TESTING FOR POTENTIAL TREATMENT OF THE HELL CREEK SANDSTONE FORMATION AT POMPEYS PILLAR NATIONAL HISTORIC LANDMARK, YELLOWSTONE COUNTY, MONTANA

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ABSTRACT

Cores of the Hell Creek Sandstone from Pompeys Pillar National Historic Landmark, located along the Yellowstone River in Yellowstone County, Montana, were treated with ethyl silicate. Measurement of the resulting physical properties, when compared to untreated cores, showed the treatment substantially increases the compressive strength and freeze-thaw resistance of the stone without sealing the pore system or discoloring the stone. As such, the treatment increases the durability of the stone and provides a method for preserving the signature of the explorer William Clark.

INTRODUCTION

Mention of the early exploration of our country and searching for a road west to the ocean certainly brings to mind the Lewis and Clark expedition. As William Clark traveled along the Yellowstone River, he took the time to carve his signature and the date, July 25, 1806, into a prominent landform, thus giving us one of our most important pieces of historical graffiti. The physiographic feature on which he carved his signature is now known as Pompeys Pillar National Historic Landmark. Clark reportedly named the pillar after the son of Sacajawea, the now-legendary Indian woman who accompanied Clark's group. Although the "pillar" is only 120 feet high, its location along the floodplain of the river allowed it to be seen from some distance as a guiding landmark. From a defense standpoint, Pompeys Pillar provided a lookout over the area.

Initial protection of the Clark signature was in the form of an iron grate installed in 1883. The prongs of the grate were either coated with lead or else covered with lead sleeves and then driven into place. Upon removal, some evidence of iron oxidation was noted. In 1964, the present cover was installed, a brass case with a cover of bullet-proof glass. In recent years, block displacement has opened up a nearby crevice; movement has changed the drainage of the rain water and sometimes, leakage has occurred into the protective case. This observation, coupled with the recently completed study using ethyl silicate to consolidate sandstone-bearing petroglyphs in Ellsworth County, Kansas, prompted the late John Taylor, then archeologist with the Billings Resource Area of the Bureau of Land Management, to contact the author and led to this study. Taylor also noted that the nearby Indian petroglyphs seemed to be fading from weathering.

With regard to historical sites that have Indian rock art and/or historically important names and dates, vandalism is a continuing problem throughout our country. People spray paint, carve initials, burn fires, scratch the surface, etc. and such action has certainly taken its toll. Even in relatively desolate areas such as Barrier Canyon in eastern Utah, graffiti has defaced some classic Barrier Canyon pictographs. Recently, the public and laws have begun to address such problems, and recent events such as the above-mentioned Barrier Canyon case and at Pompeys Pillar, the guilty parties have been caught and prosecuted. Small wonder that private landowners, the National Park Service, the Bureau of Land Management or whoever has charge of such sites, are either reluctant to tell people their location or have taken precautions to protect the site.

Some sites have been subjected to varying forms of vandalism, but as a whole, the most destructive force acting on all outdoor sites is natural weathering. Outdoor sites are gradually attacked by a variety of phenomena, including freeze-thaw, wet-dry and heat-cool cycling, wind and water erosion, biological growth, salts, atmospheric pollution, and mineral weathering. Naturally, the geographical location of a site (with regard to its climatic characteristics) and the degree of protection provided to the site play major roles in determining which agent or agents are most detrimental.

Despite the attempts to protect sites from vandalism, little work has been done in finding a suitable treatment to increase the durability of the stone itself. However, before treating any stone, it is necessary to understand the nature of the stone. For example, there is little point in treating a stone with a chemical solution if the stone has no absorption capacity. Thus, it is important to understand certain basic mineralogical and physical characteristics of the stone and be able to evaluate the changes of such properties as a result of any type of treatment.

There are natural reservations to treating outdoor sites since such sites are irreplaceable. An untested treatment could produce more problems than cures. However, while debating the merits and durability of a treatment, nature continues to erode such sites, and many sites cannot afford to wait much longer before destruction is complete. Even those sites that appear relatively unscathed today may require preservation at some point in the future.

Greater emphasis has been placed on the chemical treatment of historical stone structures, particularly in Europe, than on treating petroglyphs and historic graffiti. While not identical, there are similar problems and constraints in treating a building or an outdoor rock site. Past experience with buildings provides useful guidelines for selecting a successful method for treating petroglyph sites. Some treatment methods proposed in the past border on the exotic. About 25 years ago, when epoxy cement became popular, it was proposed that holes be drilled behind petroglyphs and epoxy cement pressure-injected into the holes. Such a method has great potential to destroy rock art.

The primary objective of this research report is to use a simple testing program to understand the nature of the stone both before and after treatment with a chemical solution composed of silicic ethyl ester or ethyl silicate dissolved in the low-viscosity carrier methyl ethyl ketone and also to show the potential of this treatment to increase the resistance to weathering of the Hell Creek Sandstone in order to preserve the signature of William Clark and related carvings at Pompeys Pillar National Historic Landmark.

DISCUSSION OF THE REQUIREMENTS TO MEET THE OBJECTIVE

Simple testing can be used to determine the basic properties of the stone. To examine the chemistry and mineralogy, chemical analysis, x-ray diffraction analysis, and optical microscopy can be used. To determine the porosity/permeability characteristics, capillary and immersion absorption can be used. The physical characteristics can also be measured on treated stone. In addition, compressive strength measurements are often used to evaluate the effectiveness of a stone-strengthener treatment. Other methods to evaluate a treatment include freeze-thaw cycling and for stones that contain significant amounts of expandable clay minerals, wet-dry cycling. The important point to remember is that most of the physical property measurements do not require expensive instruments and can be done in almost any laboratory.

One may be misled into thinking that a waterproofing agent coating the surface of the stone will be sufficient to stop deterioration caused by moisture. While this may help, it must be remembered that moisture is present throughout the stone. Fractures, joints, bedding planes, and the natural permeability of the stone all provide avenues for moisture to approach the exterior surface, including moisture from the ground moving upward and outward.

Many sites, particularly those on uncemented sandstones that are held together primarily by interlocking grains or sandstones that have undergone weathering with removal of some cement, need to be treated with a cementing agent to bond the grains of the stone together before any waterproofing agent is applied. Such a cementing agent gives the stone additional strength that will enable it to better withstand the stresses caused by natural weathering phenomena. Requirements that must be met by any strengthening agent being considered for preserving a rock art site include:

a. Strengthening agent should penetrate stone to a sufficient depth to treat all of the zone of weathering.

b. Agent should increase strength and freeze-thaw resistance.

c. Stone should be able to breathe after treatment so that the stone can rid itself of moisture.

d. Treatment should not cause any color change.

Many attempts, using a variety of treatments, have been made to preserve stone on historical structures. Many of these probably have done more harm than good because of their failure to meet one or more of the above requirements, even when an increase in strength seems to have been attained. Epoxy cement would be an example.

To achieve the desired depth of penetration, the stone must have a certain amount of accessible porosity or permeability. However, one must also consider the properties of the treating agent. Depth of penetration will be enhanced by having the bonding agent be of a low molecular weight and completely dissolved in a low-molecular weight, low-viscosity hydrocarbon carrier. Such a system would be expected to achieve greater penetration than an aqueous colloidal suspension such as an alkali silicate. In addition, the latter type of agent would be more prone to cause surface enrichment of the colloidal material, producing a lightening of the stone color due to the formation of a thin crust. Also, aqueous solutions often do not have neutral pH values, and in some cases, reaction with minerals in the stone and possible discoloration may occur. In contrast, organic systems, such as the one used in this study, possess neutral pH values.

Perhaps the most overlooked requirement in a strengthening agent is its effect on the permeability or vapor transmission of the stone. The agent must not completely seal the pore system of the stone, or problems will likely develop over time because of the excess moisture trapped behind the exterior of the stone. Such moisture can become rich in soluble salts that may crystallize during dry seasons just beneath the sealed pore zone. Then, a period of wet weather may cause rehydration of an anhydrous salt, and consequent volume expansion will occur. In colder climates, trapped moisture may lead to sanding and spalling. Remember that water begins to expand once the temperature drops below 4 °C, and additional expansion occurs if the moisture freezes. One needs only to recall the cracking, spalling, and potholes that appear in roads during the winter to realize how detrimental freezing can be. In summary, any treatment of rock art must allow the stone to breathe in order to minimize the destructive effects of excess moisture trapped in the rock.

Considering the stringent requirements for a safe and effective strengthening agent for use on rock art sites, the agent chosen for this study is based on ethyl silicate completely dissolved in the low-viscosity carrier/solvent methyl ethyl ketone. The low viscosity and low molecular weight of this solution enhance the depth of penetration for any stone, providing the stone has some degree of permeability. It is a colorless solution with a neutral pH value and would not be expected to cause any discoloration of the stone. In the United States, the sole supplier of this strengthening agent, known as Conservare OH, is the Process Solvent Company, located in Kansas City, KS.

The past experience of the author with this system in testing dimension stones from historically important buildings showed no discoloration of the stone, an increase in strength, and good depth of penetration; in addition, the system did not completely seal the pores. The mechanism involves a slow hydrolysis or reaction between the ethyl silicate and moisture in the stone to produce a silica-based cement. Strength measurements indicate the system is especially effective when applied to soft, porous sandstones and has led some researchers to believe a chemical bond is formed (-Si-O-Si-) between the hydrolysis-produced silica and the silica sand grain. Considering the above, the system seemed an ideal candidate to increase the durability of the Hell Creek Sandstone where both the Clark signature and petroglyphs had been carved into the sandstone.

EXPERIMENTAL PROCEDURE

The site was visited and photographed, but in situ capillary absorption measurements were not attempted because the visit occurred during a rainy period. It was felt such measurements would be meaningless. The late John Taylor supplied a block of the sandstone for future testing purposes.

The block of sandstone was taken to the laboratory where it was fabricated into 1.5-inch diameter cores and then trimmed to obtain relatively parallel ends. All cores were between 1.5 and 1.75 inch in height in order to conform to ASTM C-170 test specifications for determining the compressive strength of stone samples. Irregular pieces from the block were examined under a reflected light microscope and then ground into -200 mesh powder with an an alumina mortar and pestle for x-ray diffraction studies. Pieces collected for chemical analyses, using atomic absorption, were powdered using a tungsten carbide grinding mill.

Randomly selected sets of eight cores were used for various treatment cycles; one set was used as a control (untreated). The treatment cycles used on the cores are shown in Table 1. All treatments were by capillary absorption using a thin layer of chemical solution in a stainless steel pan and placing the cores in a vertical position for the selected amount of time. This method of treatment was chosen since it more closely resembles field treatment conditions than complete immersion. The wet weight of each core was recorded immediately after treatment. Cores were allowed to cure in air for at least 4 weeks before any additional treatment since the reaction is nearly complete after this period of time. After 4 weeks, the cured weight was recorded. For one set of cores, additional weighings were recorded over a 6-month period to insure the completeness of reaction.

Sets of cores were evaluated for their absorption characteristics using the weight of water absorbed after 24-hr immersion and also by capillary absorption on a water-saturated sponge. For the latter method, the weight gain was recorded as a function of time.

TABLE 1

Chemical Treatments of the Hell Creek Sandstone Cores Using Conservare OH and Conservare H Products

	Treatment Time (min.) Using Capillary Absorption		
Treatment	OH*	OH*	H**
Untreated	0	0	0
1 OH	12	0	0
2 OH	12	18	0
1 OH + 1 H	12	0	18

* Conservare OH. Stone Strengthener
**Conservare H. OH Strengthener: Water Repellent in a 2:1 Ratio

The compressive strength for six cores from each set was obtained using a Riehl Precision Hydraulic Universal Testing Instrument (model KA-60). The remaining cores from each set were evaluated for their freeze-thaw resistance using a cycle of 16 hr in a freezer at -20 °C followed by immersion in room-temperature water for 8 hr. Weight losses were recorded after every 25 cycles.

RESULTS AND DISCUSSION

Randomly selected samples were first examined for gross mineralogy by means of reflected light microscopy. As expected, the field of view was dominated by quartz grains and a fine-grained matrix that seems to be calcium carbonate cement. The latter appears to be weathered and somewhat soft on the exterior surface, suggesting dissolution or reaction with acidic pollutants. Additional phases observed in small to trace quantities included mica and feldspar.

Samples were also analyzed for their mineralogical content using x-ray diffraction analyses. The samples were first ground to -200 mesh (-75 microns) powder using a chromium-doped corundum (alumina) mortar and pestle. The resulting powder was dispersed on glass slides using acetone as a volatile, inert carrier. The diffraction patterns were obtained from a Phillips diffractometer equipped with a graphite curved crystal monochrometer. The resulting patterns were analyzed by comparison to a computerized ASTM powder diffraction file. The results agree well with the above-mentioned microscopic analysis, namely a dominance of quartz with a minor amount of calcite. Additionally, diffraction patterns showed the presence of trace amounts of feldspar (mostly albite type), mica-illite (mostly muscovite) as well as other clays and dolomite. A representative x-ray diffraction pattern is shown in Figure 1.

Table 2 lists the chemical analyses obtained from the samples of the Hell Creek Sandstone using a Jarrel Ash atomic absorption spectrophotometer. Samples A and B were obtained from the interior of different portions of the large block collected at Pompeys Pillar while sample C was obtained from the weathered surface on one end of the block. In addition, the weathered sample was also examined for soluble sulfate salts using a Technicon Auto Analyzer. As shown in Table 2, little variation in composition is observed and the results agree well with the mineralogical results.

Table 3 shows the initial capillary absorption characteristics for cores of the Hell Creek Sandstone (percent weight gain as a function of time) using the saturated sponge method mentioned in the procedure section. Table 4 shows the data for longer time periods and the final column of values shows, for comparison, the percent weight gain after the cores were submerged in water for 24 hr. Although some variation in the rate of water absorption is expected, the data indicate the rate differences are relatively small. The rate of absorption is fairly rapid with over 90 percent of the 24-hr total occurring within the first 10 minutes and over half of the absorption within two minutes. The relatively uniform rates of

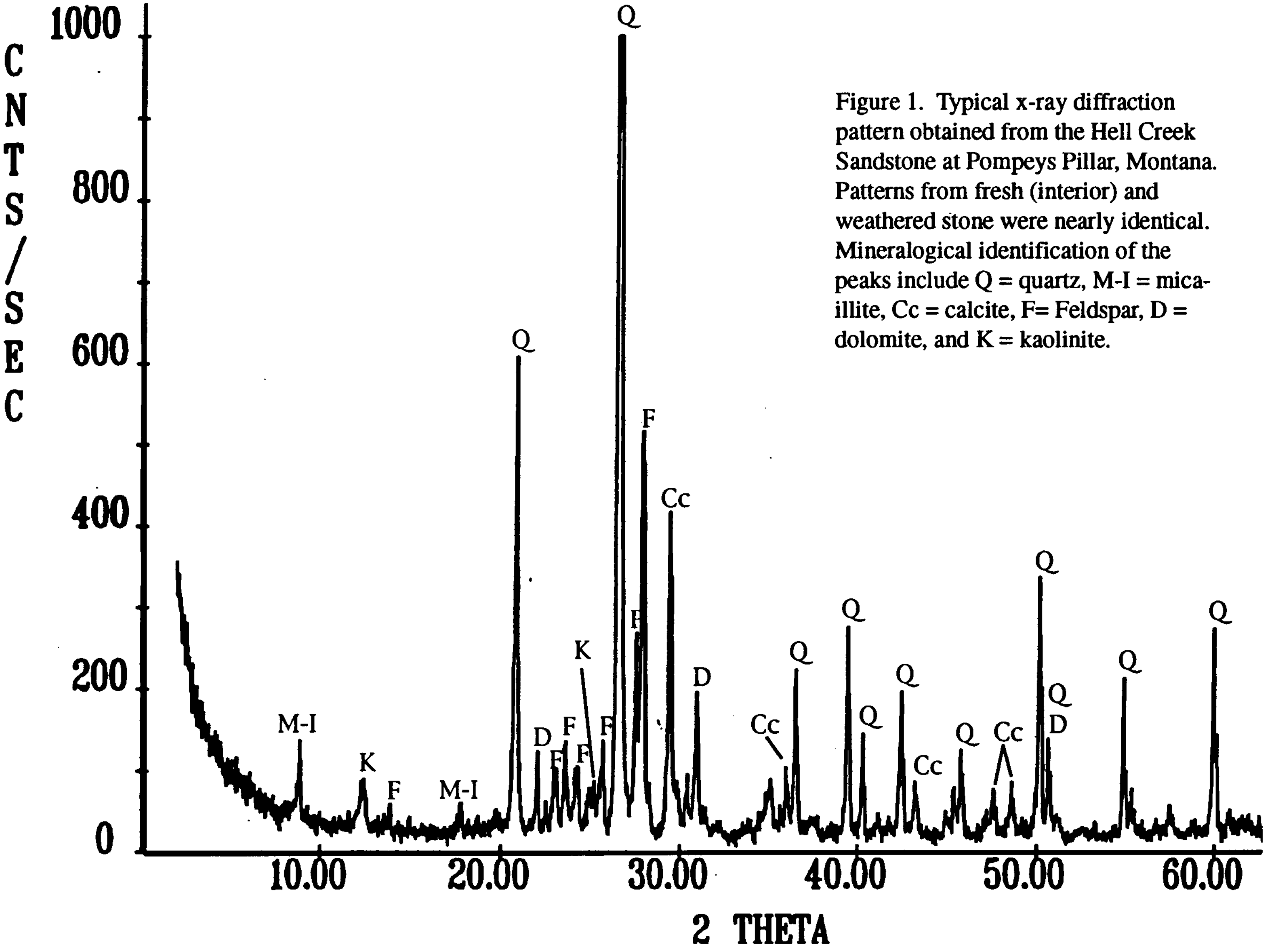

Figure 1. Typical x-ray diffraction pattern obtained from the Hell Creek Sandstone at Pompeys Pillar, Montana. Patterns from fresh (interior) and weathered stone were nearly identical. Mineralogical identification of the peaks include Q = quartz, M-I = mica-illite, Cc = calcite, F= Feldspar, D = dolomite, and K = kaolinite.

absorption and the appreciable total absorption of the Hell Creek Sandstone suggest a rather uniform stone with respect to its porosity and permeability and that a successful treatment of the stone by a consolidating agent with respect to amount and uniform distribution of the agent by spraying is likely.

TABLE 2

Summary of the Chemical Analyses of the Hell Creek Sandstone Using Atomic Absorption Spectrophotometry (Weight Percent Composition)

	Sample		
Oxide	A	B	C
SiO_2	66.09	67.91	67.22
Al_2O_3	9.24	8.76	8.36
Fe_2O_3	2.18	1.85	2.25
TiO_2	0.40	0.44	0.25
MnO	0.09	0.08	0.11
CaO	8.78	8.44	8.44
MgO	1.37	1.38	1.31
K_2O	1.71	1.71	1.87
Na_2O	1.49	1.54	1.57
SO_3	——	——	0.005
Loss on Ignition	8.24	7.97	8.67
Total	99.59	100.08	100.06

TABLE 3

Initial Capillary Absorption of the Hell Creek Sandstone

	Percent Weight Gain as a Function of Time (minutes)			
Sample	0.5	1.0	2.0	5.0
26	3.12	4.09	5.42	7.85
27	2.54	3.37	4.48	6.56
28	3.12	4.18	5.60	8.11
29	3.47	4.63	6.16	9.10
30	2.87	3.80	4.96	7.09
31	3.25	4.30	5.77	8.52
32	3.01	4.03	5.33	7.77
33	3.04	4.06	5.34	7.71
Average	3.05	4.06	5.38	7.84

TABLE 4

Capillary and Immersion Absorptions of the Hell Creek Sandstone

	Percent Weight Gain as a Function of Time			
	Capillary Absorption			Immersion
Sample	10 min.	2.5 hr.	24 hr.	24 hr.
26	9.05	9.11	9.41	9.66
27	8.72	9.13	9.49	9.91
28	9.47	9.61	9.94	10.28
29	9.68	9.89	10.30	10.76
30	8.96	9.09	9.36	9.57
31	9.38	9.50	9.95	10.44
32	9.20	9.31	9.69	10.13
33	9.09	9.19	9.54	9.89
Average	9.19	9.35	9.71	10.08

Table 5 shows the percent weight gain after treatments with the Conservare products as well as the final weight, the latter an indication of the percent of solids deposited after curing. Although the data are not shown in Table 5, the set of cores given a single treatment with the OH consolidating agent were weighed over a 6-month period. The weights were unchanged after 8 weeks, indicating the reaction was completed during that time. Each figure again represents the average of eight cores.

TABLE 5

Percent Weight Gain After Treatments

Treatment	First Treatment Wet	First Treatment 4 Wk.	8 Wk.	Second Treatment Wet	Percent Solids (Total)
1 OH	8.95	2.92	2.72	None	2.7
2 OH	8.96	2.94	—	10.00	5.2
1 OH + 1 H	9.10	3.00	—	9.93	5.0

As mentioned previously, the pore system should not be sealed by any treatment in order for the stone to rid itself of excess moisture. A simple method to demonstrate the retention of the permeability of the stone is to again measure the capillary absorption of the treated stone. The results of such measurements are shown in Table 6. Since the treatment does deposit a certain amount of solids within the pore system, the rate of moisture absorption and the total amount absorbed is lower than that for the untreated stone. A still lower uptake of moisture is observed for the cores treated with the Conservare H product due to the presence of the water repellent in this product. The results show that the stone does retain a certain amount of permeability, thus satisfying the above-mentioned requirement for any treatment.

TABLE 6

Capillary Absorption of Treated and Untreated Cores of the Hell Creek Sandstone as a Function of Time

	Treatment			
Percent Gain After Time of	Untreated	1 OH	2 OH	1 OH + 1 H
1 min.	4.06	2.38	0.31	0.03
5 min.	7.84	3.86	0.35	0.05
10 min.	9.19	4.82	0.36	0.06
30 min.	——	6.35	0.40	0.08
60 min.	——	6.94	0.44	0.10
2 hr.	9.35	7.31	0.45	0.12
24 hr.	9.71	7.71	0.69	0.22
48 hr.	——	8.13	1.73	0.26
24 hr, immersion	10.08	9.06	6.22	2.31

The above values show the expected decrease in the rate of water absorption and total water absorbed as one proceeds from untreated to one treatment to two treatments. The final column reflects the pronounced impact of the use of Conservare H which contains some water repellent. There is also a significant difference between one and two treatments using Conservare OH. In part, the difference is expected based on the amount of solids deposited as shown in Table 5 and that, in turn, is based on the length of the treatments. The first treatment (Table 1) was for 12 minutes whereas the second treatment lasted 18 minutes. Still, the rate of water absorption for cores given the two OH treatments is lower than one would expect.

Table 7 shows the compressive strength values obtained from the treated and untreated cores of the Hell Creek Sandstone. Each value represents the average of six samples. The large increases in strength as a result of the treatment(s) indicate that a successful bonding of the grains of the stone has occurred.

TABLE 7

Compressive Strengths of the Hell Creek Sandstone

Treatment	Compressive Strength lbs./in.^{2}	Percent Improvement
Untreated	1,330	——
1 OH	2,760	108
2 OH	4,700	253
1 OH + 1 H	4,020	202

With the substantial increases in the compressive strength values reported in Table 7, one would expect to also observe a pronounced increase in the freeze-thaw resistance of the stone. The results of the latter tests are given in Table 8. The cores were weighed after every 25 freeze-thaw cycles and the percent weight loss calculated.

TABLE 8

Freeze-Thaw Resistance of Treated and Untreated Cores of the Hell Creek Sandstone

	Percent Weight Loss Per Treatment			
Number of Cycles	Untreated	1 OH	2 OH	1 OH + 1 H
25	1.0	0.1	0.1	0.0
50	17.8	0.1	0.1	0.0
75	54.3	0.2	0.2	0.2
100	93.3	0.3	0.3	0.3
125	100.0	0.3	0.4	0.3
150		0.4	0.4	0.4
175		0.5	0.5	0.5
200		0.5	0.5	0.5
225		0.6	0.6	0.6
250		0.6	0.6	0.6
275		0.7	0.6	0.6
300		0.7	0.6	0.6

After 300 freeze-thaw cycles, the treated cores remain solid with a total weight loss of less than 1 percent. At this point, the testing was discontinued. Obviously, all treatments have greatly increased the freeze-thaw resistance of the stone, but 300 cycles are not sufficient to differentiate between the treatments. However, considering the correlation between compressive strength and freeze-thaw resistance of porous sandstones, one can assume that both sets of cores that were given a second treatment would be more durable than the set given a single treatment.

Shown below are two photographs of the cores after being subjected to 75 and 300 freeze-thaw cycles. Figure 2 shows what remains of the untreated cores after 75 cycles and the fresh-appearing treated cores. Figure 3 shows that all of the treated cores are sound after 300 cycles. The numbers have faded due to a gradual sanding effect (the gradual removal of the surface grains) and there appears to be a slight pitting on the cores to the left that were given only one treatment of Conservare OH. This again suggests that those cores given a second treatment will have greater resistance to freeze-thaw action.

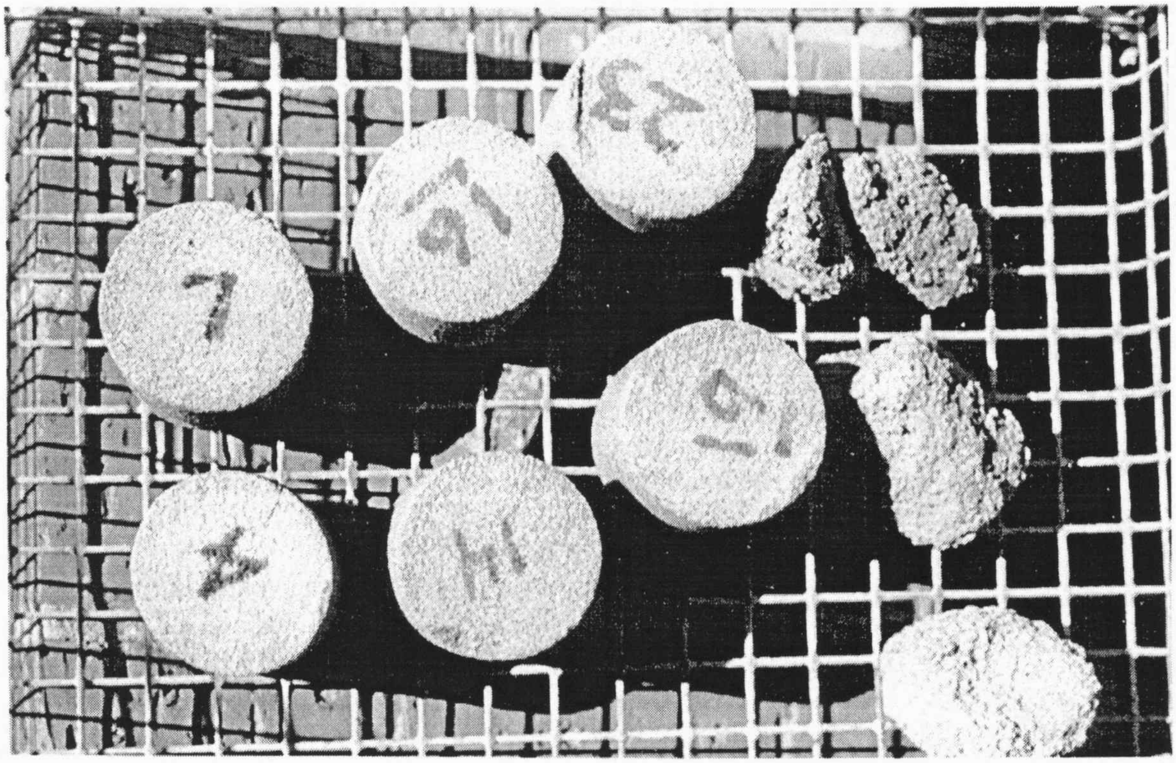

Figure 2. Cores of the Hell Creek Sandstone, Pompeys Pillar, Montana, after 75 freeze-thaw cycles. All of the treated cores appear fresh and unaffected while the two untreated cores on the right have undergone nearly complete destruction.

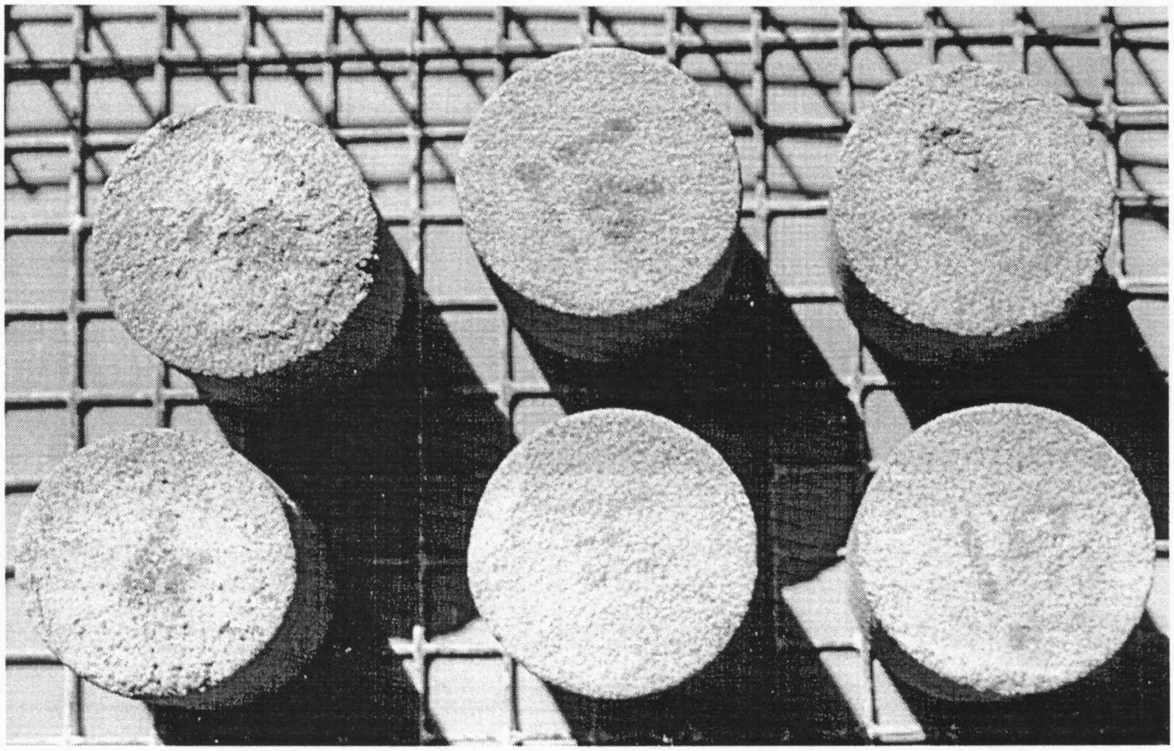

Figure 3. Treated cores of the Hell Creek Sandstone, Pompeys Pillar, Montana, after 300 freeze-thaw cycles. Although all of the cores remain intact and have lost less than one weight percent, the pair on the left that received only one treatment do show a slight amount of pitting on the top surface.

SUMMARY

When this study was undertaken, it was uncertain how successful the proposed treatment would be. Previous work had been confined to highly porous Dakota Sandstone that showed a 15 percent weight gain during absorption tests and had no chemical bonding. By contrast, the Hell Creek Sandstone has a lower porosity and a carbonate matrix bonding the quartz grains together.

The test results exceeded expectations. A single 12-minute treatment with the stone strengthener (Conservare OH) using capillary absorption doubled the compressive strength while a second treatment more than tripled the strength. Similar increases in the freeze-thaw resistance also occurred. The use of the Conservare H strengthener (two-thirds strengthener plus one-third water repellent) was also successful in increasing the strength with the added advantage of sharply lowering the rate of water absorption and thus, not allowing the stone to become saturated with water during the time frame examined, lowering the likelihood of freeze-thaw damage. At the same time, absorption values show that some permeability remains in the stone so the stone is still able to rid itself of moisture, usually in the form of water vapor that is more readily transmitted than liquid water.

RECOMMENDATIONS

Before any treatment of the Clark signature is undertaken, a test panel should be selected at the site and treated to insure that no discoloration occurs even though no color change occurs in laboratory testing. This will also give an idea of how long an area should be sprayed and the total rate of application (square feet per gallon) for a given treatment.

The stone should be given a treatment of Conservare OH to impart the desirable increases in strength and freeze-thaw resistance observed in the laboratory. If funds are available and concern remains regarding water entering the protective case, a second treatment using Conservare H would be in order.