted Salts and Mass of Salts Removed from HCT and OH100 Treated Stones						
Pre-Preconsolidation Poultice						
Sample No.	Mass Initial (g)	Final (g)	Mass Poultice	Mass Salt Removed	Avg. Conductance Reading o/oo	Standard Deviation o/oo
H22	84.57	81.96	N/A	2.61	N/A	N/A
H23	80.5	77.44	N/A	3.06		
H24	81.8	79.21	N/A	2.59		
Post-Preconsolidation Poultice Salt Analysis I						
Sample No.	Mass Initial (g)	Final (g)	Mass Poultice	Mass Salt Removed	Avg. Conductance Reading o/oo	Standard Deviation o/oo
H22	82.47	81.8	8.95	0.67	1.2 ± 0.06	.12
H23	78.06	77.3	7.23	0.76		
H24	79.69	79.02	7.94	0.67		
L34	81.22	79.57	9.59	1.65	1.6 ± 0.08	.06
L35	80.27	77.95	10.8	2.32		
L36	77.34	74.79	11.66	2.55		
Post-Preconsolidation Poultice Salt Analysis II						
Sample No.	Mass Initial (g)	Final (g)	Mass Poultice	Mass salt removed	Avg. Conductance Reading o/oo	Standard Deviation o/oo
H22	81.8	81.55	6.19	0.25	.6 ± 0.03	.12
H23	77.3	77	7.97	0.3		
H24	79.02	78.81	8.74	0.21		
L34	79.57	79.13	9.32	0.44	.8 ± 0.04	0.0
L35	77.95	77.33	10.28	0.62		
L36	74.79	74.17	9.93	0.62		
Post-Consolidation Poultice Salt Analysis						
Sample No.	Mass Initial (g)	Final (g)	Mass Poultice	Mass salt removed	Avg. Conductance Reading o/oo	Standard Deviation o/oo
H22	82.93	82.66	7.16	0.27	.4 ± 0.02	.06
H23	79.42	78.94	7.95	0.48		
H24	80.51	80.2	7.48	0.31		
L34	80.53	80.24	7.44	0.29	.6 ± 0.3	0.0
L35	79.2	78.86	6.79	0.34		
L36	76.88	76.39	6.78	0.49		

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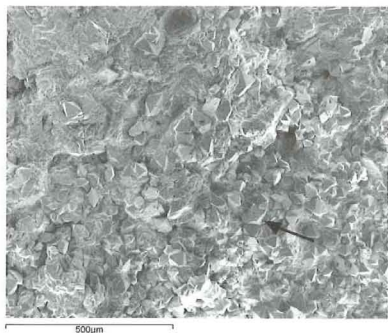


Fig. 4. SEM micrograph of the interior surface of a laboratory sample from group H (salt-contaminated and treated with HCT) after a poultice treatment. The arrow points to a single CTT grain. Note the clean faces of the CTT grains, and the good coverage on the calcite grains, mag. 100 \times , 2005.

The results were assessed by examining the untreated and salt-treated samples with SEM. Surface topography and crystal morphology were studied to ascertain the formation of CTT on the calcite grains and any potential interference from salt impregnation. Although CTT could not easily be identified with EDS on the limestone, as it is a calcium compound, it was possible to identify CTT formation through visual observation of its characteristic crystal morphology under high magnification. Original and quarry stone samples were prepared for SEM examination by breaking off an edge of the treated cube samples, mounting the interior edge on an SEM stub mount, and coating the sample with gold. The formation of CTT crystals was clearly observed in the HCT treated samples as orthorhombic grains on the calcite matrix (fig. 4). Where salts were present, these appeared to have formed around and on top of the CTT crystals, thus suggesting post CTT recrystallization (fig. 5).

4.2.2 Consolidation Treatment Testing

Consolidation testing was designed to compare the results and performance of ethyl silicate consolidation on all combinations of untreated, salt-impregnated, and preconsolidated stone (Groups G, H, K, L and M). OH100 was the ethyl silicate selected for use in consolidation. Water vapor perme-

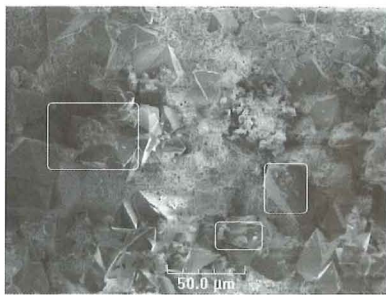


Fig. 5. SEM micrograph of a sample taken from the Sacristy Window after two applications of the preconsolidant HCT. Note salt recrystallization on the faces of the CTT grains in the outlined areas, mag. 500 \times , 2006.

ability and water drop absorption tests were performed on treated and untreated quarry stone to assess if and how certain physical properties of the stone changed in the salt-impregnated and non-salt-impregnated treated samples.

The application method was determined by the manufacturer's direction to apply the liquid consolidant in multiple cycle applications to fully penetrate the substrate. Although OH100 was applied by low-pressure spray in the field, laboratory samples were treated by capillary absorption on both sides to ensure adequate penetration. After consolidant saturation, the samples were wiped with methyl ethyl ketone to remove surface residue of the consolidant. The samples were then covered with plastic wrap and cured on a baker's rack for one month.

Poultice methodology did not change from prior testing. Rag paper pulp was soaked in deionized water overnight and then macerated. Poultices were applied before and after consolidation to test the desalination potential of preconsolidated and consolidated stone. Each sample was covered in a layer of wet pulp 1/4 in. to 1/2 in. (0.6 to 1.3 cm) thick, wrapped tightly in plastic film and left for 24 hours. The plastic film was then removed, and all samples were left on a rack to air-dry for 24 hours before removing the poultice. Only the presence of nitrates was tested, given the relative insolubility of the gypsum salts in the laboratory setting.

Each sample was also measured with EM Quant test strips and a Thermo Orion Model 105 conductance meter. The conductance meter is able to detect salt contents ranging from 0.0 to 80.0 ppt (parts per

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thousand), and has an accuracy range of $\pm 0.5\%$. Measurements can be equated to grams of salt per liter of solution. The semi-quantitative strips were used to confirm salt type and are not designed to give a numerical value, but rather a semi-quantitative range. All reported numerical values were measured with a conductance meter. The sulfate test strips detect a range from 0 to 1600 mg/L, and the nitrates from 0 to 500 mg/L.

Solutions were obtained by retaining poultices after testing. The dried poultice was weighed and placed in a beaker of deionized water (1 g poultice to 5 ml of water). Poultices were left in water for 7 days before filtering the solution. A control of deionized water was tested along with sample solutions. The ion strip value is not reported, as it is based on the median of the test strip range. Pre-preconsolidation results were not tested with the conductance meter or ion strips; the average recorded mass of salts removed was 2.75 g. The amount of salts removed was measured in grams, calculating the difference in each sample's mass before and after each poultice treatment. The mass of salts removed (g) may indicate a higher amount of salts than the conductance reading indicates, as it is possible to not solubilize all of the salts in the poultice when making the solution for the conductance meter testing. The ion strips confirmed the presence of salts after preconsolidation and consolidation. The conductance meter complemented the ion strips and gave quantitative results of salt levels in the solutions rather than semi-quantitative approximations.

The results indicate that preconsolidation did not greatly limit the efficacy of salt removal. This is evident by comparing the Group H (pre-poulticed HCT and OH100 salt-impregnated samples) with Group L (HCT and OH 100 salt-impregnated samples); Group H samples had a slightly lower reading throughout because of the pre-poulticing. After preconsolidation, 1.2 ppt salts were recorded for Group H compared with 1.6 ppt salts for Group L. This pattern of salt removal continued, and after consolidation, Group H revealed 0.4 ppt salts while Group L had 0.6 ppt salts. Results suggest that neither preconsolidation with HCT nor consolidation with OH 100 inhibits the conservator's ability to subsequently remove salts from treated stone samples (table 1).

Water vapor transmission (WVT) was measured for all samples following NORMAL 21/85 standard procedures (1985). Samples were weighed and placed on a small beaker filled with 10 ml of water. The samples were sealed with wax and placed in a desiccator for analysis. The results (table 2) indicate that both preconsolidation and consolidation treatments only slightly reduced the water vapor permeability of the quarry limestone samples. Group M (untreated control) exhibited the highest permeability (1.56×10^{-5}) while Group K (HCT and OH100 non-salt-impregnated disks) displayed the lowest permeability (1.03×10^{-5}). The non-salt-impregnated OH100 treated samples alone (Group G) displayed greater vapor permeability than the samples with the combined HCT and OH100

Table 2. Permeability and Water Drop Absorption Test Results for Control and Treated Laboratory Samples.

Performance Testing to Measure the Permeability and Water Absorption of Treated and Control Samples										
Sample Group	No.	Treatment	Water Vapor Transmission			Micro-Drop Absorption				
			Average Permeability $g/(h \cdot cm^2) \times 10^5$	Standard Deviation $g/(h \cdot cm^2) \times 10^{-6}$	Exterior Surface min. *	Standard Deviation min.	Average Evaporation Time (min)	Interior Surface min. *	Standard Deviation min.	Average Evaporation Time (min.)
G	19	OH100 disks	1.4	2.66	41.14	6.50	34.15	7.84	1.16	6.76
	20				33.72			5.53		
	21				27.16			6.93		
	22				14.33			4.56		
H	23	Pre-Poulticed, HCT and OH100 salt disks	1.36	1.15	13.18	.75	14.03	7.24	1.34	5.96
	24				14.60			6.08		
	31				42.35			7.02		
	32				29.18			6.81		
K	33	HCT and OH100 disks	1.03	1.53	42.78	7.73	42.56	8.57	.96	7.46
	34				15.34			6.18		
	35				14.66			5.29		
	36				10.02			4.47		
L	37	HCT and OH100 salt disks	1.2	2.83	16.99	2.90	13.34	4.22	.85	5.31
	38				16.73			4.98		
	39				12.19			4.57		
	Control				12.19			4.57		
M	38	Stone disks	1.56	5.51	16.73	2.50	15.07	4.98	.38	4.59
	39				12.19			4.57		
	Control				12.19			4.57		
	Control				12.19			4.57		

* (Average evaporation time of all three drops)

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treatments (Groups H, K and L). Measuring water vapor transmission ensures that consolidation treatments do not significantly reduce permeability and thus affect the entrapment of water vapor and possible condensation.

Micro-drop absorption determines the liquid water absorption rate of a porous material and is based on RILEM Test No. II. 8a (1980). Each exterior and interior surface received three water drops to ensure consistent drop size. Samples were broken in half to expose interior as well as exterior surfaces. Each sample had a total of six drops, with the exterior and interior drops performed at different times. To ensure that evaporation was not a variable, a water drop was placed on a glass surface, where it remained for the duration of testing (approximately 4 hours). Ambient conditions were 20°C and 38%RH.

Test results (table 2) indicate that the untreated control stone (Group M) displayed the lowest absorption time (highest rate) while the HCT and OH100 treated samples all exhibited reduced rate of water absorption. Group K samples (non-salt-impregnated HCT and OH100 treated) exhibited the highest absorption time (lowest rate) for exterior surfaces, followed by Group G (non-salt-impregnated OH treated). Since OH100 is reported to be hydrophobic for up to 6 months after treatment, all tests were run after 6 months to ensure uniformity across samples. Groups H and L (salt-impregnated treated samples) exhibited a lower absorption time on the exterior surfaces compared to the control probably due to the hygroscopic nature of the crystallized salts on the surfaces.

4.3 ON-SITE TREATMENT CONFIRMATION

During the treatment phase of the project, field samples were taken for analysis to confirm the results of preconsolidation and desalination. Visible salt pustules were removed from the treated basal stonework to identify the salts and treatments using XRD. The analysis revealed the following:

Calcium sulfate dihydrate (JCPDS# 33-0311)	58%
Calcium carbonate (JCPDS# 5-0586)	30%
Calcium tartrate tetrahydrate (JCPDS# 26-0330)	10%
Unknown	2%

The results confirmed that the white crystalline pustules on the flaking surfaces of the lower stonework are predominately gypsum. The identification of CTT on the pustules scraped from preconsolidated stone surfaces also confirmed the successful introduction of the HCT. SEM examination also revealed that the salts recrystallized onto and around the CTT grains in a sample taken from the window after preconsolidation. Similar results were also observed in the laboratory impregnated quarry limestone (figs. 4, 5).

4.4 TESTING CONCLUSIONS

As previously stated, SEM examination proved similar application results of HCT, in situ and in the laboratory, on salt-impregnated stone. CTT grains were clearly visible on the calcite matrix of both salt-impregnated and non-salt-impregnated stones. The crystallization of these salts (nitrates) around and on top of the CTT grains suggest post-CTT formation and also suggest that such salts can easily be removed after preconsolidation. Although it was difficult to observe the presence of ethyl silicate within the matrix of the treated stone with SEM, results from the water vapor transmission and water drop tests suggest that the permeability of the stone was altered as a result of consolidation treatments. The consolidated stone had slightly lower water vapor permeability and a lower water absorption rate, which confirmed that alkoxy-silanes polymerized to form polymers with water repellent properties, but are still water vapor permeable (Bradley 1987, 427). In both tests, the combined HCT /OH100 treatments reduced water permeability in the liquid and vapor phase more than the use of OH100 alone.

5. TREATMENT PROGRAM

The stone conservation treatment program began with emergency stabilization of the basal stonework through preconsolidation with HCT, salt reduction/removal by water poulticing, and consolidation and grouting. Scaffolding was erected before the second phase of work which included mechanical repair of the stonework by pinning, mechanical removal of previous cementitious repairs and joints, and continued preconsolidation/consolidation of selected areas. The third phase was the longest and included micro-abrasive cleaning of the stonework and conservation of the associated ironwork. The last phase included

removal of previous repairs, and repointing and mortar compensation of large areas of loss.

5.1 EMERGENCY STABILIZATION (PRECONSOLIDATION/CONSOLIDATION)

The first step of emergency stabilization involved preconsolidation with HCT followed by desalination with paper pulp poultices. HCT was sprayed in four passes onto friable areas of basal stonework. Each pass saturated the stone and was allowed to fully dry before the next pass to ensure penetration of HCT (fig. 6). After HCT was applied twice, a test poultice was applied to four areas to ensure that the poultice would not alter the color of the stone or remove a significant amount of substrate. The HCT had significantly hardened the fragile flakes and areas of delamination of stone as determined by touch in the field.

After preconsolidation, another poultice was applied to five salt-contaminated stabilized areas. After the poultice was removed, the consolidant OH100 was brush-applied in three cycles of three passes each. Methyl ethyl ketone was applied following the last cycle of OH100 to inhibit formation of surface residue. The consolidated stone was covered to protect it from rain, and cured for one month.

The preconsolidation/consolidation sequence continued in the next phase on selected areas of upper stonework and on fresh areas exposed after the removal of previous repairs and repointing. These areas were preconsolidated and consolidated using the same technique applied to the lower basal stonework. Other aspects of emergency stabilization included grouting

large voids in severely delaminating areas. Grouting techniques included cleaning the detached areas of debris and soil with mechanical tools, compressed air, and water, before injecting grout with a syringe. The dry grout was premixed and consisted of a natural moderately hydraulic lime (St. Astier NHL 3.5), fine silica sand, and ceramic microspheres. Grout was mixed on site with a 5% acrylic dispersion in water (by volume) to enhance the bonding effect of the grout. Grout was injected through 12 and 14 gauge steel and Teflon cannulas.

5.2 MECHANICAL REPAIR

After emergency stabilization was complete, carved details that were found to be detached due to micro-cracking and bedding delamination were pinned. Micro-pinning with 1/16 in. diameter pins was reserved for small and ornate areas of the carved surfaces while larger areas of detachment required 1/8 in. diameter pins.

Pinning methods were selected based on previous research by the ACL at the Second Bank in Philadelphia, and Victoria Mansion in Portland, Maine, using ceramic pins seated in a filled Paraloid B-72 adhesive (Glavan 2004; Glavan and Matero 2005). Ceramic pins of 1/8 in. and 1/16 in. diameter were inserted into holes 1/16 in. larger than the diameter of the pin, and fixed in place with an adhesive (fig. 7).



Fig. 6. Preconsolidation of the Sacristy Window limestone with HCT applied in a power sprayer.

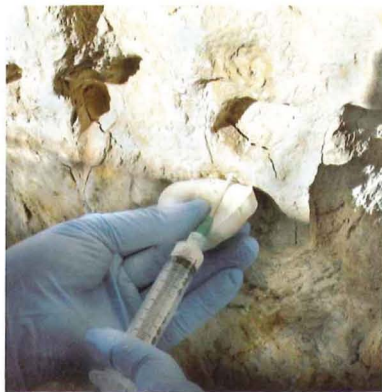


Fig. 7. Micro-pinning by filling a drilled hole with a filled B-72 injection before insertion of an alumina ceramic pin.

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A 1:1 (by weight) solution of Paraloid B-72 in acetone was prepared. Both 0.01% fumed silica (Cab-O-Sil, extra fine) and 20% precipitated calcium carbonate (Ultra-Pflex) were added to the B-72 solution (by weight) to increase viscosity, increase bond strength, and control shrinkage. Holes were drilled beyond the detachment into the sound stone; a recess of 1/4 in. was allowed at the surface of the hole for a mortar fill. The adhesive was injected into the hole through a 14-gauge Teflon cannula secured to a 10cc syringe. The pin was degreased in acetone before seating the pin in the adhesive. The area was then capped off with the same adhesive. Pins were inserted perpendicular to the direction of the detachment and at an upward angle.

5.3 REMOVAL OF PREVIOUS REPAIRS

During the initial treatment, many of the previous 1940s mortar repairs and poorly repointed joints were found to be visually disfiguring and unsound. Joints were raked back at least 1/4 in. from the surface of the stone, and defective mortar repairs were removed. Newly exposed stone was then treated with HCT and OH100.

5.4 CLEANING

Field and laboratory analysis had revealed the partial application of a pigmented cementitious wash and possible silicone-based water repellent that had darkened the stone surface, especially in repair areas. For the test trial cleaning, a portable low-pressure micro-abrasive cleaning system (Sensi-Clean) was selected because of its extreme sensitivity and control. The system utilizes a very fine calcium carbonate precipitate as the aggregate, delivered at low variable pressure and volume. The lowest settings were chosen during the pilot test cleaning, delivering approximately 10cc of medium/second at 7.5 psi (Correia 2006).

The lowest setting of 1:1 (media:pressure) was used on most areas of the stonework. Only heavily soiled, recessed, and discolored areas were cleaned with a 2:1 setting, utilizing more medium rather than higher pressure, to address heavier surface accretions. The nozzle was kept at a uniform distance of at least one inch from the surface and was not allowed to dwell in one area for more than a few seconds. Approximately 2-1/2 x 50 lb. bags of medium were



Fig. 8. Detail of the Sacristy Window during cleaning (left) with the Sensi-Clean microabrasive cleaning system.

used for the entire carved surround and metal grille (fig. 8).

5.5 REPOINTING AND MORTAR COMPENSATION

Repointing and mortar compensation were completed after cleaning. Mixes were prepared with a 1:3



Fig. 9. The outlined areas are finished mortar fills that replaced incompatible previous repairs.



Fig. 10. The Sacristy Window after conservation.

ratio (by volume) of 3.5 NHL (St. Astier) and yellow bar sand formulated to match the existing original lime mortar in color, texture, and overall properties. Where necessary, mortars were tinted with raw sienna and marble dust to match the darker cleaned stone surfaces. Larger areas of compensation, where previous repairs had been removed, needed to be applied in layers over a 2 to 3 day period. Final finishes were achieved on the molded elements with sheet metal profiles cut to match the original. Surfaces were then pressed with natural sponges to pull excess water from the mortar and leave a slightly granular finish to match the weathered stone surface (figs. 9, 10).

The final step involved integrating the repairs with the surrounding cleaned masonry. Dilute tinted acrylic emulsion washes (3%) were applied to break up large flat areas of mortar repairs and emulate the variegated color and patterns of the weathered limestone. The acrylic was also applied to integrate existing sound repairs in the same manner (figs. 11, 12).



Fig. 11. The Sacristy Window base before conservation.



Fig. 12. The Sacristy Window base after conservation.

6. CONCLUSIONS

Results from analysis and physical testing, together with observations during treatment, suggest that the application of a tartrate-based preconsolidation followed by an ethyl silicate consolidant was successful in stabilizing the fragile limestone surface, even in the presence of salts. The dual consolidating system did not significantly alter the water absorption and water vapor permeability of the stone, nor the conservator's ability to remove salts after preconsolidation. Strength changes to the stone could not be quantitatively measured as the laboratory samples were fabricated from newly quarried unweathered stone, and original stone samples were insufficient for mechanical testing. Nevertheless, field observations confirmed significant improvement to the flaking and delaminated carved basal stone without visual alteration after HCT treatment. Further testing and performance

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evaluation of HCT alone and in concert with OH100 on weathered American carbonate rocks needs to be performed. In the meantime, monitoring of conditions will continue in order to evaluate the effectiveness of the above treatments at Mission San José.

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NOTE

1. The correspondence states that Dionico Gonzales was master mason in 1776 and served until 1779 at the latest. He likely designed the sacristy's architectural details, and Antonio Salazar, hired to replace Gonzales, was likely responsible for execution of the sacristy window construction.

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SOURCES OF MATERIALS

Paraloid B-72 acrylic resin
Rohm and Haas Company
100 Independence Mall West
Philadelphia, PA 19106-2399
(215) 592-3000
www.rohmhaas.com

alumina ceramic pins
Vesuvius McDanel Co.
McDanel Advanced Ceramic Technologies LLC
Beaver Falls, PA 15010
(724) 843-8300
www.techceramics.com

chisels, points, mallets
G. Gibson & Co. Stone tools, Gibson House
Barrowey Lane
Garforth, Leeds, LS25 1NG
England
0113 2869 245, fax: 0113 2866 417
www.g-gibson.com

Hydroxylated Conversion Treatment (HCT),
Conservare Stone Strengthener OH100
ProSoCo, Inc.
Distributed through SSI
2104 Mannix
San Antonio, TX 78217
(210) 967-4796

Sensi-Clean, calcium carbonate precipitate
Sponge-Jet, Inc.
235 Heritage Avenue, Suite 2
Portsmouth, NH 03801
(603) 610-7950
www.spongejet.com

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Virginia Lime Works
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