USING ETHYL SILICATE TO IMPROVE THE DURABILITY OF THE TONGUE RIVER SANDSTONE AT CASTLE BUTTE, MONTANA: A POTENTIAL MOETHOD TO PRESERVE NATIVE AMERICAN PETROGLYPHS
Interim Report

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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 Castle Butte site is located in Yellowstone County in central Montana. The site includes petroglyphs carved onto the vertical faces of two sandstone ledges near the top of the butte that are part of the Tongue River Sandstone. Because of their location, these petroglyphs are relatively unprotected and subject to most of the weathering agents mentioned above. Prolonged weathering has undoubtedly weakened the exterior surface of the stone by dissolving some of the original cement.

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 system 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 as reported by 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 Castle Butte 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, small blocks of stone were collected for initial examination. Later, large blocks of stone were collected by Bureau of Land Management personnel from Billings, Montana, and shipped to the Kansas Geological Survey for testing. A third bed of sandstone underlying the two top beds was also sampled for comparison.

Several small pieces obtained from the exterior and interior portions of the blocks 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.

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 at 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 using cores placed with their bases on a water-saturated sponge and measuring their weight gain at periodic intervals. For comparison, cores were immersed in water for 48 hours and their percent weight gain measured at 1, 4, 24, and 48 hours.

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, some of the cores were given additional treatment(s). Based on recommendations by the supplier, a minimum curing period of 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 will indicate whether treatment by this solution is warranted in the future. Such future work would involve selection and treatment of a small test panel at the site and later, 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 in Topeka, Kansas. The diameter and height of each core was measured to the nearest hundreth 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 nine cores was used to determine each compressive strength value.

Freeze-thaw resistance was evaluated using a cycle of 16 hours at -20 degrees C. followed by thawing for 8 hours by immersion in water at room temperature. 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. The freeze-thaw testing requires the longest time of the property measurements and has just begun.

RESULTS

Chemistry

Table 1 shows the chemical analyses obtained from samples of the Tongue River Sandstone at Castle Butte. Despite the different appearance of the two ledges of stone, their chemical composition is similar. The UCB ledge contains slightly more calcium and magnesium oxides and a larger loss on ignition, all of which suggest that a greater amount of carbonate cementation may be present.

The bed of sandstone beneath the two upper ledges contains little carbonate cementation with a combined calcium and magnesium content as low as 3.5 % and a loss on ignition as low as 4.7%. Not surprisingly, this bed is very friable due to the absence of appreciable cement.

Mineralogy

X-ray diffraction patterns were obtained using samples ground to -200 mesh and dispersed on glass slides using acetone as a volatile, inert carrier to form the slurry. A Philips diffractometer equipped with a graphite, curved crystal monochromator was used to scan the samples, and the resulting diffraction patterns were analyzed using a computerized ASTM mineral database. In general, the samples are quartz with small amounts of carbonate, dolomite with lesser calcite, as the major matrix component. The samples also contain small amounts of clay and feldspar. Typical patterns are shown in Figure 1.

Absorption

Capillary and immersion absorption measured in terms of percentage weight gain of water are presented in Tables 2 and 3 for the treated and untreated cores obtained from the UCB and LCB sandstone beds at Castle Butte. Each value is the average of three cores. As expected, both the rate of absorption and the total absorption are lowered by the ethyl silicate treatments. However, the multiple treatments have not sealed the pore system. The values show that the LCB bed has a larger permeability with a water absorption over twice as great as the UCB bed during the first hour for both untreated and treated samples.

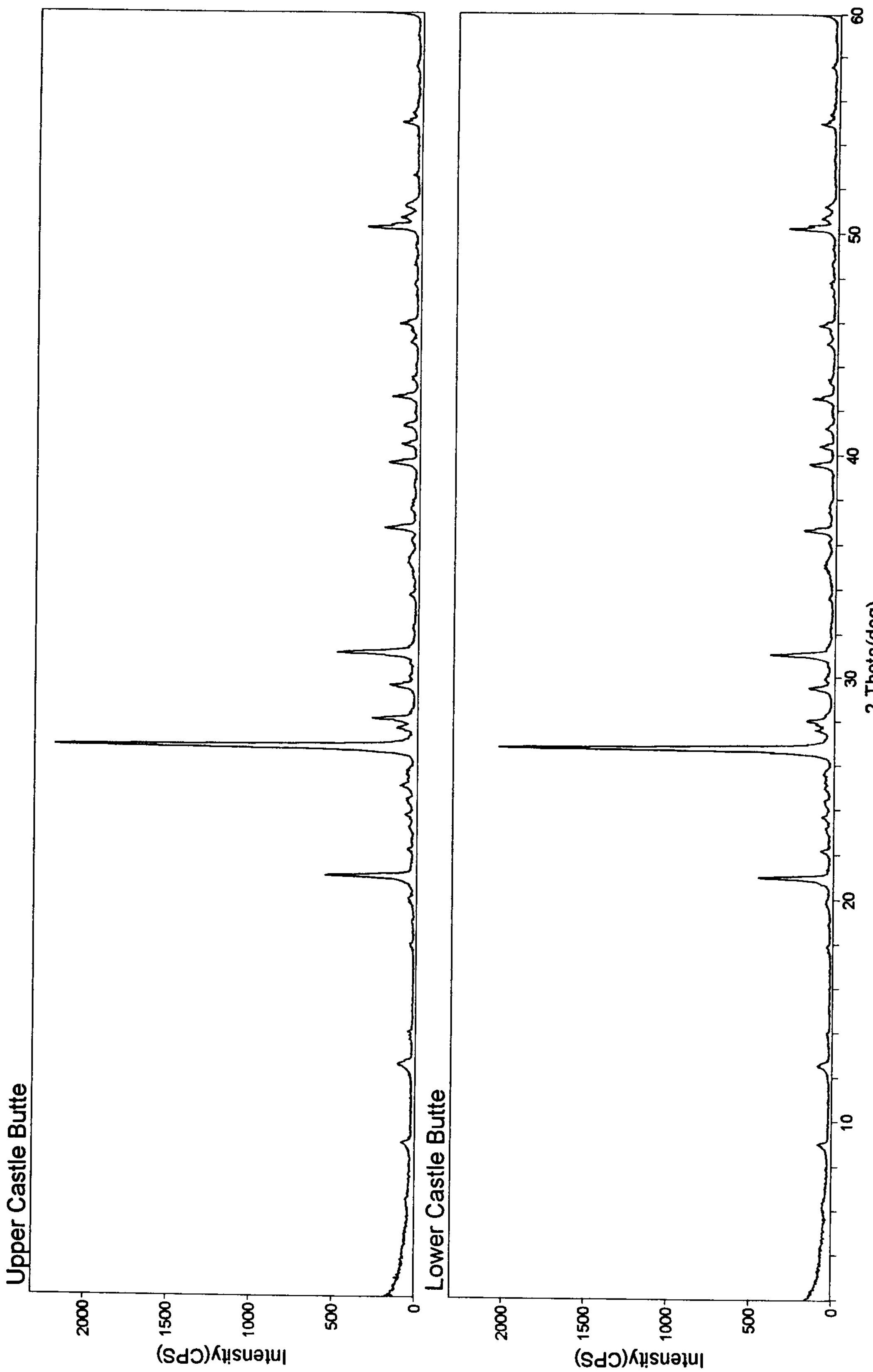

Figure 1. X-Ray Diffraction Patterns from Sandstone Ledges at Castle Butte.

Table 1

Summary of Chemical Analyses of Sandstones by Atomic Absorption

(Weight Percent Composition)

Oxide	Sample							
	UCB-1	UCB-2	UCB-3	AVERAGE UCB	LCB-1	LCB-2	LCB-3	AVERAGE LCB
SiO_2	63.29	63.01	63.28	63.19	64.65	63.14	63.31	63.70
Al_2O_3	6.89	8.57	7.12	7.53	8.66	7.93	8.18	8.26
Fe_2O_3	2.52	2.31	2.81	2.55	3.29	2.92	2.96	3.06
TiO_2	0.51	0.51	0.53	0.52	0.54	0.54	0.54	0.54
MnO	0.02	0.02	0.02	0.02	0.03	0.02	0.03	0.03
CaO	7.72	7.39	7.53	7.55	6.76	7.52	7.69	7.32
MgO	4.16	3.38	4.09	3.88	3.08	3.32	3.12	3.17
K_2O	1.72	1.64	1.14	1.50	2.08	1.98	2.11	2.06
Na_2O	1.35	1.36	1.31	1.34	1.15	1.60	1.61	1.45
Loss on ignition	11.71	11.59	12.14	11.81	9.79	10.60	10.56	10.32
Total	99.89	99.78	99.97	99.89	100.03	99.57	100.11	99.91

For comparison, Table 3 shows the weight percent absorption obtained by immersion. Since a greater surface area is in contact with the water during immersion, the rate of absorption is normally higher than that for capillary absorption for a given time and treatment during the early stages of absorption. With sufficient time, the values obtained by the two methods are similar. These figures illustrate why capillary absorption is used for laboratory treatment of the cores because it more closely resembles field application.

Table 2

Average Weight Percent Capillary Absorption Values as a Function of Time and Treatment for Sandstone Samples

Treatment	Percent Weight Gain (per Unit of Time in Hours)					
	0.5	1.0	2.0	4.0	24	48
UCB Bed						
Untreated	4.2	5.7	7.6	8.9	9.6	9.9
1 OH	1.4	1.8	2.4	3.3	5.9	6.4
2 OH	0.7	1.0	1.4	2.1	3.3	4.0
LCB Bed						
Untreated	10.7	10.8	10.8	10.8	11.1	11.9
1 OH	9.0	9.4	9.6	9.8	9.9	10.0
2 OH	3.8	4.5	5.2	5.8	6.2	6.3
3 OH	0.6	0.7	0.7	0.8	1.0	1.2

Table 3

Average Weight Percent Immersion Absorption Values as a Function of Time and Treatment for Sandstone Samples

Treatment	Percent Weight Gain (per Unit of Time in Hours)			
	1.0	4.0	24	48
UCB Bed				
Untreated	8.8	9.0	9.7	10.1
1 OH	5.1	6.5	6.9	7.2
2 OH	2.6	3.9	4.8	5.0
LCB Bed				
Untreated	10.6	10.8	11.8	12.0
1 OH	7.9	8.5	9.2	10.2
2 OH	5.4	6.0	6.6	7.2
3 OH	5.2	5.3	5.7	6.1

Compressive Strength

The compressive strength values obtained from the untreated and treated cores of the three sandstone ledges are given in Table 4. All values represent an average of 9 cores.

Table 4

Compressive Strength of Sandstone Beds of
at the Top of Castle Butte, Yellowstone County, Montana

Bed		Compressive lb/in^2	Strength kg/cm^2	Percent Improvement
UCB				
	Untreated	2,960	208	--
	1 OH	5,850	411	98
	2 OH	8,200	570	177
LCB				
	Untreated	1,520	107	--
	1 OH	2,330	164	53
	2 OH	4,480	315	195
	3 OH	5,910	416	289
Bottom (brown)				
	Untreated	1,210	85	--
	2 OH	3,230	227	167
Bottom (gray)				
	Untreated	470	33	--
	1 OH	1,280	90	172
	2 OH	1,800	127	283

The results show that treatment with the ethyl silicate solution produces large increases in the compressive strength in all of the sandstone beds. Repeated treatments produce even greater strengths. Obviously, the stone consolidation appears successful using ethyl silicate. However, it is possible to have a stone with a high compressive strength that performs poorly under freeze-thaw conditions.

CONCLUSIONS

Based on the results obtained to date, the ethyl silicate treatment has potential for increasing the durability of the sandstone, and hence the lifetime of the petroglyphs, at Castle Butte. However, the freeze-thaw testing needs to be completed before we can state with certainty that the ethyl silicate prolongs the life of the stone. In addition, the treatment produces a slight darkening of the stone color. At this point, we are uncertain as to the cause because previous studies have never encountered the problem.

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