PROSOCO
Technical Bulletin 1102-HCT

Protecting *and* strengthening carbonate stone *with* Conservare® HCT

- **Protection against acid rain and weathering**
- **Consolidation of deteriorated stone**

This technical bulletin describes Conservare® HCT (Hydroxylating Conversion Treatment), a treatment for protecting and strengthening limestone, marble and other carbonate substrates. The bulletin includes results of laboratory testing to evaluate the performance of carbonate stones treated with HCT. Treated stones were tested for resistance to acid rain, and strength increase. Additional tests measured freeze/thaw resistance, depth of HCT penetration, and water-vapor permeability. Though not a water repellent, HCT was also tested to determine what effect, if any, it has on carbonate stone water absorption. Test procedures are briefly described.

For more information about consolidation and restoration of historic masonry and stone, contact PROSOCO toll-free at (800) 255-4255 for consultation or to schedule on-site assistance.

The threat to limestone, marble, travertine and dolomite

Carbonate stones, e.g., marble, limestone, travertine and dolomite, are among the world's most beautiful and widely used building and sculptural stones. However, they are extremely vulnerable to weathering and pollution. In addition, they are often damaged by well-intentioned but ill-suited maintenance practices. Placed in contemporary urban environments, carbonate stone deteriorates at a progressive rate. During the past century, the phenomenon of acid rain has accelerated the decay of buildings and monuments constructed of these acid-sensitive materials.

The most widely used stone consolidation treatments rely on alkoxysilane technology which has limited effectiveness on carbonate building stone. This leaves many of the world's most valued monuments and buildings at risk. This technical bulletin describes the evaluation of Conservare® HCT, a new treatment developed specifically for the protection and consolidation of carbonate building stone.

Deterioration due to acid dissolution.

New treatment for carbonate stone

HCT is a novel, waterborne conservation treatment that protects and strengthens deteriorating carbonate building stones such as marble, limestone and travertine. The treatment reacts on contact with carbonate building stones. It forms an insoluble and well-adhered "hydroxylated conversion layer" on the surface of carbonate minerals that make up such stones. The chemistry, although well-known and confirmed by x-ray diffraction analysis, is new to the field of stone conservation.

Developed by MCC Materials Inc., HCT was granted US patent No. 6,296,905 *"Method for protecting and consolidating calcareous materials."* Patent applications are pending in 30 other countries.

For purpose of this technical bulletin, "calcareous materials" will refer to building stones consisting largely or entirely of calcium carbonate.

Requires no special precautions for handling or cleanup

- HCT is an odorless waterborne treatment that contains no organic solvents or polymers.
- HCT is safe to use and is harmless to the environment.

Trial application at State House, Boston.

Assessing deterioration of Reigate stone at a project in the UK.

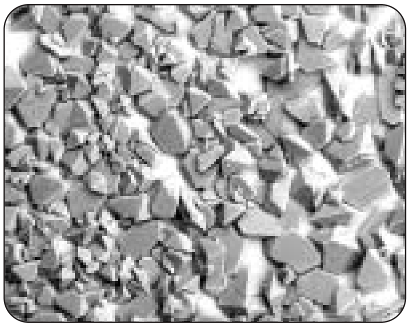
Protects against acid rain

When uniformly deposited, the HCT conversion layer protects carbonate building stone from damage caused by exposure to environmental acidity.

The methods of assessment reported here are the stirring of treated and untreated calcite aggregates in an acid rain simulant, and the acid drop test.

Strengthens deteriorated stones

As the HCT conversion layer forms on the surface of individual carbonate mineral grains, intergrowth of the conversion layer at points of grain contact cements the grains together. This restores strength and weathering resistance to the crumbling surface of deteriorated carbonate building stones, and strengthens unweathered stone. Assessment methods include Phillips microabrasion and cross-axial chisel splitting tests.



The conversion layer on Iceland spar (calcite) as seen by SEM at 500X magnification.

HCT can provide the following

(depending on stone type and conditions)

- Up to a 40-fold increase in resistance to simulated acid rain
- More than 100% increase in abrasion resistance on weathered surfaces
- More than 40% increase in resistance to destructive freeze/thaw cycles

HCT Testing Program

MCC Materials Inc., a research and development firm specializing in product evaluation and formulation for the architectural and conservation industry, conducted laboratory testing to evaluate the performance of Conservare® HCT. MCCM's laboratory collaborates with architects, engineers and specialty contractors to develop material-and-method recommendations for conservation treatments.

Testing program goals

- To evaluate HCT's ability to protect carbonate building stone from the damaging effects of acid rain
- To evaluate HCT's ability to increase strength of weathered carbonate building stones

Because there are few standard test methods for evaluating conservation treatments, these goals were challenging. In most cases, MCCM modified existing procedures such as ASTM D 5731, *Determination of the Point Load Strength Index of Rock* for strength testing and ASTM C 97 *Standard Test Methods for Absorption and Bulk Specific Gravity of Dimension Stone* for water absorption. In the absence of suitable standard test methods, e.g., resistance to acid rain, MCCM devised appropriate procedures for evaluating the performance of HCT. Copies of these procedures are available upon request. Contact PROSOCO, toll-free, at 800-255-4255.

Substrates tested

A variety of carbonate stones from the United States and the United Kingdom were used to test HCT. Danby (Vermont) marble, Stockbridge (Massachusetts) marble and Adams (Massachusetts) marble were selected because of their widespread use in historic buildings and monuments in the U.S. Testing also was conducted on Indiana limestone, the most commonly used U.S. limestone, and several Texas limestones (e.g., Calico, Western Ivory, Lueders, Cordova, Coral and Classic) with a range of water absorption characteristics.

Stones from the U.K. included oolitic limestones (Ketton stone and Monks Park) and a dolomitic limestone (Tadcaster stone). Reigate stone, a cretaceous sandstone with micritic calcite, was also used in the testing program. Reigate stone was included because of MCCM's participation in a multi-year project on the conservation treatment of Reigate stone employed on several significant historic sites in the United Kingdom.

Treatments tested

Conservare® Hydroxylating Conversion Treatment (HCT) is a novel, waterborne treatment which protects and strengthens deteriorating carbonate building stones such as marble, limestone, dolomite and travertine.

Conservare® OH100 is a ready-to-use consolidation treatment that stabilizes masonry by replacing the natural binding materials, lost due to weathering, with silicon dioxide.

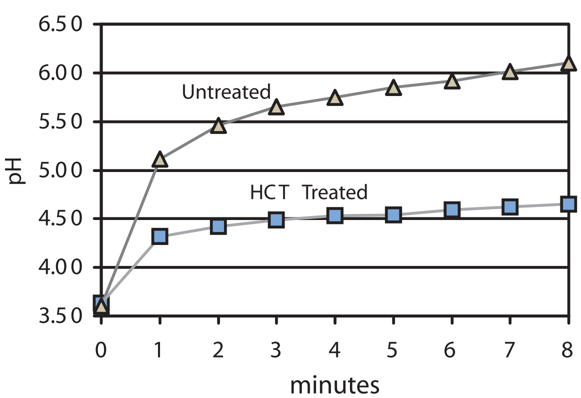
Testing carbonate building stone resistance to acid rain

Because there is no standard method for evaluating the resistance of building materials to acid rain, MCCM devised methods that provide reliable, reproducible results.

Aggregate test

This test is based on the sensitivity of carbonate building stones to acid rain. The procedure evaluates the change in pH of a solution of dilute acid after exposure to carbonate aggregate. This change occurs when the carbonate aggregate reacts with the acid solution, raising its pH.

Aggregate is prepared by crushing carbonate building stones and sieving the resulting particles through U.S. Standard sieves to collect aggregate that passes a No. 50 screen and is retained on a No. 100 screen. The retained aggregate is separated into two fractions. One aggregate fraction is treated with HCT; the other remains untreated.



Aggregate test – The graph demonstrates that HCT inhibits the attack of an acid rain simulant on Danby marble.

The acid solution is prepared by adding carbonated distilled water to dilute sulfuric acid. With a pH of 3.5 - 3.6, the solution simulates acid rain.

Treated and untreated aggregate fractions are separately stirred in beakers containing the acid rain simulant. Because HCT creates a conversion layer that protects treated aggregate from acids, the pH of acid rain simulant stirred with treated aggregate is relatively stable. Conversely, acid rain simulant stirred with untreated aggregate reacts quickly to raise the pH.

The pH is recorded over an 8-minute period. The reaction is plotted on a graph with pH on the y axis and time in minutes on the x axis.

This test measures the ability of HCT to reduce damage caused by environmental acidity to specific carbonate building stones.

Acid drop test

The Acid drop test uses a hydrochloric (HCl) acid solution which is many times stronger and more aggressive than acid rain. The test is qualitative and is used for demonstration purposes.

The test also requires thin wafers of intact building stone, 1.5 mm x 40 mm x 50 mm (approximately 1⁄16 in x 1 ½ in x 2 in), to maximize surface area to weight.*

Identical wafers harvested from the same stone are divided into two sets. One set is protected with HCT. The second set remains untreated.

Acid drop test – This test demonstrates resistance of HCT-treated marble (left) to a hydrochloric acid solution, compared to an untreated control sample after 132 minutes of exposure.

Using a buret, 0.1 M HCl acid is dripped onto the surface of treated and untreated wafers at a slow and controlled rate. The test is timed and continues until the acid dissolves a hole through the wafer.

When conducted on marble wafers, this test produced a hole through untreated marble after 132 minutes. An identical marble wafer protected with HCT survived for 184 minutes. This represents a significant increase in acid resistance.

*Because expensive equipment is required to cut wafers to precise specifications, this test is not routinely conducted.

Testing HCT strengthening of carbonate stone

In addition to protecting carbonate stones from the damaging effects of acid rain, treatment with HCT provides strengthening. ASTM E 2167 *Standard Guide for Selection and use of Stone Consolidants* suggests several test methods for estimating the improvement in mechanical properties following consolidation treatment. These include ASTM C 70 *Compressive Strength of Dimension Stone,* C 99 *Modulus of Rupture of Building Stone,* C 880 *Flexural Strength of Building Stone,* and C 1353 *Taber Abrasor for Abrasion Resistance of Dimension Stone Submitted to Foot Traffic.* Each of these destructive test methods requires a significant number of representative stone samples to produce reliable results. Since the number of samples available for testing is often limited, these tests are not routinely used to evaluate consolidant treatments.

Phillips microabrasion test

Evaluating strength improvements by HCT requires a test that can be performed on relatively small samples of historic building fabric. The test should provide quantitative results of the effects of consolidants in strengthening weathered carbonate building stones.

For this program, MCCM used a microabrasion test first reported for evaluation of conservation treatments by Morgan W. Phillips in 1982. Based on ASTM 418 *Abrasion Resistance of Concrete by Sandblasting,* this test is conducted using an SS White Airbrasive Unit and fine alumina powder.

The optimum sample size is 5 cm x 5 cm x 2 cm (2" x 2" x ¾"). A minimum of three samples for each proposed treatment is required.

The microabrasion stylus is positioned perpendicular to the sample with the orifice held a fixed distance from the sample surface. Fine blasting media (alumina powder) in a narrow stream of compressed air is propelled at the sample surface for 10 seconds at a pressure of 40 psi. The blast media erodes a small crater in the sample surface. The amount of stone eroded from the surface can be determined by weight loss.

Phillips microabrasion test – This test compares the weight loss from microabrasive blasting of HCT-treated limestone (left) to that of an untreated control sample.

A total of five 10-second blast exposures, creating five small craters, was conducted on each stone sample. Samples were weighed before and after the blasting and comparative soundness (abrasion resistance) was determined by comparing the average weight loss for treated and untreated samples.

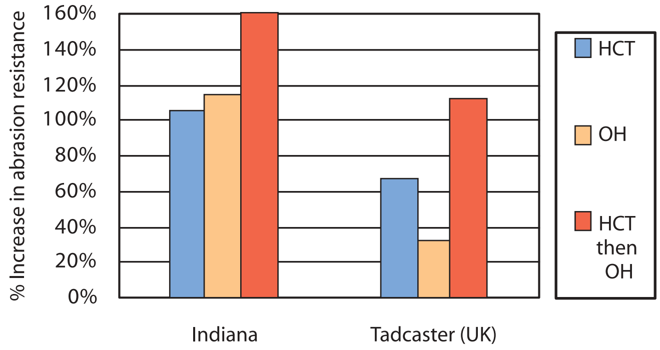
Cross-axial chisel split

This method is a modification of the diametral test of ASTM D 5731, *Determination of the Point Load Strength Index of Rock,* using a single, chisel-shaped platen to apply a concentrated load.

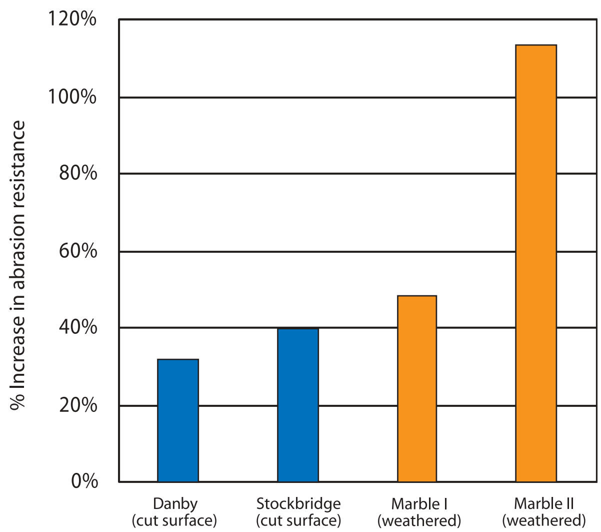
Measurement of the applied load is with a digital force gauge. The technique is particularly suited to the testing of small cores, 14 mm in diameter (approximately ½ inch).

For the standard core diameter, each breaking value is recorded as the load at failure. Data sets for treated and untreated specimens are compared and the result reported as percent strength increase. The chart presents data for Indiana limestone.

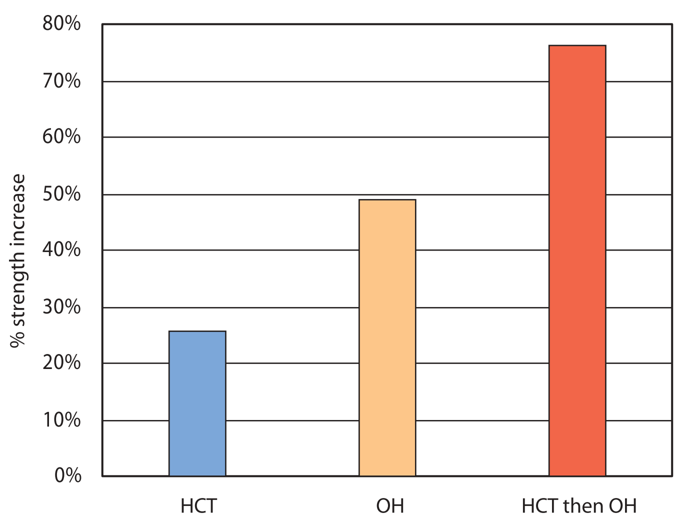
Cross-Axial chisel split test – A digital force gauge measures the applied load in testing small cores.



Phillips microabrasion test – This chart compares the % increase in abrasion resistance on limestone treated with two different consolidants, HCT and Conservare® OH100, separately and sequentially.



Phillips microabrasion test – This chart shows that weathered marble surfaces usually have a greater % increase in abrasion resistance due to HCT treatments than freshly cut surfaces.



Cross-Axial chisel split test – For the standard core diameter, each breaking value is recorded as the load at failure. Data sets for treated and untreated specimens are compared, and the result reported as % strength increase This chart presents data for Indiana limestone.

Additional tests

Additional tests conducted to determine other improvements imparted by HCT, and to rule out possible adverse effects, include the following:

Depth of penetration

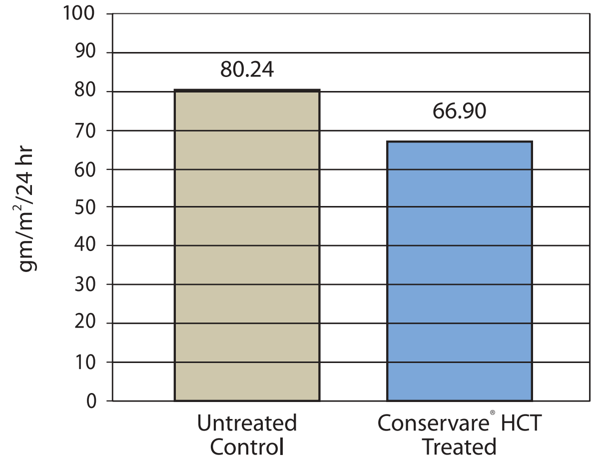
The depth of penetration achieved by consolidation treatments varies as a function of stone type and condition. Successful treatments are typically those that fully penetrate the zone of deterioration. For this testing program, depth of penetration of HCT was evaluated visually immediately following application of the treatment by capillary uptake.

Depth of penetration – Cubes of Ketton (left) and Indiana limestone, split immediately after capillary uptake, show varying degrees of HCT penetration..

The photo of Ketton limestone (typically 24% porosity) and Indiana limestone (typically 18% porosity) illustrates this point. Ketton limestone is wetted by HCT to nearly its full height after 1 minute of capillary uptake. Indiana limestone absorbs the treatment less rapidly.

Water vapor transmission

Conservation treatments should not seal the surface or block the pore structure of treated stone. Treatments that substantially reduce water vapor transmission are associated with accelerated deterioration.

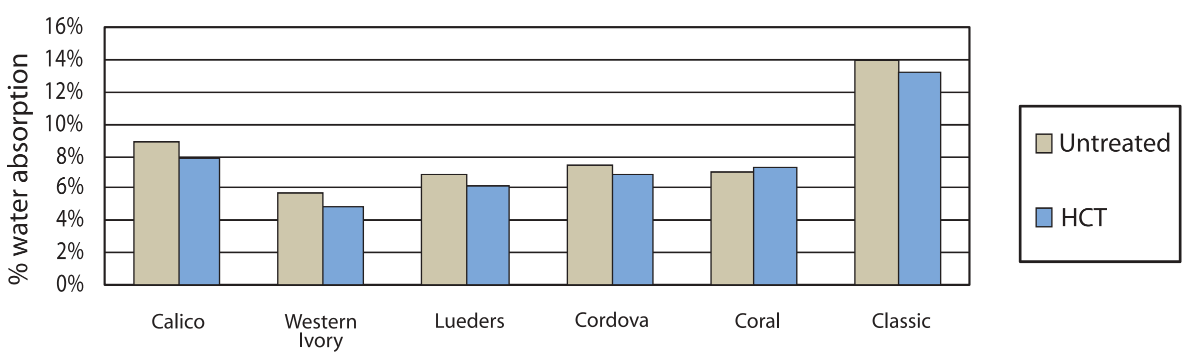


Water vapor transmission – The results of this standard test show that Indiana limestone retains its ability to "breathe" after treatment with HCT.

To measure of the ability of the HCT-treated surfaces to "breathe," water vapor transmission rates were tested for treated and untreated specimens of Indiana limestone using ASTM E 96-00e1 *Standard Test Methods for Water Vapor Transmission of Materials.* In the tests conducted, the water vapor transmission rate for untreated limestone was 80.24 grams per square meter per 24 hours and for treated limestone the rate was 66.90 grams per square meter per 24 hours. The percent retention in water vapor transmission is calculated by comparing the rate for treated with that of untreated specimens. The percent retention following HCT treatment was 84%, confirming that the limestone's ability to "breathe" was not significantly compromised by HCT.

Water absorption

Though not a water repellent, HCT was tested to find what effect, if any, the treatment has on water absorption characteristics of carbonate stone. Effects on treated and untreated specimens were measured using ASTM C 97-02 *Standard Test Methods for Absorption and Bulk Specific Gravity of Dimension Stone.* Comparing the results for treated and untreated specimens demonstrated that water absorption characteristics are not significantly altered by HCT. The chart shows results for several Texas limestones.



Water absorption – This chart compares the water absorption characteristics of untreated Texas limestone with HCT-treated Texas limestone.

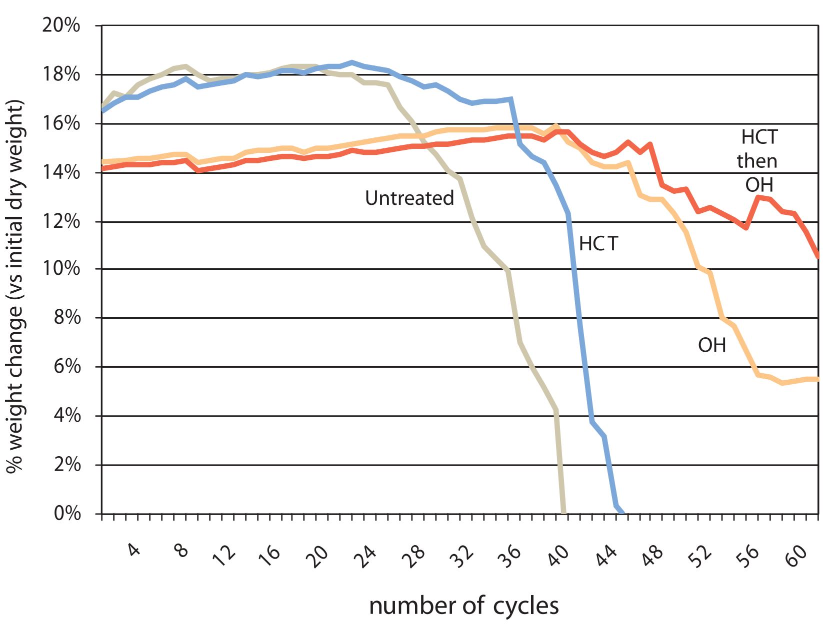
Freeze/Thaw resistance

Ice formation in the pore network of stone is an important mechanism of deterioration in some environments. Stone specimens subjected to freeze/thaw cycling in the laboratory often exhibit failures remarkably similar to that of stone on buildings. For these reasons, freeze/thaw testing has long been considered a useful measure of durability for both treated and untreated stone.

There are several standard test methods for evaluating freeze/thaw resistance of other building materials (e.g., ASTM C 666-97 *Standard Test Method for Resistance of Concrete to Rapid Freezing and Thawing)*. Currently, however, there is no ASTM standard method for freeze/thaw resistance of treated natural building stone. In the absence of a widely accepted test method, MCCM devised a freeze thaw test which could produce reliable, reproducible results.

Testing is conducted on 2.5 cm (1 inch) cubes. Treated and untreated test specimens are conditioned at room temperature and relative humidity to constant weight. The specimens are then submerged in water for 48 hours, re-weighed, and frozen. Thawing takes place in water at room temperature. Samples are re-weighed at the end of each freeze/thaw cycle.

Freeze/Thaw resistance – Treated cubes (background) and untreated cubes (foreground), after 29 cycles of freezing and thawing.



Freeze/Thaw resistance – In this graph, the initial upward curves indicate the gradual uptake of additional water beyond the amount absorbed in 48 hours. As testing progresses, samples begin to lose weight due to material losses from frost shattering, and the curves descend, sometimes dramatically.

Technical Bulletin 1102-HCT

Conclusion

In the tests conducted by MCCM, HCT increased the resistance of limestone and marble test specimens to a simulated acid rain solution. Treatment with HCT also increased strength, abrasion resistance, and durability of the test specimens. Depth of penetration and water absorption testing indicates that HCT reacted with the test specimens without adversely affecting their pore structures.

Several of the tests described in this technical bulletin are now used to evaluate samples submitted to PROSOCO's stone testing laboratory. MCCM continues to conduct laboratory tests to evaluate HCT's performance on limestone and marble as well as other building materials.

Since 1998, these tests and dozens of successful field tests and field treatments have demonstrated the ability of Conservare® HCT to protect and strengthen limestone and marble from the damaging effects of acid rain.

Further reading

The United States Geological Service publication *Acid Rain and Our Nation's Capital* defines acid rain and explains its deleterious effects on marble and limestone buildings. Available on-line (http://pubs.usgs.gov/gip/acidrain/), this booklet focuses on the impact of acid rain on historic buildings in Washington, DC.

HCT field trial on Tadcaster limestone at Howden Minster, UK.

PROSOCO
SINCE 1939

3741 Greenway Circle • Lawrence, KS 66046
1-800-255-4255 • www.prosoco.com