PRESERVING THE NAME OF W.F. CODY (BUFFALO BILL) INCISED INTO RED DAKOTA SANDSTONE IN ELLSWORTH COUNTY, KANSAS, USING ETHYL SILICATE SOLUTION

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A laboratory examination of the effect of ethyl silicate solutions (Conservare OH and Conservare H) on red Dakota sandstone (Cretaceous) cores from Red Rock Canyon, Kanopolis Lake, Ellsworth County, showed the treatments improved the compressive strength and freeze-thaw resistance of the stone without sealing the pore system or causing discoloration. The solution then was applied to the signature of W. F. Cody in order to prolong the lifetime of this important historical graffiti.

INTRODUCTION

The advent of the industrial revolution in Europe led to atmospheric pollution and acid rain. After withstanding centuries of natural weathering without appreciable change, statuary and detailed carvings on buildings made from stone and exposed to the elements began to lose detail. This process nearly destroyed much of Europe's artistic stonework.

During the twentieth century, European scientists began searching for a suitable method to consolidate the chemically weathered stone and restore stonework, as well as possible, to its original condition. One of the products that resulted from this research was an ethyl silicate solution. Ethyl silicate was not new and was patented as a stone preservative by Laurie (1925). However, what was needed was a suitable nonaqueous solvent capable of dissolving an appreciable amount of ethyl silicate that could transport the chemical into the stone. During the 1970's, a suitable solvent mixture was made available by Wacker Chemie in Germany, a ketone mixture consisting mostly of methyl ethyl ketone. Once in the stone, the solvent would evaporate and the ethyl silicate would react with moisture in the stone to form a siliceous bond and the volatile by-product, ethyl alcohol.

The product in the United States is named Conservare OH and the sole supplier is the Process Solvents Company (Lawrence, KS). It has been used for over 20 years as a stone consolidant on historically important buildings that have suffered from the effects of acidic pollution. The product is very effective when used on sandstone and an example of how it improves the strength of sandstone is given by Zinsmeister, Weis, and Gale (1988). In 1988, the product was applied to weathered Native American petroglyphs in Ellsworth County, Kansas as reported by Grisafe (1996). The solution improved the strength and freeze-thaw resistance of the stone. Grisafe (2000) found similar improvements in the laboratory on the Hell Creek Sandstone from Pompeys National Historic Landmark, located along the Yellowstone River, Yellowstone County, Montana, where the explorer William Clark carved his name.

The W. F. Cody inscription is located in Red Rock Canyon on the north side of Kanopolis Reservoir (Kanopolis Lake). The canyon's name is appropriate: the walls are formed by the Cretaceous Dakota sandstone that contain iron oxide, hence their red color. The area is on U.S. Army Corps of Engineers managed land and is not accessible to the general public. Cody was stationed at nearby Fort Harker when he carved the inscription.

Because the sandstone at this location is rather friable, the Corps decided the testing and possible treatment might benefit the preservation of this historic graffiti.

PROCEDURE

During the initial visit to the site, photographs were taken and samples collected. A photograph of the signature is shown in Figure 1. Most of the sample collected for testing was in the form of a block of fallen sandstone adjacent to the signature area. A few small pieces at the base of the site were also collected. In situ absorption was measured using a capillary tube like the one shown in Figure 2.

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 the two largest samples using atomic absorption spectroscopy. Samples of a thin white coating or salt, which appeared in small patches on the stone face at the site after the 1993 flood were gently brushed (camels hair brush) from the surface and x-rayed.

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 the block 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 base down 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 one surface inward, than completely immersing the cores in the solution. Because sufficient permeability or porosity existed after one treatment, the cores were

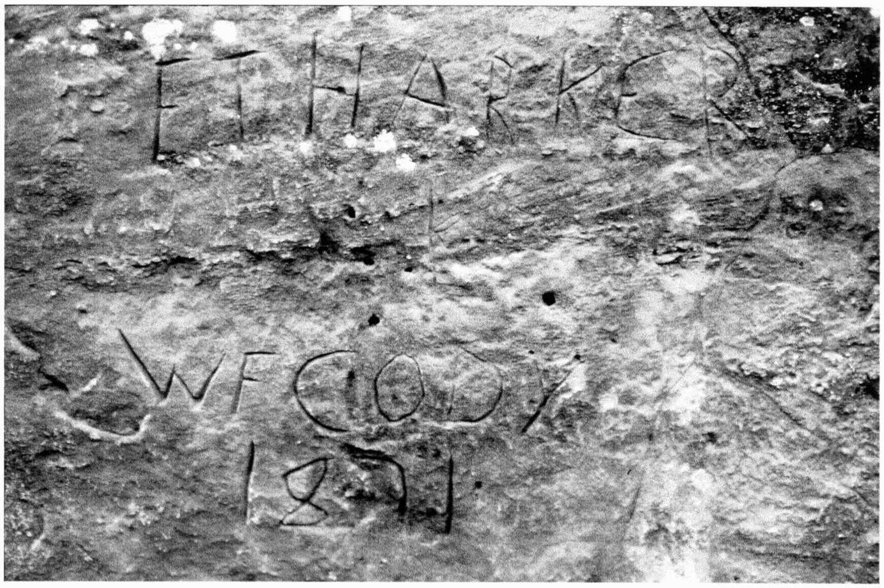

Figure 1. Photographs of the Cody Signature Taken in 1990.

Figure 2. Capillary Tube for Measuring in situ capillary absorption.

given repeated treatments. 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 signature.

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 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-170. 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 six 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. Due to sample limitations, an average of two cores from each set of cores was used to determine the absorption characteristics and freeze-thaw resistance.

RESULTS

The highly permeable nature of the sandstone permitted short treatment times. A summary of the treatments is given in Table 1. Initial and second treatments were with the Conservare OH that is entirely ethyl silicate while the third and fourth treatments were with Conservare H, a combination of the OH plus a water repellent. In each treatment the cores were wet within the allotted treatment time.

Mineralogy

A combination of reflected light microscopy and x- ray diffraction examination indicated the sandstone was largely quartz but optically also contained iron oxide(s), and a few grains of mica and rarely, feldspar and opaques. Representative diffraction patterns for the dark and light red stone are shown in Figure 3. Because the iron oxide is present in such a small amount and iron oxides are often poorly crystallized or amorphous, x-ray diffraction patterns did not show their presence. Figure 4 shows the diffraction pattern

Table 1

Chemical Treatments and Times of Sandstone Cores Using Conservare OH and H Products

	Treatment Time Using Capillary Absorption (in min.)			
Treatment	OH	OH	H	H
Control	0	0	0	0
1 OH	2	0	0	0
2 OH	2	2	0	0
2 OH + 1 H	2	2	5	0
2 OH + 2 H	2	2	5	5

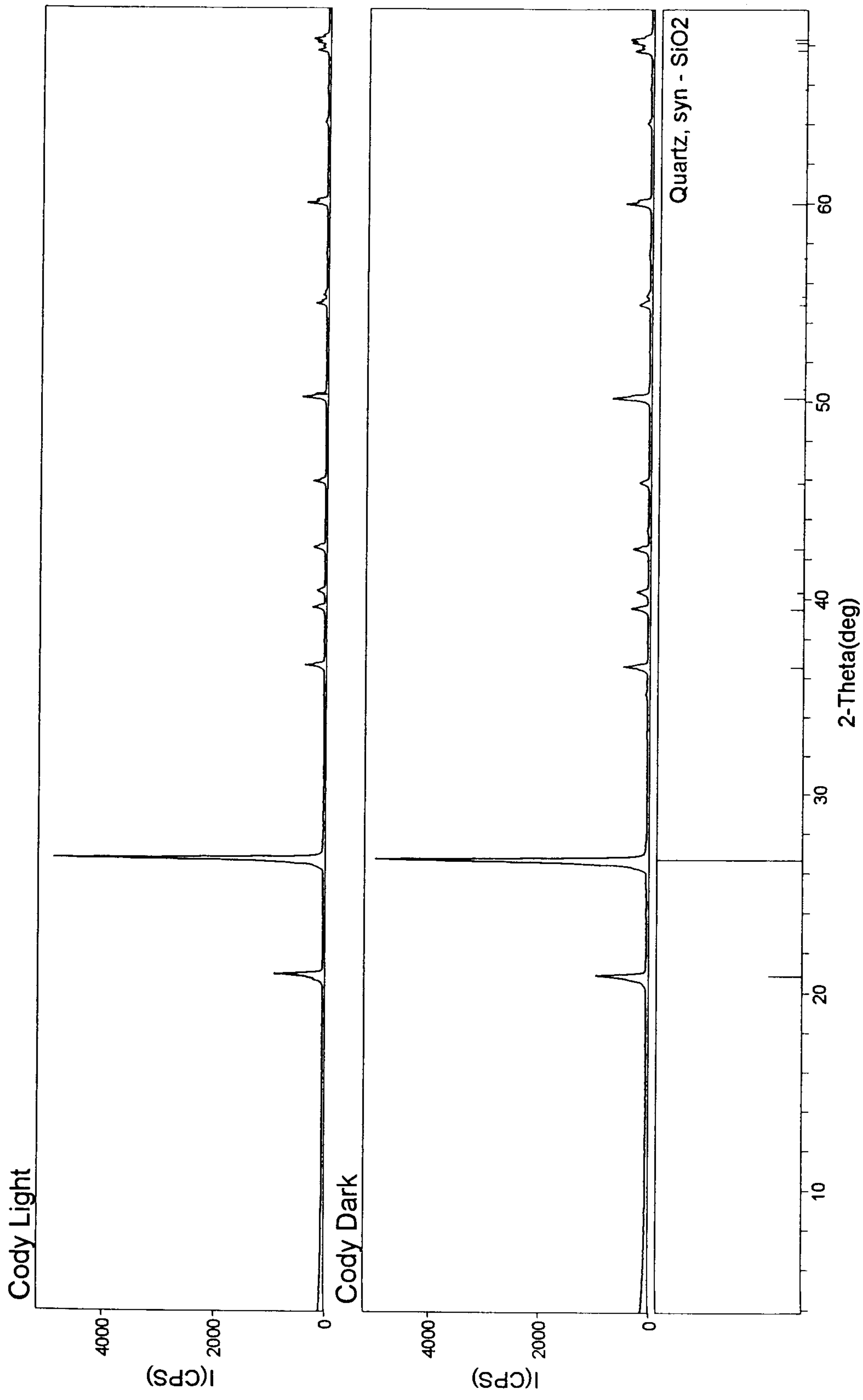

Figure 3. X-ray Diffraction Patterns for light and dark red Dakota Sandstone.

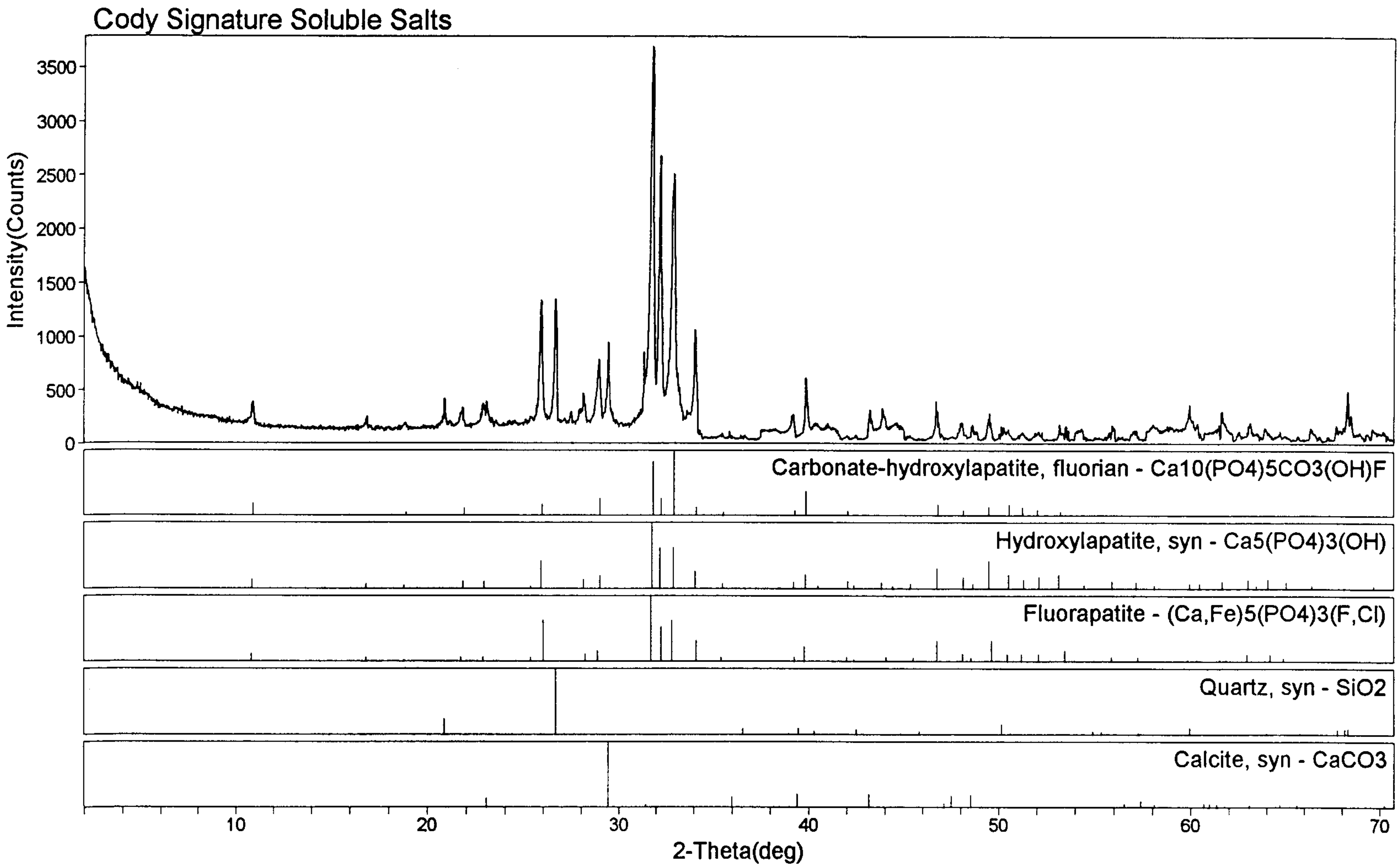

Figure 4. X-ray Diffraction Pattern for “Salt” that Appeared in Patches after the 1993 Flood.

obtained from " salt" that appeared in small patches on the surface of the Cody panel after the 1993 flood inundated the area. The pattern indicates the presence of an apatite phase. By 1999, this material had disappeared, presumably washed off by rain water, and the only white material on the panel was due to a few small, circular patches of lichen that were present since the site was first examined in 1990.

Chemistry

Table 2 summarizes the chemical analyses obtained from the red sandstone. Two blocks were examined with each value representing an average of three analyses. In general, the results are similar to those obtained from the Faris Cave site as reported by Grisafe (1996). At both locations, the stone is about 96% silica. At the Cody site, the iron is clearly trivalent as evidenced by the red color. The two blocks at the Cody site have similar chemistries with the redder of the blocks containing over 0.4% more iron oxide.

Absorption

Absorption of 5 ml of water using the capillary tube device shown in Figure 2 required less than one minute and indicated a highly porous, permeable sandstone. Likewise, using core samples in the laboratory placed on a saturated sponge, a very high rate of capillary absorption occurred. Eight untreated cores showed an average weight percent gain of 13.8% in only 15 seconds and 16.6% in 30 seconds. After 24 hours, the capillary absorption weight gain was 16.7% while the 24 hour gain using submerged samples was 16.9% This indicates the stone is nearly saturated after 30 seconds and permitted the short duration treatments shown in Table 1.

With treatments, material is deposited within the stone that naturally lowers both the rate of water absorption and the total absorption. A sharp decline in the rate of water absorption is caused by the use of Conservare H due to the presence of the water repellent. A summary of these data are given in Table 3. For comparison, Table 4 shows the capillary and immersion absorptions for two of the treatments. Because of the greater surface area exposed during immersion, the rate of water absorption is greater than for capillary absorption. Immersion absorption values also give an indication of the available porosity more rapidly than capillary absorption values.

Compressive Strength

The compressive strength values for treated and untreated cores are summarized in Table 5 and provide an indication of the effectiveness of the stone consolidation treatment. A single two minute treatment increased the strength by over 80% while subsequent treatments continued to increase the strength. Clearly, the ethyl silicate treatment is highly effective in consolidating the sandstone. The percent solids column, using the final cured weights and the original weights of the respective cores, shows the expected trend of increasing amounts with increasing treatments.

Table 2

Chemical Analyses of red Dakota Sandstone at the Cody Site
Determined by Atomic Absorption
(Weight Percent Composition)

Oxide	"low" iron sample	"high" iron sample	Average
SiO_2	96.82	95.98	96.41
Al_2O_3	0.58	1.09	0.84
Fe_2O_3	0.87	1.31	1.09
TiO_2	0.53	0.32	0.42
MnO	<0.01	<0.01	<0.01
CaO	<0.01	<0.01	<0.01
MgO	0.03	0.03	0.03
K_2O	0.30	0.32	0.31
Na_2O	0.03	0.03	0.03
Loss on Ignition at 1000°C	0.91	0.72	0.82
Total	100.07	99.80	99.94

Table 3

Average Weight Percent Water Capillary Absorption Up to One Hour as a Function of Time and Treatment for Sandstone from the Cody Site

	Percent Weight Gain in Minutes					
Treatment	0.5	1.0	2.0	5.0	10.0	60.0
Untreated	16.6	16.6	16.6	---	----	----
1 OH	6.2	8.6	12.1	13.4	13.5	13.5
2 OH	2.0	2.7	3.9	5.8	8.2	10.6
2 OH + 1 H	<0.1	<0.1	<0.1	0.1	0.1	0.2
2 OH + 2 H	<0.1	<0.1	<0.1	0.1	0.1	0.1

Table 4

Comparison of Average Percent Weight Gain by Capillary and Immersion Absorption in Water

Treatment	Capillary Absorption 1 Day	Capillary Absorption 7 Day	Immersion Absorption 1 Day	Immersion Absorption 7 Day
Untreated	16.7	-----	16.9	-----
2 OH	10.6	-----	13.6	13.9
2OH + 2 H	0.4	0.9	2.6	5.0

Freeze-Thaw Resistance

Considering the large strength increases in Table 5, one would expect a significant increase in the freeze-thaw resistance of the sandstone treated by ethyl silicate. The results of the freeze-thaw testing are given in Table 6. Untreated cores are basically reduced to piles of sand after only 50 cycles. By contrast, treated cores withstood the freeze-thaw cycling much better, in particular those given three and four treatments. The small weight loss recorded after the first 25 cycles is common for all cores because there are usually some relatively unbonded or loose grains on the surface that are removed by the first few freeze-thaw cycles.

Treatment at the Cody Site

A small area adjacent to the Cody signature was treated with the ethyl silicate solution to insure no discoloration of the red sandstone occurred. Neither cores in the laboratory or the test panel area showed any change in color.

The signature and surrounding area was treated at an approximate rate of 1 gallon per 10 square feet during each cycle and a total of four cycles (2 OH + 2 H) were used. Because of the highly volatile nature of the ketone solvent/carrier, application times were selected when there was little wind or direct sunlight on the panel area. In addition, the hottest portion of the summer and winter was avoided. Too much heat will cause a rapid drying and risk concentrating the chemical at the surface while the hydrolysis reaction will not occur in cold weather. It is also important to select a time of relative dryness since the ethyl silicate will hydrolyze upon contact with moisture. Applying to a wet surface increases the chances of concentrating the siliceous product on or near the surface instead of obtaining a good depth of penetration. Thus, applications were done during dry spells in the spring and fall.

With respect to the application, a one gallon, hand-pumped sprayer equipped with a fan jet was used for all applications. This allowed low pressure, finely dispersed droplets to be applied without damaging the surface of the stone. This method is far preferable to alternate methods of high pressure, a narrow stream, or brushing, all of which would likely remove some sand grains on such a porous, permeable sandstone.

SUMMARY

Cores of red Dakota sandstone were cut from a block collected at the Cody signature site, Red Rock Canyon, Lake Kanopolis, Ellsworth County. The cores were examined for their chemistry and mineralogy, absorption characteristics, compressive strength and freeze-thaw resistance. Sets of the cores were treated with Conservare OH, a stone consolidant consisting of ethyl silicate dissolved in a ketone mixture, primarily methyl-ethyl ketone. Two sets were given additional treatment with Conservare H, a combination of OH and a water repellent. After curing, the physical properties (compressive strength, absorption and freeze-thaw resistance) were measured and compared to the untreated cores. Results

Table 5

Compressive Strength of Red Dakota Sandstone, Cody Site

Treatment	Percent Solids	Compressive Strength		
		lb/in^2	kg/cm^2	Percent Increase
Untreated	----	850	60	---
1 OH	5.5	1,560	110	84
2 OH	9.8	2,940	207	246
2 OH + 1 H	13.3	3,860	271	354
2 OH + 2 H	15.4	4,240	298	399

Table 6

Percent Weight Loss from Freeze-Thaw Cycling
Cody Signature Site in Red Rock Canyon

	Number of Cycles			
Treatment	25	50	75	100
Untreated	76.0	96.2	100.0	100.0
1 OH	0.9	4.4	6.0	11.0
2 OH	1.2	3.0	3.6	4.3
2 OH + 1 H	0.6	0.7	0.8	0.8
2 OH + 2 H	0.5	0.6	0.7	0.6

show the ethyl silicate produces a large increase in the strength and freeze-thaw resistance without discoloring the stone or sealing the pore system. A low pressure application of the solutions (2 OH + 2 H) was used on the Cody signature in order to reduce the weathering of the stone and prolong the lifetime of this historic graffiti.

ACKNOWLEDGMENTS

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LIST OF SUPPLIERS

Chemicals

Process Solvents Company (ProSoCo), Inc.
3741 Greenway Circle
Lawrence, KS 66046

Sprayer

B & G Equipment Company
P.O. Box 130
Plumsteadville, PA 18949

LITERATURE CITED

Grisafe, D.A. 1996. Preserving Native American petroglyphs on porous sandstone. Plains Anthropologist 41, (158): 373-382.

Grisafe, D.A. 2000. Improvement of sandstone durabilty: evaluating a treatment's suitability for preserving historic inscriptions. Technology and Conservation, Spring 1999-2000: 20-26.

Laurie, A.P. 1925. Preservation of stone. U.S. Patent 1,561,988, Nov. 17, 1925. Also U.S. Patents 1,583,103, May 18,1926, and 1,607,762, Nov. 23, 1926.

Zinsmeister, K.J.H., N.R. Weiss, and F.R. Gale. 1988. Consolidation treatment: Massillon (Ohio) sandstone. Jour. Preservation Tech. 20: 35-39.