TESTING FOR POTENTIAL TREATMENT OF PETROGLYPH-BEARING SANDSTONES AT ST. VICTOR PROVINCIAL PETROGLYPH PARK, ST. VICTOR, SASKATCHEWAN, CANADA

Final Project Report

by

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Kansas Geological Survey
Open-file Report 99-42

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INTRODUCTION

Native American rock art sites provide links to our past and should be preserved for future study. Although many sites have been vandalized, the destructive force acting on all rock art is natural weathering. Such sites are attacked by freeze-thaw, wet-dry, and heat-cool cycling; wind and water erosion; biological growths; salts; atmospheric pollution; and mineral weathering. Naturally, climatic characteristics, the degree of protection from the elements, and the properties of the stone play important roles in determining which of the agents is detrimental at a given site. The placement of a suitable bonding agent in liquid form into the stone would improve the durability of the stone and retard the effects of such weathering, thus prolonging the life of the petroglyphs.

The St. Victor site is located south of the town of St. Victor in southeastern Saskatchewan. The site is unusual because of the orientation of the petroglyphs. Most sites have petroglyphs located on a more or less vertical exposure on the stone. At St. Victor's the petroglyphs are carved into the cap rock (top horizontal surface) of a calcite-cemented sandstone cliff, which is part of the Ravenscroft Sandstone. The site is one of only a handful of sites in central and eastern Canada where the petroglyphs are on a horizontal surface and is the only known such site in the Great Plains of Canada. Because of their orientation, these petroglyphs are unprotected and subject to most of the weathering agents mentioned above. Prolonged weathering over the centuries has undoubtedly weakened the exterior surface of the stone by dissolving some of the original calcite cement. Some salt appears to have formed. Underlying the cap rock along the vertical face of the cliff, abundant joints (vertical partings) are observed. In addition to natural weathering, potential treatment of the site may be complicated by the presence of a thin remnant film of latex that was once used to create molds of some of the petroglyphs. Under hand lens magnification, the surface of the latex contains large numbers of pin holes. Characteristics of the site are shown in Figures 1-8.

Figure 1. Weathering of the sandstone has produced the rolling hills at St. Victor.

Figure 2. View of the St. Victor site including the stairs to reach the petroglyphs.

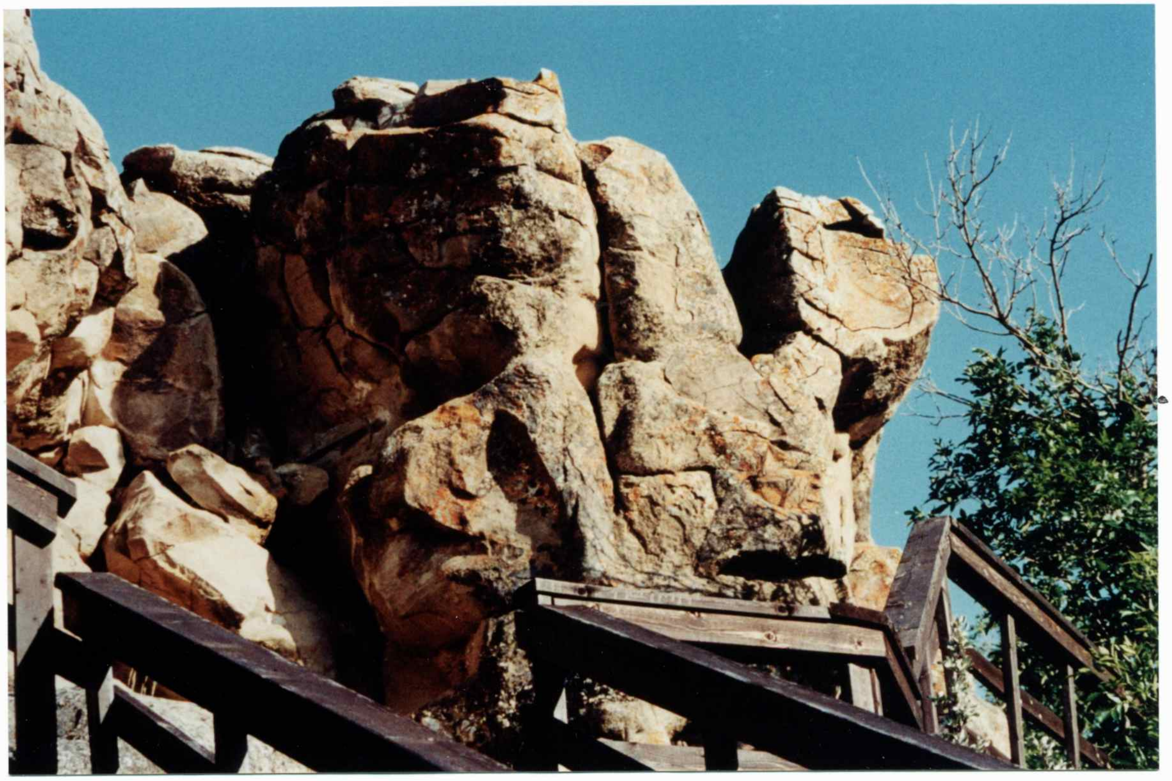


Figure 3. Fractures and joints are abundant in the Ravenscroft Sandstone at St. Victor.

Figure 4. A portion of the St. Victor site.

Figure 5. Petroglyphs that remain coated with white latex years after application for purposes of making impressions.

Figure 6. Closer view of a few of the petroglyphs.

Figure 7. The white mineralization below these petroglyphs was first thought to be soluble salts but x-ray diffraction suggests a coating of solution and redeposition of the calcite cement.

Figure 8. Most of the white (and red-orange) matter in the picture is lichen growth. Such growth is common at the St. Victor site.

In order to be effective at consolidating the stone and thereby increasing its resistance to weathering, any potential chemical treatment should meet the following criteria:

1) The treatment must penetrate the stone so that the entire zone of weathering is treated.
2) The treatment should improve the compressive strength of the stone, an indication of successful bonding.
3) No discoloration of the stone should occur. This means that no coloring ions should be present and that the solution should have a neutral pH to avoid possible reaction with the mineral components of the stone.
4) The treatment should not completely seal the pore system of the stone; the stone should be able to breathe and rid itself of excess moisture.

At present, one chemical system that meets the above criteria is known commercially as Conservare OH; the chemical solution is primarily composed of ethyl silicate (silicic ethyl ester) dissolved in a methyl ethyl ketone/acetone mixture. The ketone mixture acts as both a solvent and a volatile inert carrier and the low molecular weights of the compounds and low viscosity of the solution promote penetration into the stone. The solution has a neutral pH. Developed by Wacker Chemie in Germany, this solution in the United States is supplied by ProSoCo, Inc. or Process Solvents Company, Inc., of Kansas City, Kansas, and they have successfully used this solution for consolidation purposes on many historic buildings. Treatments have produced increased strength of the stone and no appreciable discoloration has occurred. Based on improvements in the compressive strengths of stone treated with Conservare OH, the stone consolidation is particularly effective when used on sandstones. An example of the effect on the properties of sandstone has been reported by Zinsmeister et al. (1988). Perhaps most important is the fact that with proper application, the pore system of the stone is not sealed, and the stone can rid itself of any excess moisture. The basic mechanism of the chemical treatment is quite simple; the ethyl silicate hydrolyzes upon exposure to moisture within the stone to form a siliceous cement and the volatile by-product, ethyl alcohol.

Conservare OH was used for the first time on Native American petroglyphs at the Faris Cave Site, Ellsworth County, Kansas, as reported in Grisafe (1996) and produced outstanding results. Core samples treated in the laboratory showed large increases in strength and resistance to freeze-thaw cycles, no discoloration occurred in either lab samples or on-site test panels, and the stone retained some of its permeability, thus allowing the stone to breathe and eliminate excess moisture. A recent laboratory study on the Hell Creek Sandstone collected from Pompeys Pillar National Historic Landmark in Montana, where the explorer William Clark carved his signature in 1806, yielded similar results (Grisafe, 1999).

The primary objective of this laboratory study was to determine the chemistry and mineralogy of the stone and then measure the absorption, compressive strength, and freeze-thaw resistance of both untreated and treated stone. These measurements will determine the suitability of treating the stone at the St. Victor Site with the ethyl silicate solution consolidating agent in order to increase the resistance of the stone to weathering and thereby preserve the petroglyphs.

PROCEDURE

During the visit to the site, numerous small blocks of stone were collected. One sample was a small, loose block of stone on the edge of the cliff at the petroglyph site. The remainder of the samples were collected from the top of the sandstone outcrop on the other side of the hill. In both areas a relatively thin (12 to 18 inches thick), fine-grained, brownish layer was just below the cap rock and was used as a marker bed to ensure that all samples were collected from approximately the same elevation. However, it was not possible to accurately measure the distance between the petroglyph surface and this marker bed, so an error of 1 to 2 feet is possible with regard to the elevations of the samples. It is worth mentioning that this brownish layer appears to be weathering more rapidly than the overlying sandstone on which the petroglyphs are located. In time, sufficient undercutting of the petroglyph-bearing stone may occur and become another element of potential destruction at the site.

Several of the samples were examined by x-ray diffraction to determine the mineralogy of the test specimens. In addition, samples were also examined under a reflected-light microscope and whole-rock chemical analyses of major components were obtained from some of the samples using atomic absorption spectroscopy. Samples of a thin white coating or salt, which was occasionally present at the site, were collected and examined by x-ray diffraction.

Key physical properties were determined, including the capillary and immersion absorption, compressive strength, and freeze-thaw resistance. All physical properties were measured on core samples cut from blocks of stone collected near the site, such cores being approximately 1.5 inches in diameter and 1.5 to 1.75 inches in height. Capillary absorption as a function of time was determined by placing the cores (base side down) on a water-saturated sponge and measuring their weight gain at periodic intervals. For comparison, cores were immersed in water for 24 hours or longer and their weight gain measured.

The capillary absorption characteristics (amount and rate of water uptake) of the stone were determined; these served as a guide to the treatment times to be used on the test cores. All cores were placed in a stainless steel pan containing a thin layer of the ethyl silicate solution, allowing the chemical solution to be absorbed through their bases. This method more closely simulates field treatment, where the solution would be absorbed from the surface inward, than completely immersing the cores in the solution. Because sufficient permeability or porosity existed after one treatment, the cores were given a second treatment. Based on recommendations by the supplier, a curing period of at least one month was allowed between treatments or before property measurements were undertaken to insure the reaction was at least 95% complete.

Initial weights before treatment and final treated weights were used to determine the amount of solids precipitated within the stone cores. Absorption, compressive strength, and freeze-thaw resistance were also measured on both treated and untreated cores in order to evaluate the effectiveness of the treatments. In summary, the test results indicated whether future treatment by this solution is warranted. Such future work would involve selection and treatment of a small test panel at the site, followed by actual treatment of the petroglyphs.

Compressive strength was measured on a Riehl Dynamometer located at the Materials Testing Laboratory of the Kansas Department of Transportation (located at 2300 N. VanBuren in Topeka, Kansas). The diameter and height of each core was measured to the nearest hundredth of an inch. The height measurement was done to insure the height to diameter ratio of the sample fell within the range of values specified in compressive strength test ASTM C-109. The load required to break each core was recorded and the compressive strength of each core was calculated by dividing the load at failure by the cross-sectional area of the core. Values were calculated in both pounds per square inch (lb/in^2) and kilograms per square centimeter (kg/cm^2). An average of five cores was used to determine each compressive strength value.

To evaluate freeze-thaw resistance the cores were subjected to a cycle of 16 hours at -20°C followed by 8 hours of immersion in room temperature water. Weight loss of the cores was determined after every 25 cycles. An average of three cores from each set of cores was used to determine the absorption characteristics and freeze-thaw resistance. In this study we used a total of 400 freeze-thaw cycles, and several days were required to obtain cores of constant weight after every 25 cycles. As a result this test required nearly 2 years, far longer than the other property measurements.

RESULTS

Although approximately 200 pounds of sample were collected at the site during the visit, this was not enough to complete the original research plan. During the coring of the blocks in the laboratory, two unexpected problems were found that effectively lowered the supply of stone available for testing, namely variable porosity and abundant fracturing. Further samples were not available despite requests for additional blocks of stone.

Because the porosity of the sandstone samples varied so widely, the cores were divided into three general types. The first type is relatively porous, medium- to fine-grained sandstone possessing a medium, yellowish-brown color. The second type of core is light gray and relatively dense. The third type is a mixture of the first two types, with the boundary between the two types often relatively sharp. A thin, irregular, dark line presumed to be a stylolite is present in the cores between the two zones. Although the grouping of the cores in this manner was arbitrary, it was useful for this study. In reality, some cores have a porosity intermediate between the porous and dense cores without a sharp boundary, such as the small sample obtained from the outcrop bearing the petroglyphs.

Another problem was that many of the blocks and subsequent cores contained fractures not visible during the on-site sample collection. Such cores were unsuitable for porosity, strength, and freeze-thaw evaluations. In fact, many of the samples split during coring. As expected, some of these fractures are parallel to the bedding plane but some run vertically or at an angle to the bedding plane.

Since there was no way to determine which type of sandstone core most closely matches the petroglyph-bearing sandstone (without collecting samples directly from the site), it was necessary to conduct tests on each of the three types of core. This reduced the number of cores available for testing by one-third. There were not enough samples to satisfy the original research plans of using different treatments. We ended up with only 16 to18 cores of each type; we were left with only 8 to 9 treated cores of each type on which to determine compressive strength, absorption and freeze-thaw durability, the other half being left untreated as a control set. The treated samples were given two 30-minute, capillary absorption cycles in the stone strengthening agent, Conservare OH.

Mineralogy

Field examination (hand lens and 10% hydrochloric acid) suggested the stone to be a carbonate cemented sandstone. Reflected light microscopy indicated the stone consisted largely of quartz grains imbedded in a light, fine-grained matrix. Some quartz grains are clear while others have some color, probably of iron mineral origin. A small number of other grains are quite dark, resembling smoky quartz. Another opaque mineral, biotite mica, is also present, as are a few grains of opaque material that could not be identified.

X-ray diffraction patterns were obtained from samples ground in a corundum mortar and pestle to -200 mesh and dispersed on glass slides using acetone. The resulting diffraction patterns indicated a carbonate-cemented sandstone, primarily quartz and calcite, that also contains small amounts of dolomite and mica-illite. As expected from microscopic examination, little feldspar is present. As a whole, the clay content of these samples is relatively low. Based on the major diffraction peak intensity ratios of quartz to calcite, the primary difference between the cores is the amount of carbonate cement. The denser, light-gray cores are simply better cemented with calcium carbonate. Examples of the diffraction patterns obtained from dense and porous cores are shown in Figure 9.

The small amount of what resembled a white salt deposit, collected at the site, was also examined by x-ray diffraction but only phases found above were detected in the diffraction pattern. It is probable that the coating is the result of a long-term dissolving and redeposition of the calcite matrix of the stone.

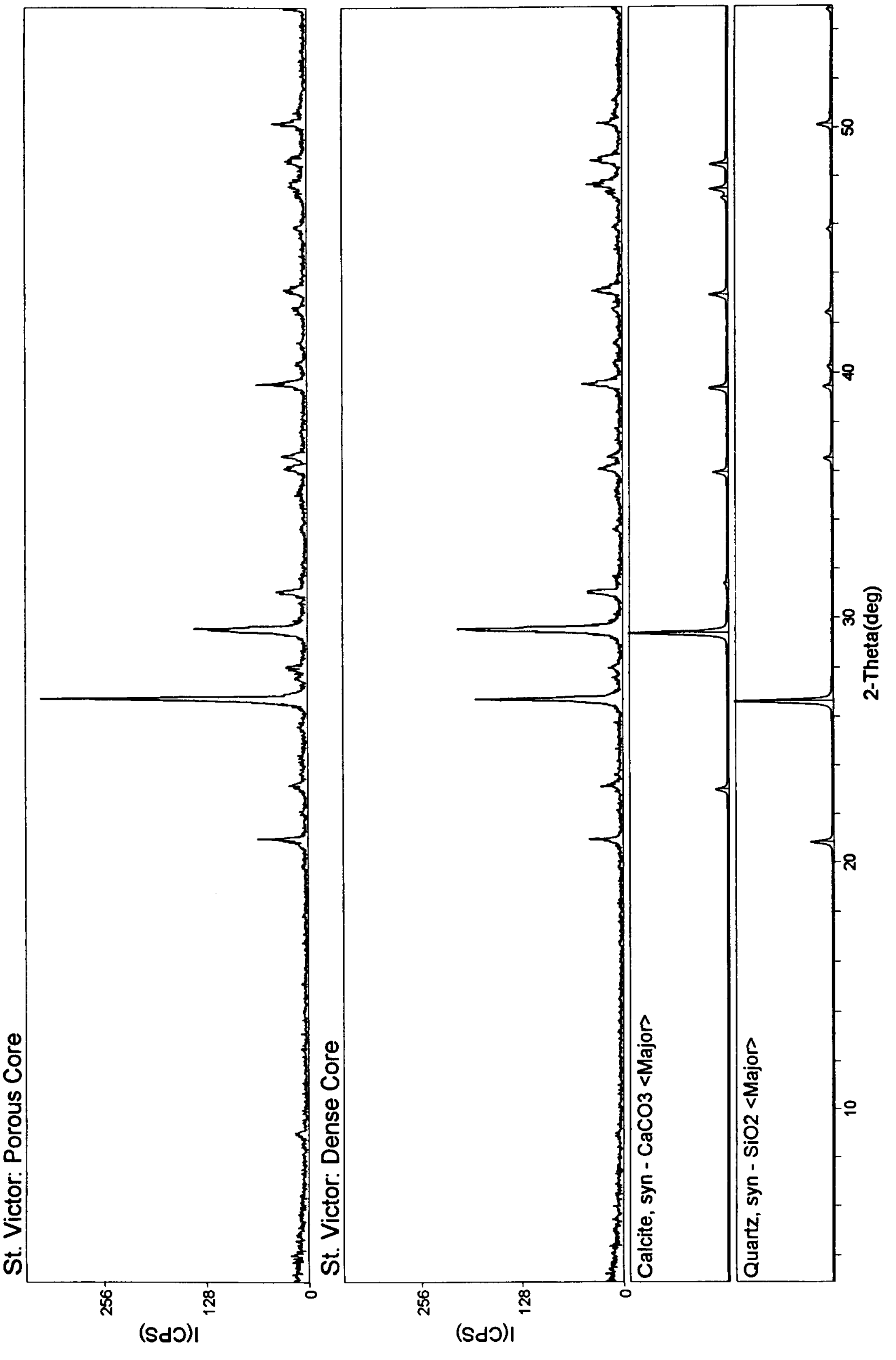


Figure 9. X-ray diffraction patterns of the Ravenscroft Sandstone at the St. Victor site. The stone is mostly quartz and calcite with the denser cores containing more calcite cement.

Chemical Analyses

Representative chemical analyses in weight percent of major oxides are shown in Table 1. The results agree with the x-ray diffraction results with regard to the relative amounts of quartz and calcite in the dense and porous cores. The higher calcium oxide content of a dense core results in lower amounts of silica and most other oxides. These results certainly show the variability of the Ravenscroft Sandstone at this site. The small sample collected at the petroglyph site contains calcite and silica levels whose values lie between the porous and dense cores in Table 1.

Table 1

Chemical Analyses of the Ravenscroft Sandstones by Atomic Absorption at the St. Victor Site (Weight Percent Composition)

	Sample Core		
Oxide	Dense	On-Site	Porous
SiO_2	28.07	38.88	52.56
Al_2O_3	3.02	3.85	5.27
Fe_2O_3	0.90	1.04	1.64
TiO_2	0.28	0.17	0.42
MnO	0.11	0.08	0.07
CaO	35.94	28.38	18.90
MgO	2.35	1.45	2.07
K_2O	0.64	0.88	1.19
Na_2O	0.40	0.55	0.73
Loss on ignition (1000° C)	28.22	25.15	17.50
Total	99.93	100.43	100.35

Capillary and Immersion Absorption

The capillary absorptions of cores were determined by placing the base of each core on a saturated sponge and measuring the weight gain of the core over time. Such information is useful to obtain an idea of how rapidly the stone would absorb liquid. The test was performed on the three basic types of cores. In addition, cores that contained what appeared to be a transition zone between porous and dense natured stone were examined from both sides. Finally, immersion absorption of the cores was done to compare the total weight gain of the stone to that obtained by capillary absorption.

Table 2

Percentage Weight Gain of Cores from the St. Victor Site During Capillary Absorption and Immersion Testing
(all times in hours)

Cores	Capillary Absorption				Immersion
	0.5	1.0	4.0	24	24
A	8.9	9.0	9.1	9.5	9.5
B	0.6	0.8	1.8	3.1	4.6
C	4.8	5.3	5.4	5.6	5.4
D	1.2	1.6	2.4	2.6	2.7

A = porous cores.
B = transition cores with dense side down.
C = transition cores with porous side down.
D = dense cores.

Partial results of these tests are summarized in Table 2 with each value being the average of three cores. The porous cores absorb most of the liquid (almost 95%) within the first 30 minutes. The differences between sets B and C confirm the apparent density and permeability differences in the two ends of the cores. The early absorption rate of set D was higher than expected and was primarily due to one core in the set that was not well cemented on one end of the core. The core also had a higher 24-hour capillary and immersion absorption Eliminating the one core gave absorption versus time values close to set B during the first hour of measurements. Again, the variation in these values highlights the variability of the Ravenscroft Sandstone at St. Victor.

The last column in Table 2 shows the weight gain after the cores were submerged in water for 24 hours. The values are similar to the capillary absorption values, except for set B in which the cores were placed dense side down, causing the lower capillary absorption values relative to immersion values. After 24 hours of capillary absorption, one of the cores in set B was still dry on the top portion, indicating the permeability of the densely cemented zones was relatively low.

Compressive Strength

The average values for the compressive strengths of the treated and untreated cores are presented in Table 3. It is apparent from the values for the porous and mixed-type cores that the treatment of two cycles of the stone consolidant has greatly increased the compressive strength of the stone. No change (within experimental error) was observed for the dense cores but this is not particularly surprising considering the low porosity of the cores and the accompanying fact that the dense cores only increased by 0.9 weight percent (compared to 4.1 percent for the porous cores) as the result of two consolidation treatments. Because of the limited number of cores and the wide scatter of the strength values obtained for the dense cores, the dense core averages are the least reliable.

Table 3

Compressive Strength of Treated and Untreated Cores of Ravenscroft Sandstone from the St. Victor Petroglyph Site

Type of Core	Untreated		Treated	
	lb/in^2	kg/cm^2	lb/in^2	kg/cm^2
Porous	1,830	129	4,660	327
Mixed	3,800	267	7,030	494
Dense	8,620	606	8,510	598

Freeze-Thaw Resistance

Although the weight loss for each core was measured after every 25 freeze-thaw cycles, the changes were small, especially in comparison to many other sandstones. Table 4 shows the average weight loss of core sets after every 100 cycles.

Table 4

Freeze-Thaw Resistance of Treated and Untreated Cores of the Ravenscroft Sandstone from the St. Victor Site

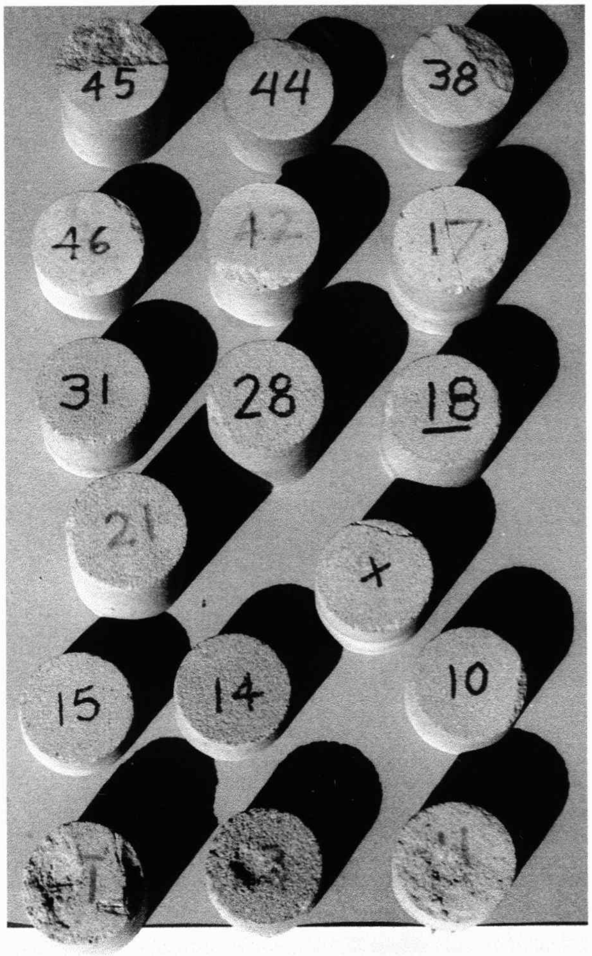
	Percent Weight Loss After Cycle			
	100	200	300	400
Porous Cores				
Untreated	0.5	0.9	3.1	4.7
Treated	0.3	0.4	0.7	0.7
Mixed Cores				
Untreated	0.2	0.2	0.3	0.3
Treated	0.1	0.2	0.3	0.4
Dense Cores				
Untreated	0.1	0.2	0.3	0.3
Treated	0.1	0.2	0.3	0.3

The values in Table 4 clearly show an improvement in the freeze-thaw resistance of the porous sandstone that was treated with stone consolidant. Although the untreated percent weight loss of 4.7% is undesirable, it is relatively good compared to many weakly or unbonded sandstones that may completely disintegrate in less than 100 freeze-thaw cycles; sometimes as few as 25 cycles is sufficient to disintegrate cores of this type of stone (Grisafe, 1996). Surprisingly, no significant difference was observed for the mixed cores although some difference might be observed with larger numbers of freeze-thaw cycles. The lack of differences between treated and untreated dense cores is not surprising given their low porosity and their inability to absorb meaningful amounts of the ethyl silicate consolidant. Figure 10 shows the cores after 400 freeze-thaw cycles.

SUMMARY

The results of this study show the core samples collected from St. Victor have similar mineralogical content but differ significantly in their porosity and permeability values due to differences in the amounts of the calcium carbonate cement present. The more porous samples allowed more ethyl silicate to be incorporated into the stone and produced larger increases in strength as a result of treatment relative to the denser cores. The treatment also improved the freeze-thaw resistance of the porous stone. However, no change in freeze-thaw resistance was observed in the dense stone. Any difference in resistance would require more than the 400 cycles used in this study.

Because the small piece of stone collected from the edge of the petroglyph surface resembles the porous type of stone, it suggests that the petroglyph-bearing sandstone



400 CYCLES

Figure 10. Freeze-thaw test results after 400 cycles. The bottom row are the porous, untreated cores and show the greatest damage. Missing stone and cracks on the other cores were present on the original samples.

would benefit greatly from the ethyl silicate treatment. However, differences in elevations of the petroglyph surface and the relatively abrupt changes in porosity and permeability that may occur with small elevation differences make it impossible to guarantee that all of the petroglyphs are located on porous stone. Obviously, coring the site would provide such information, but this is not an option at a petroglyph site. Wetting the surface to determine areas of rapid water absorption is not reliable because of the latex film coating many of the petroglyphs.

The latex coating cannot be mechanically removed without some surface damage caused by plucking sand grains from the surface. This is naturally undesirable. Any agent that could be used to dissolve the latex would undoubtedly transfer the material into the stone and affect the porosity and permeability, a similarly undesirable result.

Because the stone is relatively strong and withstands freeze-thaw cycling reasonably well, the best option is to do nothing at this point in time. With additional aging, the latex coating will likely become brittle, crack, and wind and water will eventually remove the latex from the site. Once the surface is relatively free of latex, then the petroglyph surface could be treated with ethyl silicate for consolidation and improved freeze-thaw resistance.

ACKNOWLEDGMENTS

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