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AN ASSESSMENT OF THREE CONSOLIDANTS FOR USE ON MUSEUM ARTEFACTS IN COMPARISON TO ORGANO SILANES

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Abstract

Organosilanes are consolidants that have been praised for their effectiveness on stone both in the internal and external environment. Their success on limestone, however, has been debated and there are also significant drawbacks with the health and safety requirements for working with silanes. Inorganic consolidants can address compatibility issues with limestone, and are often safer to use and dispose of. In the past, inorganic consolidants have been considered less effective to their organic counterparts. With the advent of new technology and the development of nano-limes, there has been a resurgence in interest in inorganic consolidants.

This paper presents the findings from investigation into three inorganic consolidants being considered for use at The British Museum; Calcite In-situ Precipitation System (CIPS); CaLoSil; and ammonium oxalate treatment. A range of measures of the effectiveness of these consolidants, in comparison with a previously used silane; SILRES® BS OH 100 (Wacker OH), has been taken on 40, artificially pre-eathered, limestone replicates.

Keywords carbonate stones, consolidation treatment, effectiveness, inorganic consolidants

1. Introduction

The British Museum has a large collection of stone artefacts some of which have reached a state of deterioration such that application of a stone consolidant would be the only way to prevent further disaggregation.

Over the last few decades, emphasis in conservation has been on the importance of the reversibility of treatments (Rodgers 2004). However, consolidation treatments for stone are rarely truly reversible. Therefore, stone conservation has started to focus more on compatibility of a treatment with the stone substrate (Sasse and Snethlage 1996). Along with compatibility, a consolidant usually undergoes testing to check how it measures against a range of performance requirements including durability, depth of penetration, effect on stone porosity, moisture transfer and effect on appearance (Cnudde et al. 2004).

Organosilanes consolidants have been popular in the past, and are still used by many stone conservators. Used in the British Museum in the 1980’s, there are a number of treated artefacts in its collections that demonstrate the success of consolidants. However, the condition of some stone artefacts, mainly limestone objects, has worsened since being treated with organosilanes. This phenomenon has been seen elsewhere and effectiveness of silanes on carbonate stones is a debated topic (Wheeler 2008). One suggested reason is a lack of affinity with the stone substrate (Favaro et al. 2008). Other difficulties associated with silanes include safety of application and environmental sustainability.

Inorganic consolidants address compatibility issues with limestone artefacts, but have been considered less effective than silanes, predominantly due to poor penetration depth and deposition within pore spaces (Favaro et al. 2008). Recent scientific advancements, in particular the development of nano-limes, have led to a resurgence in interest in inorganic consolidants.

The British Museum has instigated an investigation into new inorganic consolidants to be used on their stone collections, in particular on limestone. Presented here are results from an assessment of three inorganic consolidants for use on the limestone collections: Calcite In-situ Precipitation System (CIPS); CaLoSil; and ammonium oxalate treatment, in comparison to a previously used and well-known silane: SILRES® BS OH 100 (Wacker OH). 40 50 mm cubes of limestone were cut to give 10 replicates per consolidant investigated. All 40 replicates were artificially weathered using a furnace. The four consolidants were then applied as directed by the manufacturers and after discussion with BM stone conservators. All replicates were tested before and after weathering and results analysed to determine effectiveness, and, which (if any) consolidant had the potential to be used in the future in the museum. This paper focuses on results from the non-destructive testing of the replicates.

2. Materials and Methods

2.1 Stone Materials

The stone types for the replicates used in these experiments were Elm Park and Hartham Park. These two types of stone are both Bath stones from quarries near Corsham in Wiltshire. Pale buff in colour, with occasional blue flecks or veins, they are oolitic limestones of middle Jurassic age. The 40 replicates were freshly cut into 50 mm cubes, after which artificial weathering was undertaken. The replicates were heated to 250˚C and left for half and hour before being removed and held under cold running water for 5 minutes in a method similar to those used in McCabe et al. 2007. This was repeated for 5 cycles.

2.2 Consolidants

2.2.1 CIPS

The ‘Calcite In-situ Precipitation System’ or CIPS is one new inorganic consolidant under consideration by The British Museum. The CIPS method (developed by Lithic Technology Pty Ltd) is based upon precipitation of calcite within granular materials from loose sand to disaggregated stone in order to create high strength bonding between the grains (Price 2010). The calcite is precipitated from a solution that is mixed and then permeated through the material to be consolidated. Calcite crystals form around the edges of grains, creating bridges between them. Along with compatibility, particular advantages of CIPS are its ease of use and low toxicity.

The CIPS is formed from two solutions mixed in equal proportions just prior to application. The exact composition of the solutions, and their production methods, are proprietary to Lithic Technology Pty Ltd.

Multiple applications of the CIPS can be undertaken to further strengthen the stone; 6 are recommended for sufficient consolidation without inducing a highly noticeable change in the surface appearance (Price 2010). Of the ten replicates eight were treated by spraying with six applications every twenty-four hours; and two were kept as controls.

2.2.2 Ammonium Oxalate

Calcium oxalate films are naturally occurring patinas on calcareous stones (Cariati et al. 2000). Oxalate films provide a thin, compact, non-porous shell highly resistant to acid attack and atmospheric pollution. Due to this, there has been a large amount of research conducted into methods of producing this layer artificially (Doherty et al. 2006, Doherty et al. 2007) including a method involving the application of ammonium oxalate. The ammonium oxalate reacts with the stone substrate to form calcium oxalate.

Whilst the majority of recent research has focused upon the use of oxalate films as protective layers, there have been suggestions they could also have consolidation properties (Matteini 2007). To test this, ammonium oxalate monohydrate was mixed with water at 5% w/v and then applied to eight of the ammonium oxalate replicates using a cellulose poultice as recommended by Cezar (1998). A layer of Japanese tissue paper was placed between the poultice and the stone surface as protection. After application, the poultice was covered with cling film and left for twenty-four hours before removal. After 3 weeks the process was repeated for a second time.

2.2.3 CaLoSil

CaLoSil is a new, commercially available (from IBZ Frieberg), nano-lime stone consolidant developed specifically for consolidating calcareous historic material (Campbell and Hamilton 2011). Nano-particles of $Ca(OH)_2$ are suspended in different alcohols. After application, the alcohol evaporates to leave solid calcium hydroxide behind. This reacts with atmospheric carbon dioxide to form calcium carbonate. Due to the small size of the particles, CaLoSil can penetrate deeply into the stone. CaLoSil E25 (calcium hydroxide particles dispersed in ethanol at 25g/L) was applied by spraying to 8 of the 10 replicates. After 3 weeks a second application was undertaken.

2.2.4 Wacker OH 100

Organosilanes have been commonly used since the 1960's (Wheeler 2008), and have been a popular choice for consolidation, especially in Europe (Price 2006). The British Museum began using them in the 1980's but to a lesser extent than institutions on the continent, and has not used them for several years. Silicone-based consolidants are solely used to improve internal cohesion (Bradley 1986).

SILRES® BS OH 100, also known as Wacker OH 100. Produced by Wacker Chemie AG, SILRES® BS OH is a solventless ethylsilicate that penetrates into the stone forming a glass-like silica gel binder ($SiO_2 \cdot aq.$) (Wacker Chemie AG MTDS). It was applied by pipette until saturation and left to cure. After three weeks a second application was undertaken.

2.3 Testing methods

To investigate, and compare the four different consolidants, several analytical methods were used; some non - (or minimally) destructive, others destructive. Table 1 summarises the methods used and the property of the replicate that they assess.

Method	Data Provided	Destructive?
Equotip	Surface hardness of stone; Leeb rebound method	Minimally destructive
Pundit	Ultrasonic Pulse Velocity to calculate E Modulus	Non-destructive
Scanning Electron Microscopy	Depth of penetration, deposition within pores. Elemental mapping of consolidant distribution	Destructive
Karsten Tubes	Water penetration depth into stone	Minimally destructive
Drilling Resistance Measurement System	Internal strength and, depth of penetration of consolidants	Destructive
Mercury Intrusion Porosimetry	Pore size and distribution	Destructive
Thin-Section Petrography	Distribution of consolidant, depth of penetration and how pore spaces affected	Destructive
Spectrophotometry	Colour change	Non-destructive
Other Physical Properties	Dimesions, weight, density etc	Non -destructive

Table 1: Analytical methods used

3. Results and Discussion

3.1 Weight

All replicates were weighed before artificial weathering, after artificial weathering/before treatment, and after treatment. This was used to calculate the change in density at both stages. The density was further used in the calculation of the E modulus.

Replicate Group	Mean ΔM (g) Weathering	Mean Δ ρ (kg/m^3) Weathering	Mean ΔM (g) Treatment	Mean Δ ρ (kg/m^3) Treatment
CIPS	-0.22	-1.714732	3.14	24.54
CaLoSil	-0.57	-4.656352	0.32	2.63
Wacker	-0.42875	-3.351183	1.56	12.22
AmOx	-0.52125	-4.344182	0.61	5.07

Table 2: Change in weight and density after artificial weathering and after consolidation treatment

As can be seen from Table 2, the CIPS treatment increased the weight (and hence the density) the most out of the four treatments, at nearly double the next highest weight increase of the Wacker OH treatment. This in turn was more than double the next highest increase, which was the group treated with ammonium oxalate. The lowest weight and density increase was seen with CaLoSil.

3.2 Surface Hardness

Surface hardness was determined using a Proceq Equotip (Equotip 3); a dynamic hardness test using a rebound technique, *Leeb hardness* using change in it determines velocity (Viles 2010; Goudie et al. 2010). 10 measurements were taken per 50 mm area on the topmost surface of each replicate. Measurements were taken before artificial weathering, after artificial weathering/before treatment, and after treatment.

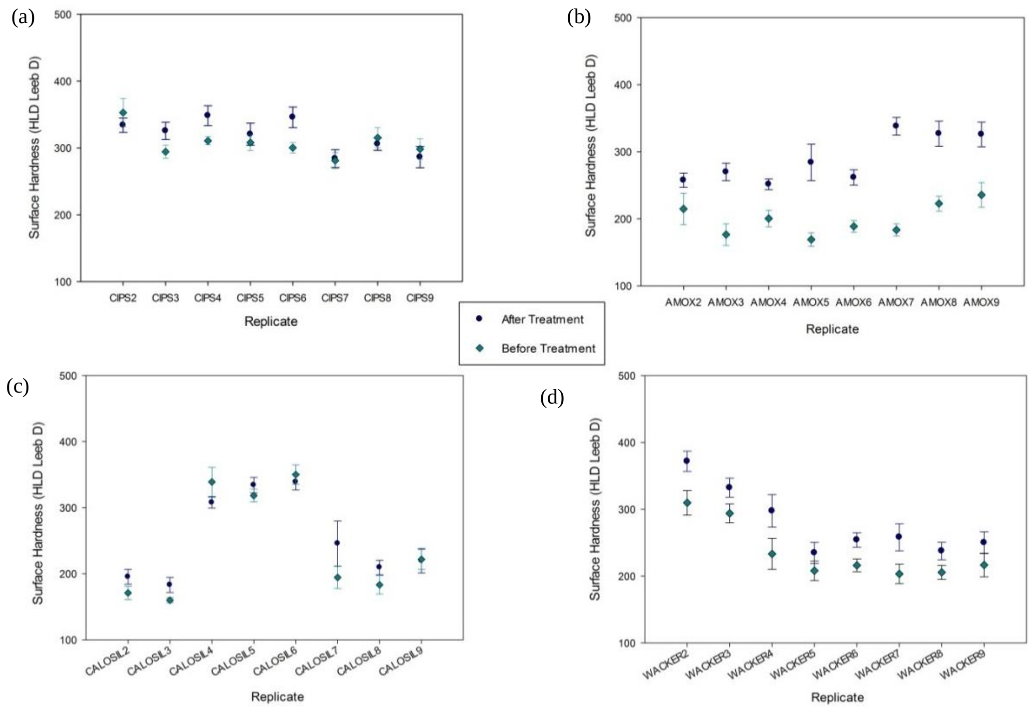

Figure 1: Graphs (a) – (d) to show change in surface hardness as measured by Equotip. (a) CIPS replicates; (b) AmOx replicates; (c) CaLoSil replicates; (d) Wacker replicates.

Figure 1 shows before treatment (u) and after (l) treatment Equotip values for each treatment, divided into consolidant groups. (a) Shows that some CIPS replicates demonstrated a noticeable increase in surface hardness, however, some did not, and overall there is not a statistically significant difference (paired t-test P = 0.237; 95% confidence interval). Similarly, some CaLoSil replicates visually show an increase (c) but overall there is no statistically significant difference (paired t-test P = 0.519; 95% confidence interval). All ammonium oxalate (b) and Wacker (d) replicates showed a clear increase in surface hardness. The increase in surface hardness demonstrated by the ammonium oxalate replicates were quite dramatic with many experiencing an increase of more than 90 HLD Leeb D.

These results clearly show that the ammonium oxalate treatment was the most effective at increasing surface hardness. However, this does not necessarily mean it is the most effective treatment – it will be important to see using other methods such as DRMS and SEM how far into the stone this consolidant has penetrated. How the consolidant has formed is also important – a solid surface layer or crust might be more detrimental than positive if there is a sudden interface with the stone substrate, or if it does not allow vapour to penetrate and allow the stone to ‘breathe’.

3.3 Internal Strength

The Pundit Lab is an ultrasonic pulse velocity (UPV) test instrument, which when used with 250kHz Sheer Wave Transducers can be used to calculate the elastic modulus of a material. This in-turn can be used as an indicator of internal strength. The control, untreated replicates were measured, along with the treated replicates post-treatment. Each replicate was measured five times and an average calculated.

Unfortunately, there was no observable difference in the elastic modulus between the control and the treated replicates. This could be due to only one surface being treated, the consolidant may not have penetrated far enough into the replicate to affect the overall UPV. Future experiments looking at the change in UPV and E Modulus when all sides of a replicate are treated could look into this factor.

3.4 Colour Change

To assess the effect of consolidation treatments on the appearance of the stone, change in the colour parameters of the limestones (CIE L*a*b*) was measured using a spectrophotometer (Konica Minolta CM 700d/600d) under illuminant D65 at a 10 degree of observation and using colour data software *SpectraMagic xs.* 10 measurements were taken on the 50 mm area on the top treated surface to give a mean colour difference. Overall change in colour (ΔE00) was determined, along with a more detailed look at change in colour such as hue and saturation.

Before analysis, replicates were observed qualitatively. Colour change between CIPS replicates and untreated blocks was difficult to detect, however, the surface had changed in appearance with treated replicates acquiring a sheen. Colour difference between the ammonium oxalate samples and the untreated samples was also difficult to detect. The Wacker replicates were slightly darker in appearance, but only on very close inspection. The biggest change was seen with the CaLoSil replicates. A white haze or ‘bloom’ was visible on nearly all treated replicates.

Replicate Group	Group Traits	ΔL*	Δa*	Δb*	ΔC*	ΔE00
CIPS	SCI	-3.15	0.31	2.65	2.67	2.72
CIPS	SCE	-3.30	0.32	2.76	2.76	2.85
AmOx	SCI	-3.74	1.09	-0.24	0.05	3.58
AmOx	SCE	-3.71	1.08	-0.23	0.05	3.57
CaLoSil	SCI	5.99	-1.47	-12.75	-12.59	9.50
CaLoSil	SCE	5.94	-1.47	-12.77	-12.60	9.50
Wacker	SCI	-5.22	1.03	3.61	3.81	4.47
Wacker	SCE	-5.20	1.29	3.65	3.85	4.46

Table 3: Summary of mean colour change per replicate group

As can be seen from Table 3, all replicates demonstrated an overall colour change (ΔE00) greater than 1; the value generally accepted as the level at which colour change is noticeable to the naked eye. The replicates that demonstrated the lowest overall colour change were ones treated with CIPS; ΔE00 of 2.72 SCI and 2.85 SCE. The ammonium oxalate replicates had the next lowest colour change with ΔE00 of 3.58 SCI and 3.57 SCE. Wacker replicates had an even greater overall colour change and most dramatically, CaLoSil replicates had a ΔE00 of 9.50 SCI/SCE. This CaLoSil result was to be expected with the significant white haze that appeared on the surface. SCI and SCE values can help to show a difference in the gloss on the surface. For all groups except the CIPS these two values are almost identical. The CIPS replicates showing a difference is likely due to the sheen now seen on the surface.

If purely considering the colour change, the choice for the preferred consolidant would be between the CIPS and the ammonium oxalate; since these two altered the colour the least. Whilst overall colour change is lower with the CIPS treatment, the change in the gloss of the surface is definitely noticeable and so the ammonium oxalate might be the better choice.

3.5 Capillary Uptake

Water penetration capacity (WPC) was measured before and after treatment using Karsten Tubes. A glass tube containing water is bonded to the surface of the replicate with putty. The drop in water level is measured over time. This was repeated 10 times for each replicate and the mean ml/minute/area of water in contact with the stone calculated.

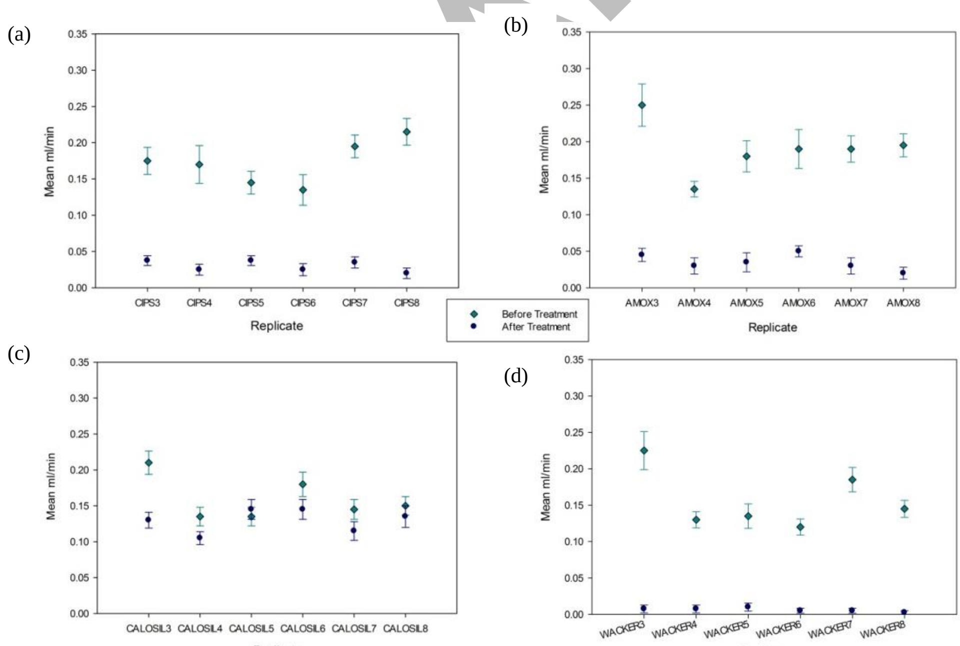

Figure 2(a-d): Graphs to show change in mean ml/min water penetration of replicates before (u) and after (l) treatment**.** (a) CIPS replicates; (b) AmOx replicates; (c) CaLoSil replicates; (d) Wacker replicates.

As can be seen in Figure 2, all replicates treated with CIPS, Ammonium Oxalate, and Wacker OH demonstrated a dramatic decrease in the average millilitres of water penetrating per minute. The Wacker replicates had the most severe decrease with hardly any water penetrating after treatment. The CIPS and Ammonium Oxalate replicates demonstrated a fairly similar decrease; after treatment water penetration was low, but some was still going in. Some individual CaLoSil replicates demonstrate a decrease in water penetration, although very slight and overall the differences are not statistically significant (paired t-test $P = 0.055$; 95% confidence interval).

3.6 Destructive analysis

The next stage in this investigation will be to undertake the destructive testing of the replicates. This will include examining thin sections on a petrographic microscope, and cross sections using scanning electron microscopy (SEM) to look at depth of penetration of the consolidants, interface between treated and non-treated areas, and distribution of the consolidants within the stone. Drilling Resistance Measurement System (DRMS) will be used to look at depth of penetration and internal strength of the stone. Mercury Intrusion Porosimetry (MIP) will be used to look at the pore spaces within the stones.

4. Conclusions

Overall colour change for all replicates was at a level detectable by the human eye. The lowest values were for those treated with CIPS, although this treatment did change the gloss of the surface in a noticeable way. Next lowest were the replicates treated with ammonium oxalate, which were below the values for the replicates treated with Wacker OH. The replicates treated with CaLoSil developed a very obvious white bloom on the surface; shown by the extremely high $\Delta E00$ values. The colour change was so severe that further experiments to try and reduce/prevent this white bloom would be needed before any recommendation for trialling on museum artefacts could be made.

Karsten Tube tests to analyse water penetration showed replicates treated with CIPS, ammonium oxalate, and Wacker OH, all had a significant decrease in water penetration with virtually no water penetrating into the Wacker OH replicates. Some individual CaLoSil replicates had a decrease in water penetration, however overall there was not a statistically significant difference. These treatments were all designed as consolidants, not as hydrophobic coatings. Whilst some decrease in water penetration could be expected, blocking all water penetration could be detrimental to an object.

No one parameter can be used on its own to make a decision about whether any of these three inorganic consolidants hold potential for use on limestone artefacts in the British Museum, or are a more preferable option than previously used Wacker OH. This decision will be made once results from the destructive tests are in. However, information from these non-destructive tests can be used to focus on certain areas during the destructive testing. The results here seem to show the ammonium oxalate treatment succeeding more than the other two inorganic consolidants and indeed outperforming the Wacker OH. However, it will be really important to analyse if this treatment is consolidating the stone substrate, or just has just formed a very hard superficial layer.

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