LITHIUM SILICATE AS A CONSOLIDATION TREATMENT ON LIMESTONE

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Abstract

Lithium silicate has been used for years to harden and densify concrete; however, little testing has been done on the use of lithium silicate to strengthen limestone. Testing on concrete has long shown that not only is there a chemical reaction between the lithium silicate and free calcium hydroxide, but the deposition of crystalline silicates in surface pores creates a tenacious mechanical bond that improves the hardness and abrasion resistance of treated concrete.

In theory, that same chemistry should be useful in the treatment of deteriorating carbonate stones such as limestone. This presentation will focus on the evaluation of lithium silicate applied to Bath limestone independently and in combination with more traditional ethyl silicate consolidation treatments. The laboratory tests revealed the limestone treated with lithium silicate exhibited a denser, harder surface that was more resistant to loss from abrasion. Phillips Microabrasion (mechanical strength), depth of penetration, color change, and artificial weathering tests were performed to determine the effectiveness of the treatments. The presentation will share the test methods used, data gathered, and ideas for future research.

1. Introduction

AMT Labs was contracted to offer recommendations for the interior limestone of a prominent coastal building in the Republic of Ireland. The goal of the testing was to identify a sensitive and controlled means of preparing the limestone for conservation treatment, as well as to recommend an appropriate conservation treatment. The client requested PROSOCO, Inc. consolidation treatments for the evaluation.

Small pieces of the interior stone were submitted for the pre-treatment evaluation. However, rather than removing pieces of historic stone from the building, samples of new Bath limestone were submitted for evaluation of the consolidation treatments. A Petrographic Examination was conducted on the limestone to compare the mineralogy of the new limestone to the stone on the building. The examination indicated both new and historic stone were Bath oölitic limestone composed of 100% calcite ($CaCO_3$).

Water solubility and acid solubility were also conducted on the new Bath limestone to help determine its suitability for chemical conservation. Water solubility of the stone was negligible, and acid solubility was 81%.

Microabrasion and depth of penetration tests were conducted to determine the effectiveness of the consolidation treatments. Results of the completed test programs are reported in the attached pages.

The conservation treatments evaluated were:

- Conservare® OH100 Consolidation Treatment
- Conservare® HCT

- T-2333 Lithium Silicate Treatment
- Conservare® HCT followed by Conservare® OH100 Consolidation Treatment
- T-2333 Lithium Silicate Treatment followed by Conservare® OH100 Consolidation Treatment

The following product descriptions are taken from the Product Data Sheets:

Conservare® OH100 is a ready-to-use ethyl silicate consolidation treatment that stabilizes masonry by replacing the natural binding materials lost due to weathering with silicone dioxide. When properly applied, Conservare® OH100 penetrates deeply, does not form a dense surface crust, and retains the substrate's natural vapor permeability. In addition to the general conservation of severely deteriorated masonries, Conservare® OH100 is an effective pretreatment for friable substrates that need to be strengthened before cleaning, patching or coating. Conservare® OH100 may be used on most types of natural stone, concrete, stucco, brick, terra cotta, etc.

Conservare® HCT is a two-step waterborne treatment that protects and strengthens deteriorating carbonate building stones such as marble, limestone and travertine. HCT reduces the vulnerability of treated stones to the ravages of air pollution, acid rain and normal weathering. HCT forms a well-adhered, hydroxylated conversion layer on carbonate mineral grains. HCT Finishing Rinse completes the chemical reaction that forms this conversion layer. The treatment dramatically increases the resistance of marbles and limestones to acid attack, and strengthens deteriorating carbonate stones.

T-2333 Lithium Silicate Treatment is a penetrating lithium silicate treatment. When applied to concrete, the treatment produces insoluble calcium silicate hydrate within the concrete pores. Treated surfaces resist damage from water and surface abrasion.

2. Treatment Application

Limestone samples for the treatment evaluation were cut with a wet masonry saw into manageable test specimens. The test specimens were oven dried until weight loss studies revealed that all integral moisture had been removed. Samples were then allowed to cool at 73°F and 50% relative humidity for a period of 24 hours until sufficient integral moisture had been regained to facilitate reaction with the conservation treatments.

The following application methods were chosen based on previous studies including weight gain and wet and dry deposition, and to simulate field application.

Application of Conservare® HCT:

In an effort to simulate field application, the method of application for Conservare® HCT consisted of immersing the samples in the conservation treatment for periods of 30 seconds. Samples were then removed from the treatment and allowed to air dry for 30 minutes before re-immersion. This process was continued until the samples had received three immersion applications, simulating a typical field treatment. Samples were allowed to air dry for 60 minutes. The samples were then immersed in Conservare® HCT Finishing Rinse for 30 seconds to remove any excess HCT. Following 24 hours of drying, two cycles of Conservare® OH100 were applied to some of the HCT-treated samples in the manner described below.

Application of Conservare® OH100:

In an effort to simulate field application, the method of application for Conservare® OH100 consisted immersing the samples in the conservation treatment for periods of 10 seconds. Samples were then removed from the treatment and allowed to air dry for 30 minutes before re-immersion. This process was continued until the samples had received three immersion applications, simulating a one-cycle field application. Samples were allowed to air dry for 60 minutes before an additional cycle was applied. Two cycles of OH100 were carried out on the Bath limestone.

Application of T-2333 Lithium Silicate Treatment:

In an effort to simulate field application, the method of application for the T-2333 treatment consisted of immersing the samples in the treatment for a period of 20 seconds. Samples were then removed from the treatment and allowed to air dry. Following 24 hours of drying, two cycles of Conservare® OH100 were applied to some of the T-2333 treated samples.

All treated samples were allowed to cure at 73°F and 50% relative humidity for a period of 21 days.

3. Testing

3.1 Phillips Microabrasion Test

The Phillips Microabrasion test was chosen as a quantitative way of evaluating the effects of the consolidants in strengthening the limestone. The test is meant to evaluate the interstitial bond between exposed surface granules of stone.

The Phillips Microabrasion Test is conducted using an SS White Airbrasive Unit (Model-K) and fine alumina powder. 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 ten seconds at a pressure of 40 psi. The blast media erodes a small crater in the sample surface. The amount of material eroded from the sample surface is determined by weight.

A total of twelve 10-second exposures was conducted on treated and untreated samples. Samples were weighed before and after blasting and comparative soundness (abrasion resistance) was determined by comparing the average weight loss for treated and untreated samples.

In the Phillips Microabrasion Test, T-2333 Lithium Silicate followed by OH100 performed the best, substantially increasing the resistance to abrasion by 80%.

Treatments	Average Grams Lost Per Blast	% Increase in Abrasion Resistance
Untreated Control	0.01965	---
OH100 Consolidation Treatment	0.00824	58%
HCT	0.02144	Negligible
T-2333 Lithium Silicate Treatment	0.01351	31%
HCT followed by OH100	0.00731	63%
T-2333 Lithium Silicate Treatment followed by OH100	0.00395	80%

Table I. Test Results: Phillips Microabrasion Test

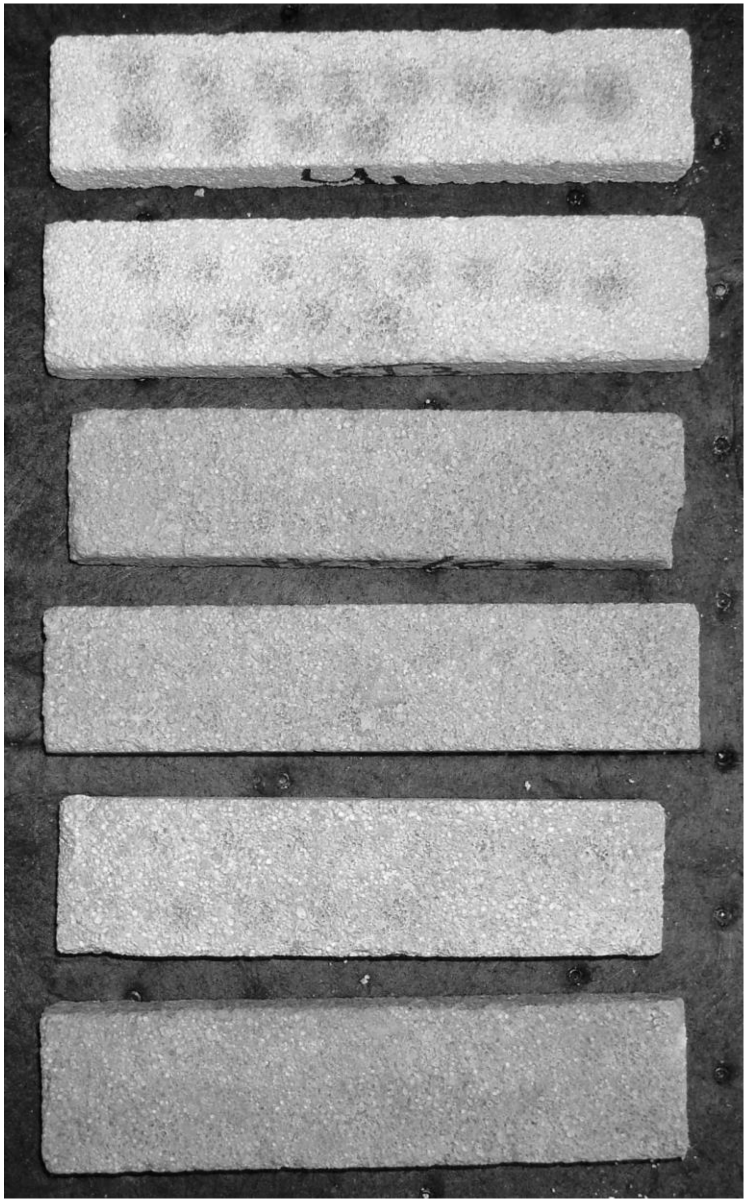

Figure 1. Limestone after Phillips Microabrasion Testing. From top to bottom: Untreated Control, HCT, HCT/OH100, OH100, T-2333, and T-2333/OH100.

3.2 Depth of Penetration

Treated samples are mechanically split and the interior faces wetted with an indicator dye specific for the treatment. A quantitative visual evaluation is then carried out to determine the depth of penetration achieved by the conservation systems on each of the treated samples. Sufficient depth of penetration ensures against the formation of hardened, superficial, surface crusts that might contribute to further deterioration.

NOTE: At this time there is no indicator dye that is effective on Conservare® HCT.

Test Results: Depth of Penetration

T-2333 reached a depth of 3-4 mm on the limestone. The comparatively shallow depth of penetration of the lithium silicate treatment is not unexpected as the chemical reaction is faster than traditional ethyl silicate treatments. As the lithium silicate treatment reacts within the pores it resists further penetration. It should be noted that the evaluation was conducted on new stone; we would anticipate a deeper depth of penetration on weathered stone exhibiting surface erosion.

The depth of penetration of OH100, when used alone and with HCT or T-2333, reached the entire depth and thickness of the treated samples.

Depth of penetration was not evaluated for HCT because the indicator dye is not effective.

Conservation Treatment	**Depth of Penetration**
OH100 Consolidation Treatment	21 mm - 50 mm (total sample saturation)
HCT	N/A
T-2333 Lithium Silicate Treatment	3 mm - 4 mm
HCT followed by OH100	22 mm - 48 mm (total sample saturation)
T-2333 followed by OH100	21 mm - 46 mm (total sample saturation)

Table II.

3.3 Color Change

Treated and untreated masonry samples were submitted to careful visual evaluation to determine color change created by application of the conservation treatment(s).

Visual evaluation for color change of treated and untreated samples revealed that T-2333 Lithium Silicate caused a very slight darkening of the limestone compared to the untreated stone. OH100 Consolidation Treatment caused a slight darkening of the limestone. This effect may dissipate over time.

3.4 Artificial Weathering

Limestone treated with T-2333 Lithium Silicate and untreated limestone were subjected to artificial weathering tests using a QUV Weatherometer for 3 months. The test specimens were exposed to alternate cycles of ultraviolet light using fluorescent lamps UVA-340 and 60°C temperatures and cooler, moist, dark conditions at 20-30°C. Temperature, humidity, and UV cycling are intended to replicate external weathering conditions, but are accelerated. The samples were exposed to artificial weathering for three months and then visually inspected, comparing the treated samples to the untreated samples.

Test Results: Artificial Weathering

No visual changes were evident on the samples treated with T-2333 Lithium Silicate after three months of artificial weathering.

Conservation Treatment	Color Change?
OH100 Consolidation Treatment	Slight darkening
HCT	No
T-2333 Lithium Silicate	Very slight darkening
HCT followed by OH100	Slight darkening
T-2333 followed by OH100	Slight darkening

Table III.

4. Conclusions

Based on the laboratory testing, the treatment that was most effective in improving the mechanical strength of the Bath limestone was T-2333 Lithium Silicate Treatment followed by Conservare® OH100. This treatment combination increased the limestone's mechanical strength by 80%, compared to 58% with the ethyl silicate alone.