# Back to Nature: Geologically Informed Consolidants for Stone Museum Artefacts

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# Abstract

The *Back to Nature* project was developed as a collaborative doctoral award between the British Museum and the School of Geography and the Environment, University of Oxford. The British Museum has a large collection of limestone artefacts, some of which have deteriorated to an extent that a consolidation treatment, to improve internal cohesion, has been deemed necessary to ensure the value of the artefacts is maintained. Previous consolidation practices within the museum had centred on the use of organic consolidants. In the past, inorganic consolidants had been considered ineffective chiefly due to poor penetration depth and inconsistent deposition within the stone. Recent scientific developments within conservation, particularly the development of nano-limes, coupled with a trend towards treatments offering physical and chemical compatibility, led to the British Museum reconsidering the use of inorganic consolidants.

Three inorganic consolidants: ammonium oxalate treatment, Calcite In-situ Precipitation System (CIPS), and CaLoSil have been investigated by the *Back to Nature* project to assess their potential for use on the British Museum's deteriorated limestone artefacts. The investigation involved a developmental sequence of four experimental phases to assess the effectiveness of each consolidant upon freshly cut, artificially pre-weathered, and naturally weathered stone samples. In all experiments an organic silane Wacker SILRES BS OH 100 was used as a comparison. A variety of analytical methods were used including: Equotip, GrindoSonic, Scanning Electron Microscopy, Karsten Tubes, Drilling Resistance Measurement System, spectrophotometry, X-ray Diffraction and Ion Chromatography.

Experiments show that the CIPS treatment could hold promise for use as a consolidant. Ammonium oxalate only appears to provide consolidation at the surface level, and CaLoSil would need modifying and more investigation before using in the museum environment. The differences noted between experiments on artificially weathered and naturally weathered stone indicate that a two-step process, involving testing on

both types of samples, would give the best indication of consolidant effectiveness. High variability between samples shows a large number are needed to give an accurate interpretation of change due to consolidation.

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# Chapter 1

*Introduction*

A large proportion of the material culture that surrounds us – from tools to art, buildings, and monuments, is carved from stone. Whilst often perceived as a durable material, stone can decay in a multitude of ways due to biological, chemical or physical factors (Fitzner & Heinrichs 2002). This decay is somewhat expected in the external environment where stone objects are exposed to wind, rain and polluted atmospheres, however it can also be a common occurrence in the museum environment. Conservation is the name given to both the discipline, and the methods used by specialists within it, to manage change to material culture so that the meaning and values attached can be sustained (Drury & McPherson 2008). Maintaining these often intangible aspects, is frequently achieved by preserving the items' physical, more tangible, nature. Within stone conservation this can be accomplished by both preventive and interventive or active methods, some of which are outlined in figure 1 (Doehne & Price 2010).

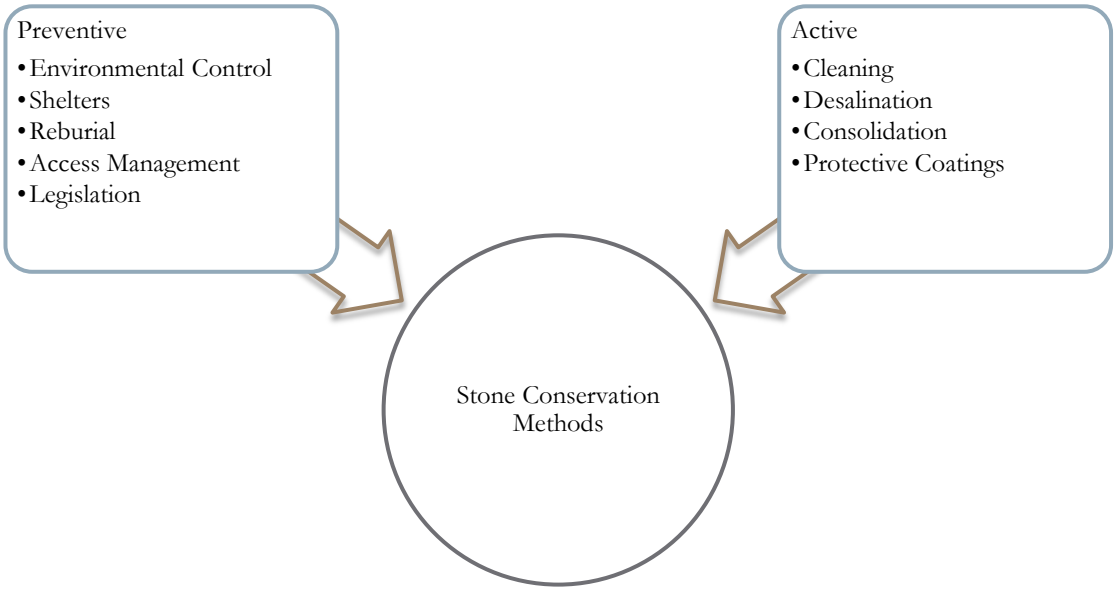



**Figure 1 Preventive and active consolidation methods (author's own)**

Over the last few decades in conservation there has been a focus on reversibility – the idea that any treatment undertaken by a conservator can be undone in the future (Rodgers 2004). Preventive methods, cleaning, desalinating, and protective coatings, may all be seen as less interventive treatments and so may be preferable options for stone conservators. However, once a stone reaches a stage where it has been seriously weakened by decay, the use of consolidants is required. A consolidant is a substance that is applied to decaying stone with the intention of restoring its chemical and physical properties and is usually used when deterioration has reached the stage where the use of consolidants to improve internal cohesion is the only method that will ensure the values attached to an artefact are maintained. (Salazar-Hernandez et al. 2010). An effective consolidant needs to meet a range of performance requirements that assess durability, depth of penetration, effect on stone porosity, effect on moisture transfer, compatibility with stone and effect on appearance (Cnudde et al. 2004). The most appropriate product to use will vary depending upon the stone involved, its location, deterioration problems, and history, as demonstrated in figure 2, (Pinto & Rodrigues 2008) .

a)  b) 

**Figure 2: Appropriate consolidation method varies - an outdoor monument with many visitors such as the Parthenon (a) will require different care to a stone sculpture in an environmentally controlled museum store with restricted access (b). Images author's own.**

Some consolidants are in theory reversible however, in practice, even soluble treatments are difficult to remove so they should be considered permanent additions (Doehne & Price 2010). With the acceptance of the difficulties posed by a solely reversible approach has come a shift in focus from reversibility to compatibility (Sasse & Snethlage 1996). Compatibility within conservation comes from both a practical and ideological standpoint. Ideologically, compatibility is associated with the premise that any materials introduced to an artefact should be as close as possible to the original material components. New materials could affect artefacts' integrity or alter the associated values. This ideology has its roots in the practicality that compatible materials will have much the same properties – for example moisture and thermal expansion, and will form chemical bonds as well as physical bonds (Dei & Salvadori 2006). With reference to stone consolidants, one of the main aims of compatibility is to limit future damage due to differing reactions to changing environmental conditions, particularly at the interface between treated and non-treated substrate (Jimenez-Lopez et al. 2008). This project fits within this current trend for identifying conservation treatments that will be compatible with the stone material of an object.

The British Museum has a large collection of limestone artefacts, a proportion of which are deteriorating to an extent that consolidation is required (Bradley & Hanna 1986). Large-scale consolidation of limestone artefacts in the museum has, in the past, involved the use of silanes. Whilst these have been very effective in some cases, in others they have not – possibly even exacerbating the situation (Thickett, Lee & Bradley 2000). A suggested reason for this variable success rate is a lack of affinity between silanes and carbonate stone (Dei & Salvadori 2006). Inorganic consolidants involving calcite, are based upon natural rock formation and cementation processes, and are a possible alternative to organic treatments. Inorganic treatments should address both ideological and practical issues of compatibility. In the past these have not been considered as effective, predominantly due to poor penetration depth and inconsistent deposition within the stone (Favaro et al. 2008). Recent scientific advances however, have led to a resurgence in development and research into inorganic consolidants (Daniele, Taglieri & Quaresima 2008, Matterini 2008, De Muynck, De Belie & Verstraete 2010a, Giorgi et al. 2010, Sassoni, Naidu & Scherer 2011).

## The Back to Nature Project

*Back to Nature* is an AHRC funded Collaborative Doctoral Award (CDA) between Oxford University, School of Geography and the Environment (SOGE), and the British Museum. The *Back to Nature* project was initiated by stone conservators at the British Museum with the aim of evaluating the potential of novel, inorganic, stone consolidation techniques based upon naturally occurring rock components in comparison to more conventional methods based upon organic chemicals. Three new inorganic treatments were selected for investigation: CaLoSil, a newly commercially available consolidant produced using calcium hydroxide nano-particles (D'Armada & Hirst 2012); ammonium oxalate, a technique developed in Italy based upon the process behind naturally occurring calcium oxalate patinas (Matteini 2007); and Calcite In-situ Precipitation System (CIPS), a treatment developed in Australia for the oil and gas industry (Price 2010). As a comparison, Wacker OH 100 (a commonly used alkoxysilane which has been utilized by the British Museum in the past) was included in all investigations (Matteini 2007, Kucharski et al. 2000, Bradley 1985). Evaluation involved extensive experimental testing of both the constituents of the various new treatments and of their effect upon stone replicate blocks and objects of more complex geometry in the laboratory. Analytical techniques used included; Scanning Electron Microscopy, Optical Microscopy and Thin-Section Petrography, Spectrophotometry, Ion Chromatography, X-Ray Diffraction, Mercury Intrusion Porosimetry, Drilling Resistance Measurement System, Karsten Tube Penetration Test, Equotip Portable Hardness Testing, and the Pundit Lab Ultrasonic Pulse Velocity System.

After providing a more detailed background to conservation and the role of consolidants, and an overview of the aims and project methodology, this thesis presents the results from the four stages of experimental investigation into future consolidation possibilities for British Museum limestone artefacts: developing an experimental methodology; investigating the potential of the Calcite In-situ Precipitation System; comparison of the three new inorganic consolidants with a previously used silane on standard samples; and comparison of the consolidants on naturally weathered samples. Following this is a discussion that draws results from the four stages together to produce guidelines for conservators and conservation scientists about the future use and investigation of all consolidants investigated.

# Chapter 2

*Literature Review*

The role of stone material culture within our modern society is multivariate and complex. This chapter provides an overview of key connotations that stone objects can hold, and the reasons for their preservation. Deterioration factors associated with stone are presented and a breakdown given of how they might be mitigated using different conservation practices. A particular focus is placed upon stone consolidation and the assessment of consolidation materials. Reference is made to the Ancient Egyptian limestone artefacts in the British Museum, their deterioration problems, and treatment history.

## The Importance of Stone Material Culture

Material culture refers to the artefacts created by a particular group of people or society. Material culture theory is used to describe the area of study that investigates the beliefs of a society using the objects they produced as the primary data (Prown 1982). Whilst increasingly studied as a discipline in its own right, material culture theory has become an important part of other studies including anthropology, art history, archaeology and geography (Tilley 2006).

Objects change over time, both physically and in their cultural meaning. The value or meaning of an object is a complex subject and cannot be reduced to a simple figure that can be easily calculated. The values attached to an object can be multivariate and depend upon who is assessing the object, their background and the current situation that both the object and the person are in. Some values are obvious and others are much more intangible. They can include economic, historic, symbolic and aesthetic. An example can be shown by the well-known artefact, the Rosetta Stone (EA24)(Figure 3). This is perhaps best known now for its contribution to Egyptology, with its role in the deciphering of hieroglyphics in the 19th century. But what about its place in the history of archaeology, specifically during the Napoleonic wars? Or what it actually tells us about Egypt during the time of Ptolemy V? To some people in Egypt it is a symbol of the

heritage artefacts that were removed from their country. If we were to consider the values people placed upon the stela during the time of Ptolemy V, they would be completely different. Along with these cultural values are the economic ones - how much is it worth if one were able to purchase it? Can you even attach a monetary figure to such an object?



**Figure 3: EA24 "The Rosetta Stone" pink and grey grandiorite stela with priestly decree concerning Ptolemy V in Hieroglyphic, Demotic and Greek. Image courtesy of The Trustees of The British Museum.**

The premise of material culture studies is that objects are a link to the people that made or used them, and from this to the values they held. By looking at a man-made object and assessing why it was made, how it was formed and the contexts in which it was used, a greater understanding of the people who were involved with the object can be gathered; this can concern individuals or a larger society (Odegaard 1995). Not only do objects provide a link to societies, but, as production of material objects can be considered a

fundamental component of culture, then to fully understand any culture of society, an assessment of their material productions needs to be examined (Tilley 2006). Stone artefacts commonly held by museums include statues, monuments and building components. As described below, the common perception of stone as a durable material has led to highly valued items being created from stone meaning that much could be gleaned from the study of these items.

Conservation manages change to an item of cultural heritage to preserve its significance and to protect values attached to it. According to Caple (2000) conservation has three aims; *Revelation* "cleaning the object to reveal its original form at some point in its past"; *Investigation* "to discover information about the object"; and *Preservation"* to maintain the object in its present form*"*. Depending upon the object involved, the conservation action undertaken may involve any one of the three areas mentioned above, or a mixture of two or all three. Each of these three areas are inextricably linked with material culture theory as demonstrated in Figure 4. Preservation of the intangible aspects of an object such as meanings is often achieved by preventing physical changes (Eastop 2006). When first encountering an object which is to be conserved, there are usually many decisions to be made; for example which method to employ, and which characteristic to conserve (sometimes at the expense of others) "The recurrent problem of conservation is to decide on the 'best' method of intervention. This decision usually leads to questions about what aspects should be conserved and for whose benefit." (Eastop 2006: 526). Conservation, in a similar way to material culture studies, is interdisciplinary, drawing from disciplines including archaeology, anthropology, chemistry and geography among many others. It protects the subjective, intangible, and intensely theoretical by preserving the material, using predominantly scientific and physical methods.

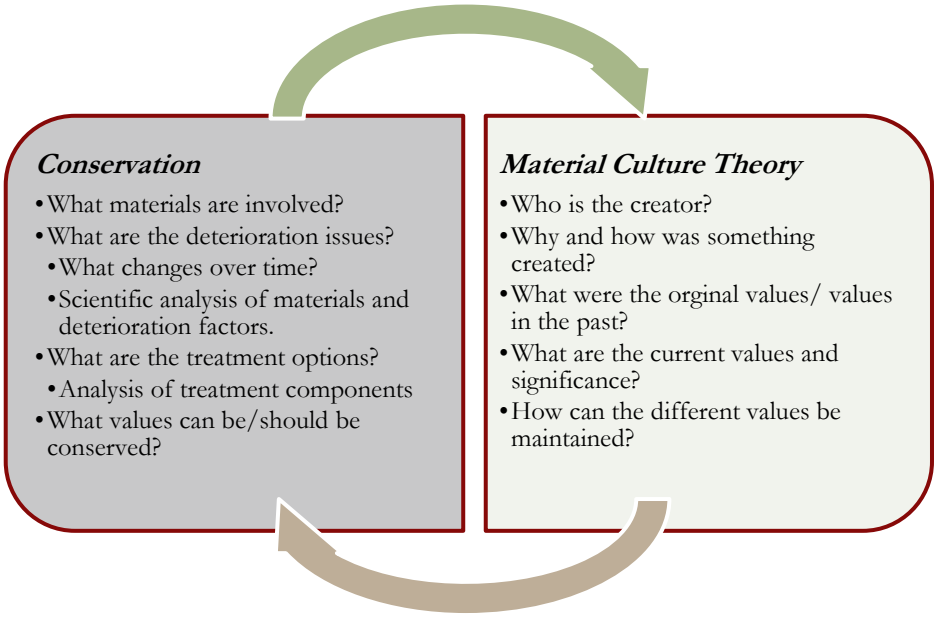



**Figure 4: The intertwined nature of conservation and material culture theory (author's own)**

From the earliest societies stone has been worked by humans and has been intertwined with all aspects of life – from tools, to shelter, to art. A large share of the tangible cultural heritage the world possesses is formed from stone; indeed the further back one reaches into human occupation, the more we rely on stone heritage to inform us about the past as it is often one of the few physical remnants (Ashurst & Dimes 1998). However, stone is more than just a material with which to make an axe or a building, it is loaded with cultural significance. The impact of stone can be clearly demonstrated by the way in which its various cultural meanings have become incorporated into everyday language; we say a meeting is 'set in stone' or that something is 'as hard as a rock'. The most prevalent symbolism attached to stone is stability and permanence – it is this perception of stone surviving for eternity that is the reason behind its use for items of great importance such as gravestones or monuments (Berleant 2010). Whilst the durability of stone, particularly relative to other materials, has indeed allowed for many stone artefacts and buildings to survive, the allegory of omnipresent stone is flawed; stone does, and indeed can at a rapid rate, deteriorate.

## Stone Decay

Stone, for the purposes of this thesis, will be defined as rock or mineral substance used for a specific, cultural, purpose. Stone can vary immensely depending upon how, when, and where it was formed. Decay of stone is, in turn, just as variable, and can be based upon physical, biological and chemical factors for example freeze-thaw cycles, acid attack, and crystallisation of soluble salts. Decay can affect stone in a number of ways, and there are a range of terms and definitions to describe the form it takes. Equally, there are many terms in English used often interchangeably with *decay,* which can actually hold slightly different meanings. Decay is defined by ICOMOS (ICOMOS-ISCS 2008) as "any chemical or physical modification of the intrinsic stone properties leading to a loss of value or to the impairment of use". Deterioration is defined as the "process of making or becoming worse or lower in quality, value, character, etc…; depreciation" (ICOMOS-ISCS 2008). Fitzner and Heinrichs (2002) divide stone deterioration into four phenomena:

**1st: Loss of stone material**: Describing the cause of loss of compact fragments. Removal can be from a range of causes including: natural (e.g. earthquake), anthropogenic (e.g. vandalism, war), or stress from constructional issues.

**2nd**: **Discolouration/ Deposits**: Change in the appearance of the stone surface, often involving change in colour. This could be a result of chemical weathering, salt efflorescence, animal waste, pollution, or biological colonisation.

**3rd**: **Detachment**: From a single grain upward, this category describes the process of removal of stone material and includes: flaking, scaling, disintegration and detachment of layers.

**4th**: **Fissures/ Deformation**: Individual cracks, or multiple resulting from a natural issue to do with the stone structure or constructional issue, or buckling/bending of stone (especially stone slabs).

Stone deterioration is often seen to result from a change in the external environment (Herrera Videla 2009). Because of this perception it may be thought that controlling environmental conditions will prevent

deterioration, and thus museum environments (usually thought of as highly controlled) could be thought to be a safe place for stone artefacts. However, it is not always possible to effectively control an environment; this can be very expensive and can increase pollution due to the energy required to power air conditioning. Even if it were possible to control temperature and relative humidity, this does not mean a stone will avoid deterioration, as shown in Figure 5; the greatest misconception about stone artefacts in museums is that they will require little conservation (Larson 1998).




**Figure 5: Block statue of 'Hati' with two squatting figures of Anuris and Mehyt (EA1726) attributed to Abydos or Thinis. (Bradley, Middleton 1988).**

In the series of images depicted in Figure 5, an artefact from the British Museum Ancient Egyptian collections provides an example. Acquired by the museum in 1898, the first image was taken in 1920 where minimal deterioration can be seen. In the 1940 image large fissures are apparent especially in the head, and by 1983 over half the head is missing. This is despite the best efforts of conservators in the museum; different treatments have been attempted, the statue is housed within a case in an environmentally controlled store.

The main causes of decay of a stone museum artefact can be seen in Figure 6. As previously mentioned even within a museum temperature and humidity may not be completely controlled. Many objects enter the museum environment with pre-existing problems, such as salt contamination, that may not be apparent upon first inspection. These issues can remain undetected for a long time and may only become obvious when severe damage has occurred. A further problem museum conservators face when trying to prevent deterioration is the long, and often unrecorded, history of an object. Past environmental conditions the object has been subjected to or previous treatments applied could be affecting the current situation and could negatively interact with any future ones (Larson 1998). The objects are on display with the purpose of being seen by visitors, however they themselves can affect a museum object – primarily by touching (stone objects are often displayed in the open and not in cases) but also in the way they can alter the environment – visitors entering from a wet or humid external environment could raise the RH inside the museum significantly; a sudden influx of a large amount of visitors could affect the temperature within a gallery space.

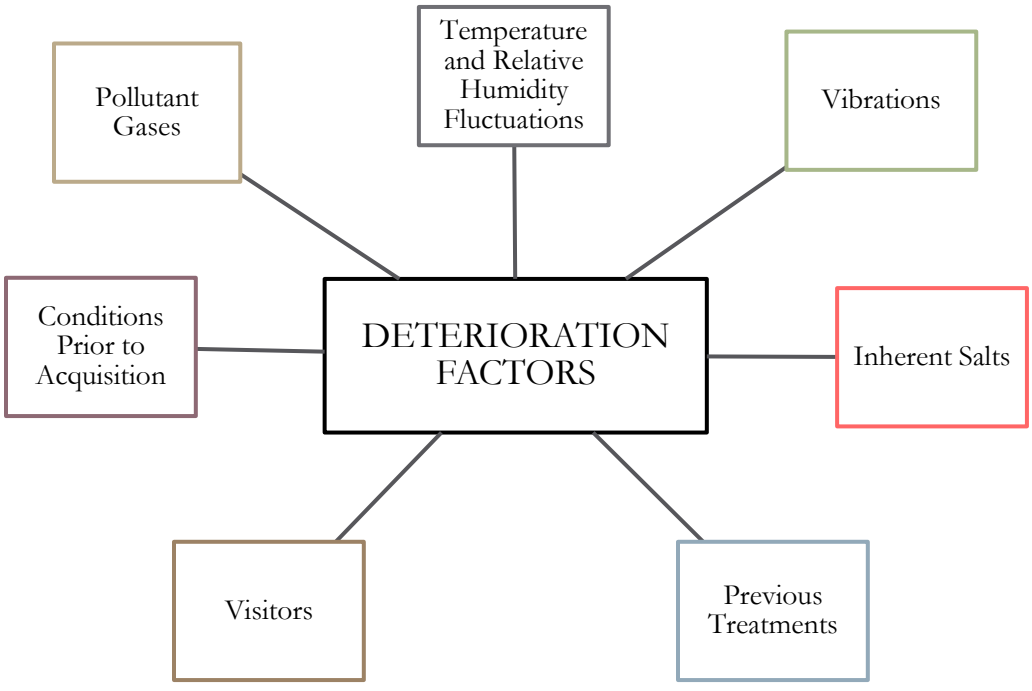



**Figure 6: Deterioration factors for museum artefacts (author's own)**

## Limestone in the British Museum

Limestone is a sedimentary rock often formed in marine, though occasionally in freshwater, environments which consists mainly of calcium carbonate ($CaCO_3$); commonly in the form of calcite. There are usually also fossils (themselves often formed of $CaCO_3$) and impurities including; dolomite ($CaMg[CO_3]_2$), quartz, iron oxides and clay minerals (Aston, Harrell & Shaw 2000) contained within. Typically limestone will be grey or white in colour, however it often weathers to a yellow-buff colour. The strength and durability of limestones can vary greatly, however many younger limestones are relatively soft, with the advantage that they are easy to work, yet with the consequence that they are not very weather resistant.

Limestone has been used as a building stone and as a medium for sculpture and monumental constructions in Egypt from pre-Dynastic times ( Lucas 1915, Lucas 1962, Middleton & Bradley 1989), with some of its most famous uses being the Sphinx and the Pyramids on the Giza plateau. Its use exponentially increased from the 3rd Dynasty with the growth of Egypt as a state and the technological revolution that accompanied this leading to some to describe Egypt as a state grown out of stone or "staat aus dem stein" (Evers 1929). Certainly, stone (including limestone, sandstone and granite) is the dominant substance in the surviving examples of Ancient Egyptian material culture (Abu-Jaber et al. 2009).

Limestone outcrops occur in Egypt along the Nile valley from Esna (just south of Luxor) to the Mediterranean, and also along the desert plateaux to the East and West of the Nile Valley (Abu-Jaber et al. 2009, Aston, Harrell & Shaw 2000) . Egyptian limestones were formed in periods from the Upper Cretaceous to the Pleistocene (Klemm & Klemm 2008). The main exploitation of limestone in Pharaonic times took place along the Nile Valley from Qurna to Cairo. Limestones here predominantly date from the Eocene (Klemm & Klemm 2008). In the time of the Ptolemies, the principal material used in construction projects was an oolitic Pleistocene limestone (Klemm & Klemm 2008). Egyptian limestones are very fossiliferous and virtually all contain clay minerals although in varying quantities. Those limestones from

south of Giza also contain sand, particularly quartz but also feldspar and other minerals (Klemm & Klemm 2010).

The British Museum has a large and important collection of Egyptian limestone sculptures. Using archival information, and an analytical study conducted by Middleton and Bradley in the late 1980's (Middleton & Bradley 1989), the Egyptian sculptures can be divided into three geographical groups (see figure 7) based upon their limestone characteristics:

- Cairo: The limestones present in the museum from the Cairo area are usually fine-grained, compact, and show no obvious lamination or bedding (Middleton & Bradley 1989). They have been petrographically categorised as fossiliferous micrites (Middleton & Bradley 1989).
- Thebes/Abydos: Two different varieties in the museum come from this area; fossiliferous micrites and biomicrites. Both are fine-grained buff limestones, however differ in the quantities of fossils and the type and alignment of clay inclusions (Middleton & Bradley 1989).
- El Bersha: These biomicrite limestones are distinct from those from the other two areas in appearance (being white and chalky) and in the form of the calcite grains (euhedral (sharp, well defined, crystal faces) rather than anhedral (undefined crystal faces)) (Middleton & Bradley 1989).




**Figure 7: Map to show provenance of British Museum Egyptian limestone artefacts**

Limestone in Egypt is subject to large diurnal temperature cycles and abrasion from sand, both of which cause deterioration. However, disintegration of stone buildings in Egypt mainly occurs in a zone up to 1.5 metres above ground level and is accompanied by a marked white efflorescence (Lucas 1962, Lucas 1915, Anonymous 1993). Such deterioration is attributed to crystallisation of various salts, in particular sodium chloride, beneath the surface of the stone (subflorescence) (Anonymous1993, Lucas 1915, Lucas 1962).

Whilst it is often thought that a museum environment would be safe, in particular for something perceived as durable as stone, some of the limestone artefacts in the British Museum have deteriorated significantly since their acquisition. The existing high soluble salt content of many Egyptian limestones is no doubt a

contributing factor to this. There is a vast difference between the environment of Egypt and that experienced in the UK, particularly in relation to the humidity. Both the initial change in relative humidity, combined with the fluctuations experienced in the UK's maritime climate will have led to movement of soluble salts within the stone, which in turn will have caused degradation. However, not all limestone in the museum is degrading, suggesting there is likely to be a variation in deterioration depending upon limestone source. According to a study conducted in the British Museum (Bradley & Middleton 1988), the chemical and physical properties of the limestone the sculptures are made from have significantly affected their propensity to decay, and the way in which the decay manifests. Three factors were identified, that especially when combined, would affect the deterioration of a limestone object:

- A high clay proportion of acid insoluble fraction would increase likelihood of structural decay.
- High soluble salt content; in particular a large amount of nitrate salts, that would especially affect localised powdering and pitting.
- A high proportion of micropores would lower durability (Bradley & Middleton 1988).

Out of the three different types of limestone identified above, the Thebes/Abydos demonstrated the highest amount of decay. These stones had both a high clay acid insoluble fraction and a high soluble salt content that was predominantly nitrates (Bradley & Middleton 1988). The Cairo group showed evidence of some pitting, powdering, and flaking, but were generally sound. Despite having a high soluble salt content, the soluble salts were mainly chlorides rather than nitrates. The El Bersha group contained low acid insoluble fractions (hence little clay content), and low soluble salts, so were relatively solid (Bradley & Middleton 1988).

A database of the British Museum Ancient Egyptian limestone artefacts that are seriously deteriorated and deemed in need of consolidation, along with some of those previously consolidated, has been compiled during this project using archival research within the museum and in consultation with the museum's stone conservators. This is discussed more at length in Chapter 4 and can be found in Appendix A.

## Treatment of Stone Decay

Before any action can be taken to prevent stone decay or to remedy the effects of it, an artefact needs to be assessed to see what the causes of decay are and whether deterioration is on going. This is achieved by a combination of artefact inspection, surface condition recording, and analysis of the stone including salts present and their concentration (Durnan 2006). Then, as with other materials, the first line of defence when it comes to stone decay is with preventive measures. In a museum this can include environmental control, limiting physical access to an artefact and careful monitoring of condition to catch any deterioration at an early stage. The importance of regular monitoring and maintenance is highlighted by Domaslowski (2003) to ensure environmental parameters are being controlled and to check any past treatments are remaining effective.

### Cleaning

After the condition of a stone object has been assessed, it may be decided that preventive conservation is not enough to prolong its life. Interventive, or active conservation, which will alter chemical or physical aspects of the stone, is sometimes necessary. One of the most common forms of active conservation is cleaning. Cleaning can be used to improve the appearance of a stone object by removing superficial dirt or microbial growth, to improve assessment of the condition of the stone, to prevent further degradation, or to see original tooling (Durnan 2006).

There are a variety of cleaning techniques employed by conservators – some physical such as dry brushing, some chemical such as applying a biocide. Whilst the appearance of a stone object may be improved in the short term by cleaning, careful consideration of the method used and its effects upon a stone surface is needed as it can also be highly detrimental. Consequences of cleaning can include loss of fragile surface detail; mobilisation of soluble salts, and irreversible change in colour (Maxwell 2007). Removal of one particular type of micro-biota may encourage the growth of others (Siegesmund & Snethlage 2011, Piñar & Sterflinger 2009). To limit negative impacts of cleaning, conservators assess four different aspects of the

surface: mineralogy and chemistry; morphology and texture; chromatic parameters; durability (Delegou et al. 2008)

## Desalination

One of the main causes of decay within stone is the presence of soluble salts (Scherer & Jimenez Gonzalez 2008, Goudie & Viles 1997). and they have long been recognised as a factor in the deterioration of stone heritage (Lucas 1925, Goudie 1977, Rodriguez-Navarro & Doehne 1999). Decay can manifest as efflorescence, powdering, and blistering at the surface, or structural weakening due to the stress exerted upon pore walls during crystallisation (Bradley & Hanna 1986, Scherer & Jimenez Gonzalez 2008). Where salts are thought to be actively leading to deterioration, attempts can be made to try and remove them, or at least reduce their concentration. Within the museum setting this may be achieved by immersing an artefact in water or by using poulticing, however care must be taken as such actions could prove difficult if an artefact is extremely fragile or if there are pigments on the surface (Doehne & Price 2010).

## Surface Coatings

A surface coating is, at its most basic, either a protective layer that prevents entry of unwanted materials such as pollutants that may exacerbate decay, or a sacrificial layer. There are a wide range of surface coatings with varying purposes for example water repellents, anti-graffiti coatings, salt inhibitors and biocides (Doehne & Price 2010). They are commonly used when stone material culture is at risk from being in the external environment and cannot be moved to a more controlled internal area. The porous nature of stone can sometimes mean that such surface coatings cause more problems than they solve. For example, a hydrophilic layer on the surface of stone can induce stress if there are internal salts that cannot reach the surface to crystallize out, leading them to build up under the surface (Cezar 2011).

## Consolidation

When the structural integrity of a stone artefact reaches a very weakened state to which values or significant could be lost, a conservation option is to apply a consolidant; a substance that penetrates the stone and strengthens by increasing internal cohesion, retarding future deterioration (Clifton & Frohnsdorff 1982). In some cases, a consolidant can act as a protective layer and vice versa (De Buergo & Fort González 2001). The methods associated with these two procedures, and the materials used, have changed and developed over time with advances in technology and changes in philosophical approaches. Doehne and Price (2010) provide a comprehensive overview of the different materials used as consolidants, both in the past and at present, including lime treatments, barium hydroxide, alkoxysilanes, epoxies, and acrylics.

Over the last few decades there has been a general trend towards reversibility within the conservation discipline as a whole, placing great importance on the idea that any action undertaken by a conservator could be put back in the future (Rodgers 2004). It can be very difficult in stone conservation to stick to this principle, particularly with the use of consolidants, so instead there has been a shift towards a focus on compatibility rather than reversibility (Sasse & Snethlage 1996). This involves ensuring that where a conservation procedure requires the introduction of a new material to an artefact, the material to be introduced will not negatively impact upon the object in an aesthetic, historic, or technical way (Quist 2009). Along with the ideological preference for compatibility, physical and chemical incompatibility with the stone has been suggested as the reason some popular conventional conservation treatments, such as silanes, have been recorded speeding up deterioration (Delgado Rodrigues 2001, Moropoulou et al. 2003, Dei & Salvadori 2006).

Efforts to ensure compatibility have led to a recent trend in treatments based upon natural rock components and coverings, and research into adapting more traditional methods. One example of this is the research into the protective nature of biological deposits on the surface of stone artefacts, for example carbonate production from bacteria (Zamarreño, Inkpen & May 2009, Jroundi et al. 2012) Whilst interactions between bacterial species and stone have often been viewed negatively in the past, research

such as that of De Muynck et al (2010b) has highlighted "self-healing" properties where calcium carbonate produced by bacteria on a stone can act as a cement to repair cracks (De Muynck et al. 2010). Another area of research, and one that particularly shows the use of cutting-edge science, involves nanoparticles. Traditional lime treatments are being adapted to include new "nanolimes" - nano sized particles of calcium hydroxide suspended in alcohol to improve the carbonation process (Daniele & Taglieri 2010, Giorgi et al. 2010, Dei & Salvadori 2006, D'Armada & Hirst 2012, Chelazzi et al. 2013). Silanes are becoming nanocomposite materials in an effort to overcome problems such as cracking whilst drying (Simionescu et al. 2009a, De los Santos et al. 2008). The Back to Nature project is firmly situated within this research trend and examines three potential consolidation treatments based upon natural rock components.

## Assessment of Consolidation Materials

The selection of which consolidation material to use for a stone artefact is highly important, but is often complicated due to the large range of products available and the variable nature of the petrophysical properties (Cnudde et al. 2007, Ferreira Pinto & Rodrigues 2008, Slavíková et al. 2012). The large variety of stone types and manifestations of decay mean that there is no one consolidant that suits every situation (Karatasios et al. 2009, Price 1982). Evaluation of which consolidant to use is normally conducted using laboratory testing to assess effectiveness, durability and any possible side effects (Ferreira Pinto & Rodrigues 2012) This is achieved by systematic monitoring of quantitative properties that are considered critical to successful consolidation (Theoulakis, Karatasios & Stefanis 2008).

The ideal consolidant will improve the internal strength of a stone, penetrate deeply and not have a sharp interface between treated and non treated substrate, will bind grains together but not completely block pore spaces; still allowing water vapour transfer, and will manage all this whilst not changing any of the object's aesthetic qualities (Doehne & Price 2010). Properties of stone samples are usually analysed before and after treatment with a consolidant to see how the consolidant measures up to these ideals. For each property there are a number of different tests that can be used to assess it, each with their own merits and disadvantages. Any modern investigation into consolidants is likely to use a range of tests, to look at as

many different properties as possible, to come to an overall conclusion (Sasse & Snethlage 1996, Moropoulou, Association of Civil Engineers of Greece. 2000, Laurenzi Tabasso & Simon 2006). The great number of properties to analyse, and methods with which to do so, can make it difficult to compare results from different conservation laboratories or studios. In an attempt to rectify this there have been suggestions for standardisation of tests (Fassina 2008). An important characteristic of a successful consolidant is its ability to remain stable, and continue to work over time. Accelerated ageing tests are often used to discern the effects of a consolidant in the long term (Moropoulou, Maravelaki & Biscontin 2008, Pamplona, Melo & Aires-Barros 2008). Other factors can affect the consolidation action achieved including application procedure (Ferreira Pinto & Rodrigues 2008, Nardini et al. 2008, Pinna, Salvadori & Porcinai 2011). Experiments with the aim of assessing consolidation effectiveness may therefore include an examination the roles such factors can play. A critique of many investigations into consolidants is that they have been conducted upon fresh stone samples which may give an unrealistic impression of how the consolidant would behave on the weathered stone it would eventually be applied to (Wheeler 2008, Theoulakis, Karatasios & Stefanis 2008) . Recently investigations have sought to resolve this issue by testing consolidants on both artificially and naturally weathered stone samples.

As described more fully in the aims outlined in Chapter 3, the Back to Nature project followed the now industry-accepted procedure of consolidant investigation/assessment using laboratory testing of stone characteristics to gather an overall picture of "effectiveness". A priority of the aims was to address the issue of testing solely on fresh stone material.

# Chapter 3

*Aims of Back to Nature*

The previous chapter detailed the various ways in which stone conservators can treat stone decay, and explained the in-depth testing carried out before any new treatments are applied to stone heritage. The main aim of the Back to Nature project was to assess the potential of three new, inorganic, consolidants, in comparison with a more traditional organic polymer, for severely deteriorated limestone artefacts in the British Museum. The end goal was to produce guidelines for conservation professionals in the selection and application of these consolidants. To achieve this, research was divided into four developmental stages; each with its own separate objective as described within this chapter:

## 1) Developing a robust experimental methodology to evaluate the comparative performance of stone consolidants.

The first objective of the Back to Nature project was to develop a set methodology for any experimental comparison of the consolidants to be investigated. The most important part of this was to assess the requirements for stone samples that would be treated; their number, size, shape, and source. The secondary focus was to compare the use of fresh and weathered samples, and how to produce experimentally weathered samples with tightly constrained weathering histories. In the past, the vast majority of experiments conducted with the aim of investigating consolidants have used stone blocks or replicates in the laboratory, in order to safeguard the artefacts that will eventually be treated, for example experiments conducted by Casadio and Toniolo (2004), Nardini et al. (2008), and Mosquera et al. (2008). The last few decades have seen progress towards standardization of methods to test the performance of consolidants

(Doehne & Price 2010, Fassina 2008). However, this process is still ongoing. Frequently, laboratory investigations into the nature and effectiveness of consolidants use stone samples solely cut from fresh, sound, stone (Theoulakis, Karatasios & Stefanis 2008) . Fresh stone has some obvious advantages over weathered; it is not only easier to obtain, but has a known history; there is less scope for unknown factors to affect the results of any investigation. However, it is extremely unlikely that in a conservation situation consolidants would be applied to fresh stone. The relevance of results from investigations into such samples for real conservation practice could therefore be questioned. By comparing results from fresh and weathered stone samples, both treated with the same consolidants under the same conditions, the first stage of this investigation was designed to gain a clearer idea of the effect of weathering of the samples upon the assessment of consolidants.

## 2) Evaluating the consolidating properties of CIPS as applied to deteriorated limestones.

Of the new inorganic consolidants under consideration for use in the British Museum, CaLoSil and ammonium oxalate treatment had either been developed specifically for stone conservation, or had been investigated and applied to heritage stone by other researchers. CIPS on the other hand was developed in Australia for the oil and gas industry and whilst subsequently used for a variety of purposes, had not been investigated in relation to heritage stone prior to this project (Geotechnical Consulting Group 2002, Soudain 2001). It was therefore decided that, before any large scale experiments to compare the different consolidants, the potential of CIPS as a museum consolidant needed to be investigated further. This was done on three levels: producing and characterising the solution, treatment of a range of unconsolidated sands, and the treatment of weathered stone.

## 3) Comparing the performance of three inorganic and one organic consolidants on experimentally weathered limestones.

Once a methodology had been designed using the first set of experiments, and CIPS had been confirmed as a potential consolidant in the second, the main project objective could be tackled. The aim of the third stage therefore was to perform an initial comparison of the three new potential consolidants; between each other and with a previously used silane: Wacker OH 100. Several different analytical techniques were used to characterise stone samples before and after treatment. The aim was to combine the results from all these different techniques to provide an overall indication of consolidant effectiveness. This initial comparison would be conducted on fresh stone samples of equal size and shape that had been artificially weathered. The aim of this was to minimise external variables not directly related to the action of the consolidants.

## 4) Comparing the performance of three inorganic and one organic consolidant on naturally weathered limestone objects.

In line with the first stage of the project, the fourth stage extended the comparison of consolidants on artificially weathered cubes onto naturally weathered stone samples. Data gathered in this stage could be examined in comparison with that from the previous to see if effects were consistent and to see if the performance varied on naturally weathered stone. These samples had a far higher degree of weathering than achieved when artificially weathering stones in the lab for the previous stage, leading to a far rougher surface. The samples for this stage would differ in shape and size, rather than being identical stone cubes. The natural weathering and variety in shape, it was hoped, would provide a more realistic indication of how a consolidant would behave on a deteriorated museum artefact. This part of the project would also provide an insight into the usefulness of the different analytical methods for use on non-standard stone samples – for example if they were to be used to analyse the museum artefacts themselves in the future.

The following chapter provides in-depth information on the materials used within this project – both the stone materials treated and the consolidation treatments themselves, and describes the project methodology and analytical methods used to achieve the aims detailed above.

# Chapter 4

*Materials and Methods*

As described in the aims in the previous chapter, the *Back to Nature* project centred on the desire to discover the potential held by newly developed inorganic consolidants, and to assess if any were suitable for future use on deteriorating limestone artefacts within the British Museum. This was achieved using a range of investigative methods and involved working with a variety of materials. This chapter provides details of the materials involved – from the artefacts that formed the base of the investigation to the variety of consolidation treatments, and provides an overview of the quantitative and qualitative methods employed in their assessment.

## Consolidants

Three new inorganic treatments were selected for investigation: CaLoSil, a newly commercially available consolidant produced using calcium hydroxide nano-particles; ammonium oxalate, a technique developed in Italy based upon the process behind naturally occurring calcium oxalate patinas; Calcite In-situ Precipitation System (CIPS), a treatment developed in Australia for the oil and gas industry. As a comparison, Wacker SILRES BS OH 100 (a commonly used alkoxysilane) was included in all investigations (Matteini 2007, Kucharski et al. 2000, Bradley 1985).

### Organic Polymers

There are numerous products that have been used within conservation in an attempt to increase stone strength; the majority of which have been organic polymers (Doehne & Price 2010, Liu & Zhang 2007). Among the synthetic organic polymers available, the most widely used in stone conservation are those based upon ethyl silicates frequently known as "silanes" short for alkoxysilanes and alkyl alkoxysilanes

(Snethlage & Wendler 2000, Doehne & Price 2010). The two main groups of silane consolidant used in stone conservation are alkoxysilanes and silicon esters (Bradley 1986). Both are derived from SiH4 with at least one Si-O bond replacing a Si-H bond, the main difference being the degree of initial polymerization (Price 2006). In terms of the conservation action achieved, the difference between the two is that alkoxysilanes form polymers with water repellent properties and are applied to strengthen a stone artefact but also to prevent entry of water and other weathering agents, whereas the polymers from silicon esters are solely used to improve internal cohesion (Bradley 1986) .

Silanes have been commonly used since the 1960s, although their history goes back to the 1840s, and they have been a very popular choice for consolidation, especially in Europe (Grissom & Weiss 1981, Wheeler, Goins 2005, Wheeler 2008, Price 2006). Silanes' popularity can be attributed to their low viscosity and a relatively long curing time which together allow for greater penetration into stone, stability, minor effect on colour, and considerable hardening of the treated stone (Dinsmore 1987). The British Museum used several different silane based consolidants in the 1980s for severely deteriorated sandstone and limestone artefacts, predominantly those from the Ancient Egypt and Sudan department, however it has not employed them since. One of the reasons the British Museum halted the use of silanes is the ongoing debate about the alleged reduced success in applying silane consolidants to limestone in comparison to sandstone. Hypotheses include the difficulty in forming bonds between silicate and calcitic material; slower reactions in the presence of calcite leading to an increased loss of consolidant through evaporation; or the fact that alkalinity of calcareous stones makes the precipitate from the silanes soft and useless, however this has been disputed (Wheeler 2008, Ferreira Pinto & Rodrigues 2008). Another major area of concern with silanes is their use on stones that have a high clay or salt content. There is a high risk of salts or clays swelling upon hydration, leading to increased pressure on pore walls and possible deterioration including cracks or fissures and delamination. There are occurrences where silanes have been applied to such stones and the deterioration has continued, sometimes at a higher rate (Thickett et al. 2000). Something to look for in an alternative treatment to silanes would therefore be success on stones with a high salt or clay content.

Aside from their interaction with the stone material of an artefact, a problem with the use of silanes is that they involve hazardous materials and as such pose health and safety risks. They need to be used in a well-ventilated area or fume cabinet and protective clothing including a respiratory mask needs to be worn (Price 2006). The hazardous materials can also pose complications for disposal of waste material and can increase pollution (Rodriguez-Navarro et al. 2003). An alternative consolidant would ideally therefore have fewer safety risks and be environmentally friendly.

Despite the range of concerns that accompany the use of silanes within stone conservation, there are numerous examples of their success and there are conservators who still promote their use within the field. This belief in the possibilities of silanes is evident from the number of recent investigations into adapting them to maximise their success (Simionescu et al. 2009b, Maravelaki-Kalaitzaki et al. 2008, Miliani, Velo-Simpson & Scherer 2007). Inclusion of a silane in the Back to Nature experiments would therefore cover two aspects: firstly it would provide a basis for comparison. Secondly, the British Museum stone conservators wanted to know if they should consider reintroducing the use of silanes for severely deteriorated artefacts.

The silane based consolidant selected for use within the Back to Nature project was SILRES BS OH 100 supplied by Wacker Chemie AG. Often abbreviated to Wacker OH, this consolidant was chosen for this project since it was one of the few used by the British Museum in the 1980s that is still available on the commercial market today. SILRES BS OH 100 is sold as a solventless ready-to-use product based upon tetra-ethoxysilane (also known as tetraethyl orthosilicate and tetraethyl silicate). TEOS is one of the most commonly used silane compounds, upon application, it reacts with atmospheric or internal moisture and hydrolyses to form silanols which then condense into a silica gel binder as can be seen in Figure 8 below (Doehne & Price 2010, Snethlage & Wendler 2000). The Wacker OH 100 was applied directly using a pipette until the surface appeared to reach saturation. Any stone treated had two applications of Wacker OH with a three week curing period in-between applications.

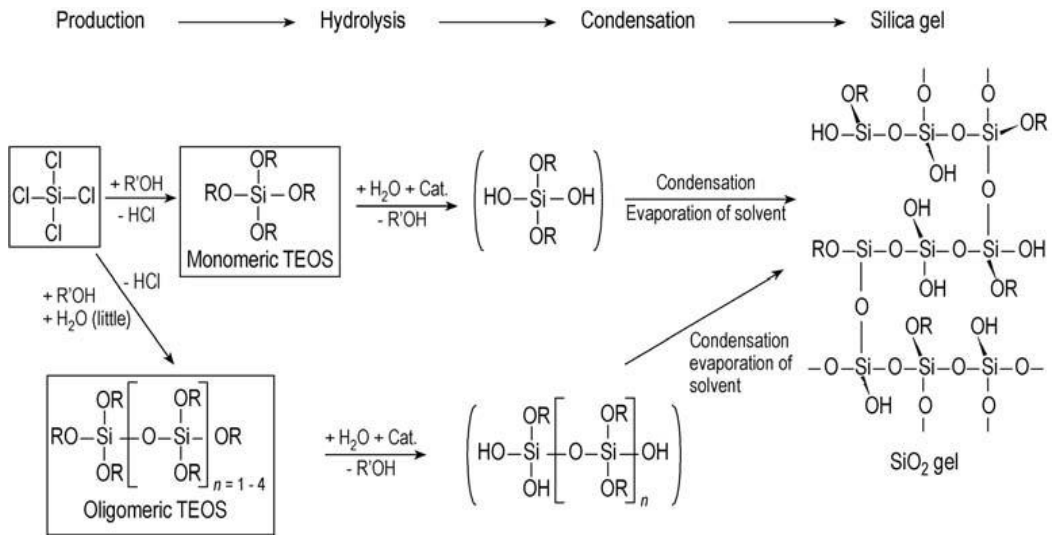



**Figure 8: TEOS hydrolysis and condensation into silical gel (Snethlage & Wendler 2000)**

## CIPS

The 'Calcite In-situ Precipitation System', or CIPS, is one of the new possible inorganic consolidant under consideration by the British Museum. The CIPS method (developed by CSIRO; marketed by Lithic Australia Pty Ltd) creates high strength bonds between grains in porous material using calcite precipitation (Price 2010). Calcite crystals form within a solution applied to the material and settle on the surface of individual grains, creating bridges between them. Repeat treatments are used to introduce more calcite, to bridge larger gaps between grains, and so to increase the strength further. Along with the attractive compatibility of using a calcite based consolidant within limestone, particular advantages of CIPS are its ease of use and low toxicity (Ismail et al. 2002). No special requirements in terms of ventilation are needed during treatment production and application, and gloves are worn to prevent treatment contamination; not to protect the user. By-products from the treatment can usually be disposed of in municipal waste or by washing down the sink (Price 2010). This treatment was originally developed for the oil and gas industry in Australia, and has since been used for a variety of consolidation purposes including beach preservation, military logistics and to shore up railway embankments (Price 2007, Geotechnical Consulting Group 2002). However, this is the first time CIPS has been used indoors, on a smaller scale.

The CIPS fluid is formed from two solutions (designated Solution A and Solution B) that are mixed 1:1 just prior to application. The exact composition of the two solutions, and their production methods, are proprietary to Lithic Australia Pty Ltd who can be contacted for more details (http://www.lithic.com.au/Company%20Profile%20and%20Contacts.htm).

When solutions A and B are mixed a defined chain of processes is set into action, these stages can be observed and timed. The rate at which calcite is produced affects the eventual strength induced, so when making up a new batch of CIPS it is recommended that a small amount of CIPS is mixed and then timed to check the different stages are occurring at the right time (Price 2010) Upon mixing, the combined solution is a translucent light yellow colour. After approximately 20 minutes the solution should have turned into until a thick white gel. It is important that the treatment has been applied BEFORE this white gel stage has been reached. This gives a fairly short treatment window so it is essential that the two liquids are mixed only as application is about to commence. After approximately 45-60 minutes from the original combining of Solutions A and B the white gel begins to break down into a white precipitate and a yellowish clear liquid (Price 2010) . The precipitate is the calcite, which in a material would settle around the grains, and the yellowish clear liquid the spent CIPS fluid that would remain in pore spaces. Once the two solutions are mixed, CIPS can be applied in a variety of ways – immersion, pipette etc. For all *Back to Nature* experiments the CIPS was applied by spraying.

## Ammonium Oxalate

A proposed alternative to ethyl silicates is ammonium oxalate treatment. Calcium oxalate films are naturally occurring patinas found on some calcareous stones (Cariati et al. 2000). The patinas have two different mineralogical phases: monohydrated whewellite ($CaC_2O_4 \cdot H_2O$) and dehydrated weddelite ($CaC_2O_4 \cdot 2H_2O$) and are colourless except if impurities are present (Doherty et al. 2007, Doherty et al. 2006).

The exact origin of oxalate films is a contested topic with the two main theories being; the by-product of microflora such as algae, fungi and lichens (Caneva, Nugari & Salvadori 2005) ; or the product of degrading past, sometimes ancient, conservation treatments (Cariati et al. 2000). Whatever the origin, the

oxalate films provide a thin, compact, non-porous shell highly resistant to acid attack and atmospheric pollution. Because of the potentially protective role of such a shell, there has been a large amount of research conducted recently 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 as shown in the equation below.

**Equation 1: Reaction of ammonium oxalate with calcium carbonate**

$$CaCO_3 + (NH_4)_2C_2O_4 \longrightarrow CaC_2O_4 + 2NH_3 + H_2O + CO_2$$

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| calcium carbonate | ammonium oxalate | | | calcium oxalate | ammonia | water | carbon dioxide |

Whilst the majority of recent research has focused upon the use of oxalate films as protective layers, there have been suggestions that it could also have consolidation properties (Matteini 2007). To test this hypothesis, it was decided to include ammonium oxalate treatment as one of the inorganic consolidants within the Back to Nature project. Ammonium oxalate monohydrate was applied using two different methods. In the first round of experiments ammonium oxalate monohydrate was mixed with water at 5%w/v and then pipetted onto the stone surface. In later experiments it was applied at the same concentration using a cellulose poultice. 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 24hrs before removal. After 3 weeks the process was repeated for a second time.

## CaLoSil

CaLoSil is a new, commercially available, nano-lime stone consolidant developed specifically for consolidating historic material (Campbell et al. 2011). Nano-particles, on average 150nm in size, of $Ca(OH)_2$ are suspended in different alcohols (Costa & Delgado Rodrigues 2012). After application, the

alcohol evaporates to leave solid calcium hydroxide behind. This then reacts with atmospheric carbon dioxide to form calcium carbonate in the following carbonation reaction:

**Equation 2: CaLoSil reaction to produce calcium carbonate**

$$Ca(OH)_2 + CO_2 \longrightarrow CaCO_3 + H_2O$$

| | | | |
|---|---|---|---|
| calcium hydroxide | carbon dioxide | calcium carbonate | water |

Due to the small size of the particles, CaloSil can penetrate deep into the stone (IBZ - Salzchemie GmbH & Co. KG 2013). Along with no limit of penetration due to particle size, advantages of CaLoSil include a high reactivity, the compatibility associated with treating limestone with a lime based treatment, no mobilisation of soluble salts, and a mixture of low toxicity that is environmentally friendly (Daehne and Herm 2013). There are several different concentrations of CaLoSil that in turn can be suspended in different alcohols. Within this project, CaLoSil E25 (calcium hydroxide particles dispersed in ethanol at 25g/l) was used. Two different application methods were investigated – spraying, in the earlier experiments, and pipetting in the last round of experiments. Three weeks after the first treatment in each round of experiments, a second application was undertaken. It is important to consider the time needed to allow the carbonation reaction (shown in equation 2 above) to occur when planning subsequent treatments and the curing time before post-treatment testing of stone characteristics. If post-treatment testing was conducted before this carbonation reaction occurred, results including changes in internal strength and pore space characteristics might not be an accurate representation of changes due to treatment with CaLoSil. Daehne and Herm (2013) recommend more than 7 days curing time for CaLoSil. The three weeks between treatments, and subsequent three weeks before post-treatment testing, used within this project should therefore have allowed sufficient time for the carbonation reaction to occur.

## Limestone

The Ancient Egyptians were prolific users of limestone, exploiting oolitic Eocene and Pleistocene outcrops in Egypt along the Nile valley and within the desert plateaux on either side (Abu-Jaber et al. 2009, Aston, Harrell & Shaw 2000) . Limestone was used during Pharaonic times and the time of the Ptolemies to create buildings, sculptures, monuments, and other objects including sarcophagi. The British Museum now holds a large number of Ancient Egyptian limestone items. More information on the provenance of these items and details of an analytical study performed by Middleton and Bradley in the late 1980's can be found in Chapter 2 (Middleton & Bradley 1989).

Sadly, some of the limestone artefacts in the British Museum have deteriorated significantly since their acquisition and now have reached the stage where the active conservation method of consolidation is likely to be the best method to save these artefacts for the future. The chief aim of the Back to Nature project was to assess new consolidants for these limestone artefacts in the museum, so any laboratory experimental work would use limestone as the material to be treated with the consolidants. Since it would prove difficult to source Egyptian limestone with a direct relation to any of the museum artefacts, exact matching of the limestone for the replicates was not the principal requirement. Instead, importance was placed upon finding a limestone, known to be prone to deterioration, of which there was sufficient quantity for all experiments - to minimise, where possible, variance due to stone type. The majority of stone replicates used within Back to Nature experiments came from two quarries near Corsham in the UK; Elm Park and Hartham Park. These are both Bath limestones. Pale buff in colour, they are oolitic limestones of middle Jurassic age. The Elm Park samples were cut from an unweathered block, obtained from the quarry a few years ago, and stored inside in a dry basement since then. The Hartham Park stone had been removed from St Edmunds Hall and St John's Colleges, Oxford during restoration and repair work in the last five years having been exposed previously in the polluted Oxford environment for over 100 years. In latter experiments, that required highly (naturally) weathered stone, samples were taken from two further sources of stone. One was stone removed from the south pavilion of the National Trust property Basildon Park, an ooidal and bioclastic limestone thought to be Middle Jurassic, Bath Stone, supplied from quarries in the Combe Down

area of Bath and North East Somerset (British Geological Survey 2008). The other was also an ooidal limestone supplied by the British Museum with unknown provenance. Tests to show characteristics of the Elm Park, Hartham Park and Basildon Park were conducted in the Oxford Rock Breakdown Laboratory and combined with standard tests, the results of these analytical tests can be seen in table 1. It was not possible to source any similar investigations into deteriorated Egyptian limestones however, as mentioned above, direct relation to Egyptian limestone was not a focus for this project.

| Characteristic | Elm Park | Hartham Park | Basildon Park |
|---|---|---|---|
| Water Absorption (WAAP) | 10.07 | 9.15 | 10.2 |
| Open Porosity (%) | 21.1 | 17.2 | 18.8 |
| Water Absorption Coefficient (WAAC) | 1.03 | 0.8 | 1.0 |
| Apparent Density (Kg/$m^3$) | 2064.2 | 2050.6 | n/c |
| Elasticity Modulus (MPa) | 18.85 | 16.00 | n/c |
| Salt Crystallisation (% Mean wt loss) | 23.7 | 27.59 | |

**Table 1: Tests conducted in OxRBL; salt crystallisation data from standard characteristics conducted by the BRE and Stanleys Quarry (BRE 2000, Stanleys Quarry 2011).**

## Methods

The *Back to Nature* project had a threefold methodological approach: archival, practical and experimental, reflecting the requirements of a Collaborative Doctoral Award (CDA) project. Such CDA projects are designed to link the needs of 'user communities' to the research capacity of academic organisations, with a hybrid project carried out by the student. The British Museum (BM), as 'user', originated the project based

on practical conservation needs and designed the approach to be followed, in association with researchers in the BM science department and researchers in the academic partner, the University of Oxford.

## Archival and practical research

The archival components of the project involved getting information, both written and oral, about both the nature of deterioration affecting Ancient Egyptian and Coptic limestone sculptures within the museum, and past conservation treatments used within the BM to try and stabilise some of these deteriorating objects. There is a database of artefacts within the museum, with information on material types and condition, which was consulted and used to produce a database of artefacts of particular relevance to this project, i.e. those made of limestone and suffering from salt contamination (reproduced in the appendix). Some records of consolidant treatments are held within the BM conservation department, and some published accounts also exist, but the records are patchy and sparse. Where information was gathered about previous consolidation treatment of the artefacts designated of particular relevance, this was added to the database shown in appendix A. A visit to the Egyptian and Sudan storerooms with members of the conservation team permitted first hand observations of a range of limestone artefacts treated with these different consolidants, and allowed discussion of the pros and cons of the various techniques. The conservators' descriptions of the state of each artefact were used to develop an improved understanding of the nature of deterioration as perceived by conservators. Issues of when treatment might be desirable or essential were discussed. Further information on current conservation treatments within the BM was gained from interviewing conservators and observing their conservation practice.

The practical components of the project focused on gaining first-hand experience of conservation practice, through working in the conservation department and learning the techniques from the conservators. Developing potential new consolidant treatments of practical value can only work if there is good liaison between scientists and conservators. Time spent in the museum working with the conservators helped to develop an appreciation of the practicalities of applying consolidants, and the decision-making process involved in selecting a suitable treatment and deciding upon any necessary pre-treatment stages (e.g.

desalination and cleaning). This component of the project also involved liaison between the stone conservation studio, conservation section and science department of the BM. Under one umbrella as the Conservation and Scientific Research (CSR) department, the three groups have slightly different priorities and work independently as well as together. The science section predominantly focuses on conducting experimental and investigative research, whilst the conservation section would work more on treatment of artefacts with different studios dedicated towards different materials. The different sections work together to achieve both the aims of research and collections care. Liaising between these different sections within the CSR department gave an insight into the complexities of working in a museum environment, the level of research information available to back up conservation decisions, and the relationship between researchers (science department) and practical conservators. The experience and insights gained from these practical engagements contributed to developing the draft guidelines for conservators presented in chapter 9. Such practical advice is a vital part of a CDA project, cementing the links between the end users and the research organisation.

## Experimental

An experimental approach has been followed to provide objective comparisons of the performance of the different consolidants. These include investigations into the treatment components themselves and comparison of the different consolidants on stone measuring performance indicators such as porosity, surface hardness, penetration depth and colour change. Statistical analyses, along with qualitative observations, have been used to examine the results of these experiments and to assess which treatments, if any, might be suitable for future use in the museum. Table 1 summarises the analytical methods used, and figures 10 to 11 detail the sample preparation steps needed for some of these methods.

### Experimental Design

Where possible, a consistent experimental design was used for all laboratory experiments. As can be seen in figure 9, large blocks of stone were cut into smaller samples. After baseline analyses these samples were

divided evenly into groups to be treated with different consolidants. For each experiment an untreated control group of samples was kept in the same laboratory conditions as the treated samples. After curing time and retreatment as required, post experimental analyses were performed. Simple statistical analyses such as paired t-tests and one-way analysis of variance (one-way ANOVA) were then used to discover if any differences between analytical results before and after, and also between replicate groups, were more significant than could be expected due to natural variation. Before statistical analysis, the normality of data was tested using the Shapiro-Wilk normality test. The paired t-test compares pairs of results within two related samples with the null hypothesis that the mean difference between the two is zero (Miller & Miller 1993). ANOVA tests the null hypothesis that samples in two or more groups are from populations with the same mean and is used when there is more than one source of variation (for example treatment and stone type) (Miller & Miller 1993). The majority of analytical tests were performed on the same samples so there could be a direct comparison between before and after treatment. However, due to the destructive nature of some tests this was not possible for all analytical methods. In these cases, after treatment tests were compared to tests on the untreated control samples.

The following four chapters (five to eight) provide the results from the four stages of experimental investigation into the consolidants detailed within this chapter. Each stage, beginning with Chapter 5 'Developing a robust experimental methodology', follows the aims outlined within Chapter 3.

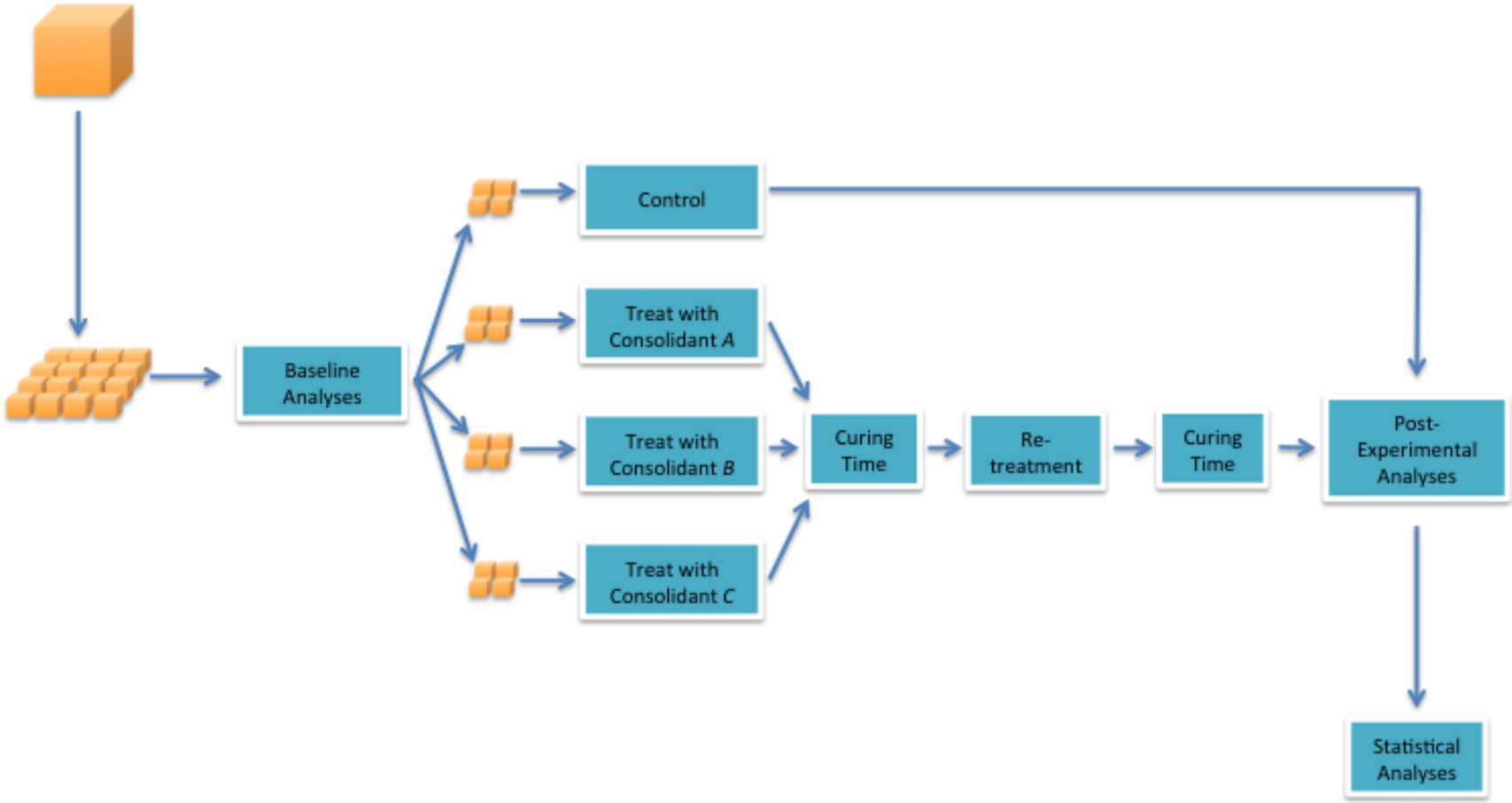



Figure 9: Schematic representation of experimental design

| Analytical Technique | Property Investigated | Equipment | Method of Analysis | Sample Requirements/ limitations | Destructive? | Initial Data Output Format | Units | Standard/ Reference |
|---|---|---|---|---|---|---|---|---|
| **Drilling Resistance Measurement System - DRMS** | Internal strength and, depth of penetration of consolidants | SINT Technology DRMS with 3mm SINT drill bit | Calculates force (N) needed to drill into stone at constant rotational speed and penetration rate | Whole sample used – drilling occurs from treated surface inwards. | Destructive | Graphical; Numerical | $Nmm^{-1}$ | (Pamplona et al. 2007) |
| **Equotip** | Surface hardness of stone | Proceq Equotip 3 and Piccolo 2 Portable Hardness Tester with D attachment | Leeb hardness based upon change in velocity between impact and rebound | Difficulties if surface too irregular. Samples <2kg or <25mm thickness should be coupled to strong base | Minimally | Numerical; Graphical | HLD Leeb D | (Viles et al. 2010) |
| **GrindoSonic** | Internal strength via E Modulus | GrindoSonic Mk5 Industrial | Impulse excitation Technique. Results translated into E-Mod using GeneMod software | Sample length ≥ 3 x sample width | Non-destructive | Numerical | MPa | ASTM E1876 |
| **Ion Chromatography** | Presence and concentration of salts | Dionex Ion Chromatograph | Separation of ions and polar molecules based upon charge | Powdered sample from stone prepared as in Figure e. | Destructive | Numerical | $mgL^{-1}$ | ... |

| Analytical Technique | Property Investigated | Equipment | Method of Analysis | Sample Requirements/ limitations | Destructive? | Initial Data Output Format | Units | Standard/ Reference |
|---|---|---|---|---|---|---|---|---|
| **Karsten Tubes** | Water Penetration Capacity (WPC) | Proceq Karstenröhrchen wasserindringprüfer (Karsten tubes) | Drop in water level in graduated, glass tube bonded to sample surface, measured over time | Dry, relatively even, dust free surface | Minimally destructive | Numerical | $mLmin^{-1}$ | BS EN 1925: 1999 |
| **Mercury Intrusion Porosimetry - MIP** | Pore size and distribution | Micromeritics AutoPore IV 9500 V1.09 with 09-0582 5ml Bulb, 1.131 Stem, penetrometer | Mercury intruded measured through changes in capacitance. Cylindrical pore geometry assumed using Washburn equation | Clean sample needed; pores measured between 500µm and 3.5nm; sample size preferably ≤ 10mm3 | Destructive | Numerical | Cumulative Intrusion/ Extrusion: $mLg^{-1}$ Pressure: MPa | (Webb 2001, Giesche 2006) |
| **Pundit** | Internal strength via E Modulus | Proceq Pundit Lab with 250kHz sheer wave transducers | Ultrasonic Pulse Velocity measurements converted into E-Mod. | Initial use suggest a minimum density of samples is necessary | Non-destructive | Numerical; Waveform | GPa | EN12504-4 |

| Analytical Technique | Property Investigated | Equipment | Method of Analysis | Sample Requirements/ limitations | Destructive? | Initial Data Output Format | Units | Standard/ Reference |
|---|---|---|---|---|---|---|---|---|
| **Scanning Electron Microscopy - SEM/VP-SEM** | Depth of penetration, deposition within pores. Elemental mapping of consolidant distribution | Hitachi S3700 and Hitachi S4800 with EDS attachment | Images acquired using secondary electrons (SE) or back-scattered electrons (BSE) | VP-SEM can take whole samples or chips - SEM requires samples to be made into cross-sections and/or gold or carbon coated as described in Figure d. | Destructive | Digital Image; Elemental Map; Spectra | N/A | (Stutzman, Clifton 1999) |
| **Spectrophotometry** | Colour change | Konica Minolta CM 700d/600d; lluminant D65; 10 degree of observer | Change in colour space defined using CIE L*a*b* $\Delta E_{00}$ | N/A | Non-destructive | Numerical; Graphical | L*a*b* | CIELAB $\Delta E_{00}$ (Konica Minolta 2007) |
| **Thin Section Petrography** | Distribution of consolidant, depth of penetration and how pore spaces affected | Leica DMRX with Leica DFC500 camera | 30µm thin sections analysed using optical light microscopy | Samples need to be made into thin sections on microscopy slides. | Destructive | Digital Image | N/A | EN 12407 |

| Analytical Technique | Property Investigated | Equipment | Method of Analysis | Sample Requirements/ limitations | Destructive? | Initial Data Output Format | Units | Standard/ Reference |
|---|---|---|---|---|---|---|---|---|
| **XRD** | Mineralogical composition | Phillips PW 1120/90 diffractometer using Cu Kα radiation | Xrays diffracted from sample in characteristic pattern to demonstrate crystal types present | Sample needs to be finely powdered | Destructive | Diffraction Pattern | N/A | (Corbeil 2004) |
| **Other** | Dimensions, weight, density, photos etc | Multiple | N/A | N/A | Non - destructive | Multiple | Multiple | - |

**Table 2: Summary of analytical methods used within the Back to Nature project**

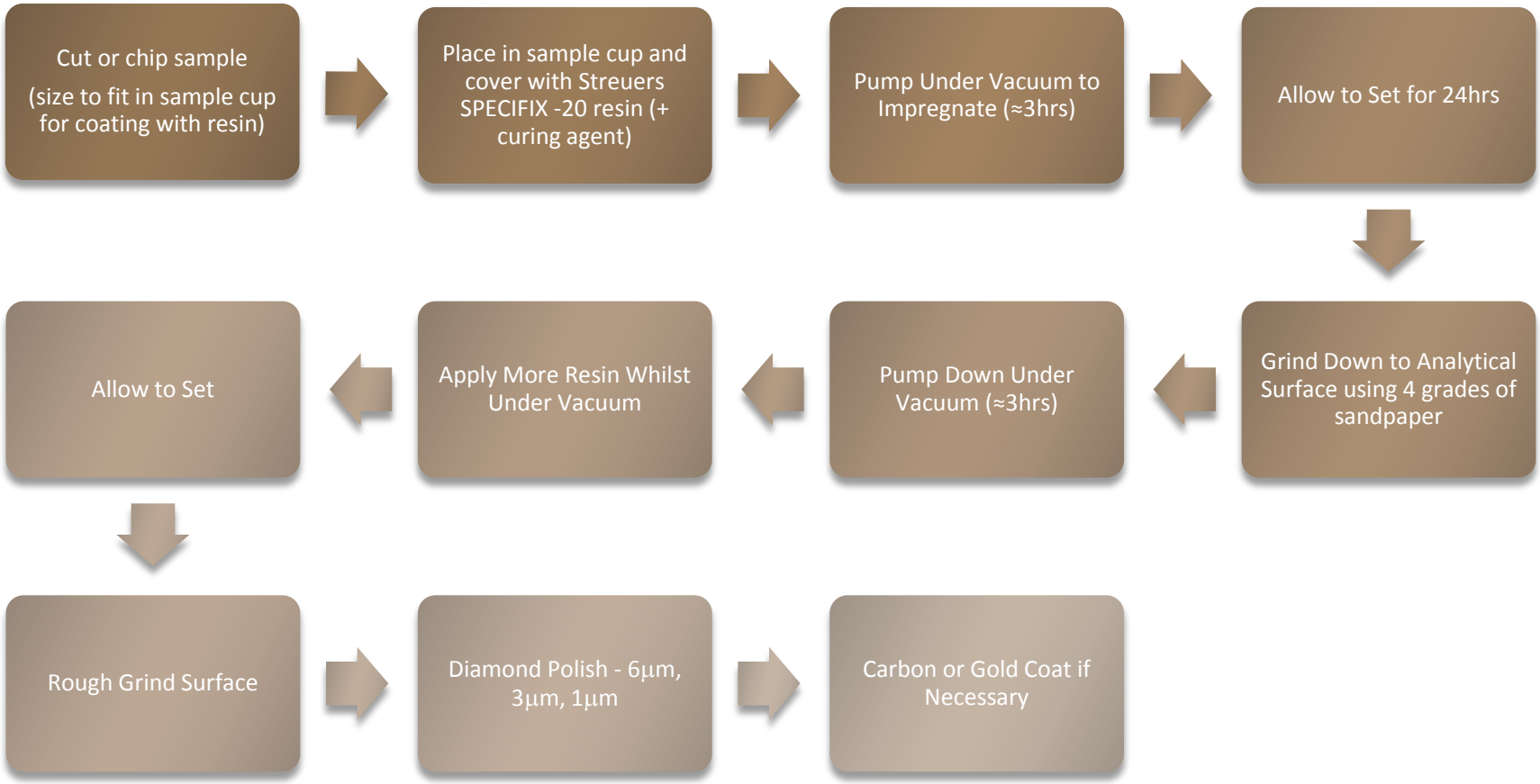



**Figure 10: SEM sample preparation**

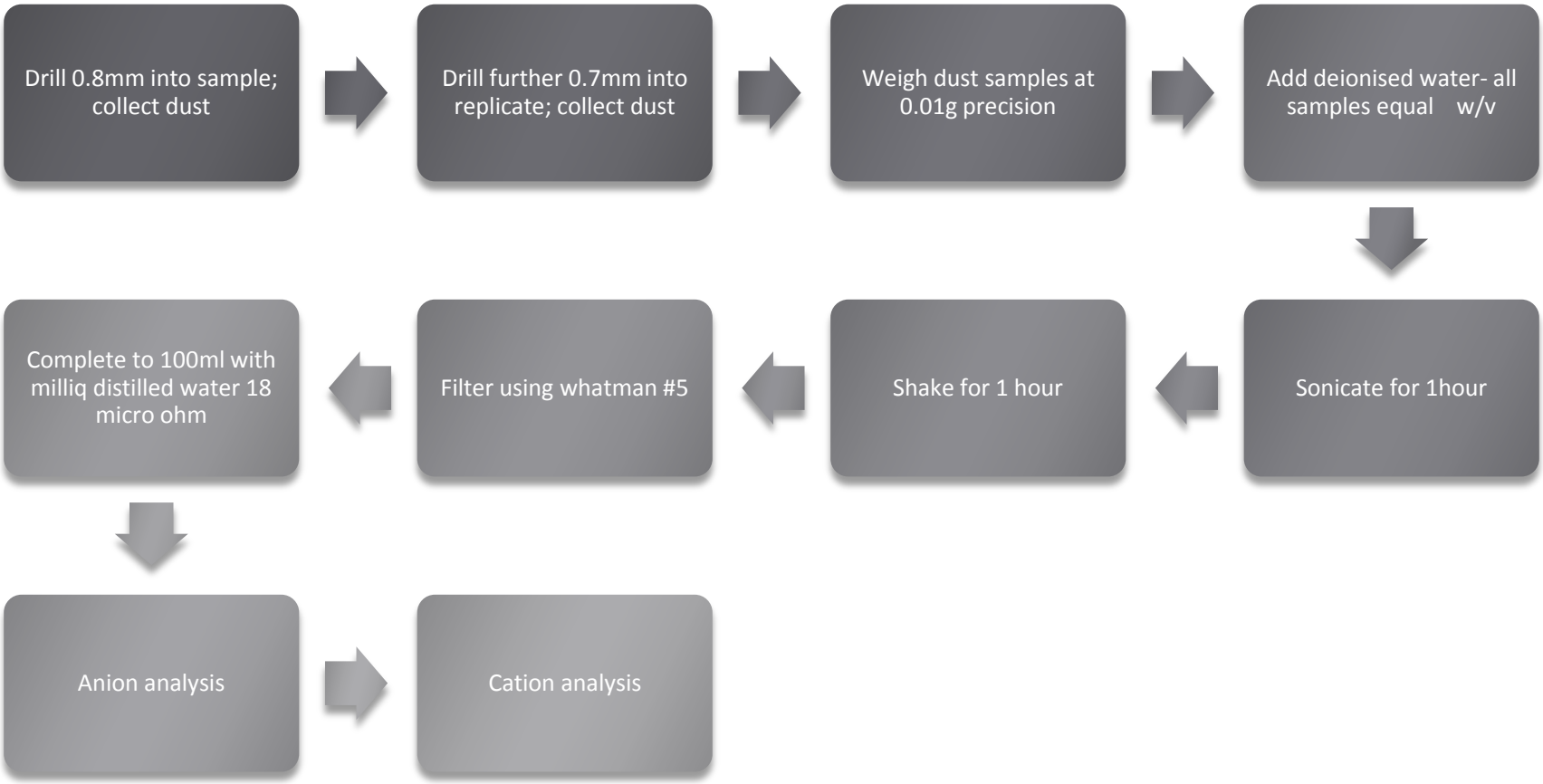



**Figure 11: Ion chromatography sample preparation**

# Chapter 5

*Developing a robust experimental methodology to evaluate the comparative performance of stone consolidants*

## Introduction

Stone has been used throughout human history to make tools, buildings and as a medium for artistic expression. Deterioration of stone, from many different agents including biological, chemical and physical, both natural and anthropogenic, can therefore represent irretrievable loss of our cultural heritage. Stone decay can manifest itself in a variety of ways; cracking, scaling, fissuring, on both a macro and microscopic level (Fitzner & Heinrichs 2002, Favaro et al. 2008). The negative effects of climatic changes, such as the influence of acid rain, have been highlighted in recent decades and this in part has led to increased research into stone conservation and the prevention of stone decohesion is a growing field (Liu & Zhang 2007, Lobovikov-Katz 2009, Herrera Videla 2009). To mitigate stone deterioration, consolidation treatments that improve internal cohesion are often applied.

There are many potential consolidants available on the market, with new ones also being developed, and studies of both the conservation products and stone substrates have shown that there is not one product for every situation (Karatasios et al. 2009, Price 1982). Therefore when undertaking a new programme of conservation it is usually advisable to test potential consolidants experimentally to decide which will be the most effective. Along with effectiveness, it is also important to check that any consolidant applied will not adversely affect the stone (De Buergo & Fort González 2001). Clifton and Frohnsdorf (1982) provide a list of requirements for categorising stone consolidants including analysis of penetration depth and the effect on permeability, moisture transfer, appearance and durability. For new consolidants, it is important to analyse how they interact with different stone types (De los Santos et al. 2008, Jimenez-Lopez et al. 2008).

Differing treatment protocols and how changing the application procedures alters the effectiveness of a consolidant, are also often the focus of investigations (Ferreira Pinto & Rodrigues 2008, Nardini et al. 2008, Pinna, Salvadori & Porcinai 2011). Building on these investigations into the stone consolidants themselves, are those into the different techniques and evaluation parameters used to analyse the materials, or to assess treatment effectiveness (Casadio & Toniolo 2004, Theoulakis, Karatasios & Stefanis 2008). Just as there is no one consolidant for all situations, there is no one method to determine effectiveness. Many researchers have therefore followed a procedure of combining data from multiple tests to reach an overall conclusion (Sasse & Snethlage 1996, Moropoulou et al. 2000, Laurenzi Tabasso & Simon 2006). The British Museum, in conjunction with the School of Geography and the Environment at The University of Oxford, developed the *Back to Nature* project to investigate potential new consolidants to use on some of the limestone artefacts in their stone collections. This process involves investigations from all across the different areas mentioned here. The first experiments, detailed in this chapter, assess methodological issues such as the type, size, shape and number of replicates to be used. The main aims of the section of the project discussed within this chapter are summarised as follows and described in more detail below:

- To investigate different analytical methods and sample characteristics such as size and weight of replicates, in order to develop a basic methodology to use in future investigations.
- To compare results between fresh and weathered stone treated with the same consolidants to see if the weathering state of stone replicates affects the interpretation of consolidation action.
- To assess the variability between replicates tested to inform on the number of replicates needed for future investigations.
- To gather initial ideas about the performance of the two different consolidants investigated

The majority of experiments involving consolidants have been conducted upon stone blocks or replicates in the laboratory. Frequently, in previous laboratory investigations into the nature and effectiveness of consolidants, the stone samples used have been solely cut from fresh, sound, stone (Theoulakis, Karatasios & Stefanis 2008) . Fresh stone has some significant advantages over weathered; it is not only easier to obtain, but has a known history; there is less scope for unknown factors to affect the results of any investigation. However, it is extremely unlikely that in a conservation situation consolidants would be applied to fresh stone. The relevance of results from investigations into such samples could therefore be questioned. Where samples for consolidation testing have been taken from both fresh and weathered stones (De Witte, Charola & Sherryl 1985) , little comparison has been made between results. The significance of the weathering status of the stone upon the results is therefore not really known. By comparing results from fresh and weathered stone samples, both treated with the same consolidants under the same conditions, the first major aim of this investigation was to gain a clearer idea of the effect of weathering of the samples upon the assessment of consolidants.

Another highly variable aspect of previous investigations into consolidants is the number of stone replicates tested. In order to calculate mean and standard deviation, a minimum of 3 replicates of each treatment on each stone type is needed. However, it is well known that stone can vary even between blocks cut from the same level in the same quarry. Three replicates may be the minimum, but not actually enough to provide a true indication of the performance of a consolidant. Many previous investigations where looking at factors such as differing stone type, consolidant or treatment procedure, may involve many replicates overall, but actually only have two or three replicates per factor (Park & Shin 2009}, Mosquera, de los Santos & Rivas 2010, Moropoulou et al. 2003). Whilst it is common practice to describe the main features of the stone type used for samples – such as origin, porosity, water absorption, and most reports specify dimensions, many do not indicate the number of samples or replicates (Salazar-Hernandez et al. 2010}, El-Midany, Khallaf & El-Mofty 2011) . Stone can be a very expensive material, and the testing of multiple characteristics can be a costly and time-consuming process, increasing with a greater number of replicates. Sometimes it is just not possible to acquire a large quantity stone of a similar type to the artefact or building to be conserved

(Simionescu, Aflori & Olaru 2009). The disadvantages therefore of having a larger number of replicates are clear. However, are these disadvantages outweighed by the possibility of misinterpreting the results? Where the number of replicates tested is not apparent, it can sometimes be estimated by other data given, but this in itself adds an element of uncertainty when interpreting the results. The second major objective of this study was therefore to assess the variability between replicates when testing different stone properties and to look at the number of samples needed for an accurate interpretation of consolidant effectiveness.

## Experimental

### Characterisation of Materials

To investigate the variability between replicates and to see if there was a difference between fresh and weathered stone, two different consolidation treatments were used. Criteria used for selection were that one would be a more commonly used organic silane treatment, and also be one that had been used in the past at The British Museum, and that the other would be one of the new inorganic treatments under consideration for future use in the museum. The two selected were: SILRES® BS OH 100 by Wacker Chemie AG, a silicic acid ester used in The British Museum during the 1980's; and the new possible consolidant based upon an application of ammonium oxalate – diammonium salt in water at 5% w/v (Matteini 2007).

As the predominant aim of the entire project is to assess new consolidants for limestone artefacts in the museum it was decided that limestone replicates should be used here to assess methodological issues. For this initial investigation the provenance of the limestones was not important, they did not have to approximate to any artefacts in the museum. Instead, the importance was placed on there being two limestones, one freshly quarried, and one old and weathered, that would be very close to one another both physically and chemically- if possible from the same source. The two selected were Elm Park (fresh) and Hartham Park (old). These are both Bath limestones. Pale buff in colour, they are oolitic limestones of middle Jurassic age. More detailed descriptions of the physical and chemical characteristics of these limestones can be found in Chapter 4. Importantly, there was a large enough supply of both within the

Oxford stone stores, to produce the large number and size of replicates involved in this study. The Elm Park replicates were cut from an unweathered block, obtained from the quarry a few years ago, and stored inside since then. The Hartham Park stone had been removed from St Edmunds Hall and St John's Colleges during restoration and repair work in the last five years and had been exposed in the Oxford environment for over 100 years.

## Preparation

The old and the fresh limestones were cut into prismatic replicates measuring 50x50x150mm. This shape was selected to allow for a range of testing methods before and after treatment. There were 8 replicates of fresh and 8 of old per consolidant, giving 32 replicates in total. This would allow for direct comparison between fresh and weathered stone for each consolidant and an assessment of each consolidant in comparison with one another.

The top surface of each replicate was divided into three and the consolidant applied to the middle 50x50mm area (figure 12). Both treatments were applied as a liquid by pipette until the surface reached full saturation. The reason for only applying consolidants to the central area was so that there would be one treated area directly comparable to two untreated (control) ones either side. For each characteristic measured, values were taken from each of the untreated areas as well as the central treated area (Figure 13).

The replicates were all kept under lab conditions in the same fume cabinet with temperature and humidity recorded with an iButton datalogger. The consolidants were allowed to cure for three weeks after application as per the recommendation from the supplier (Wacker Chemie AG). There were two cycles of this procedure.



Figure 12: First application of consolidant

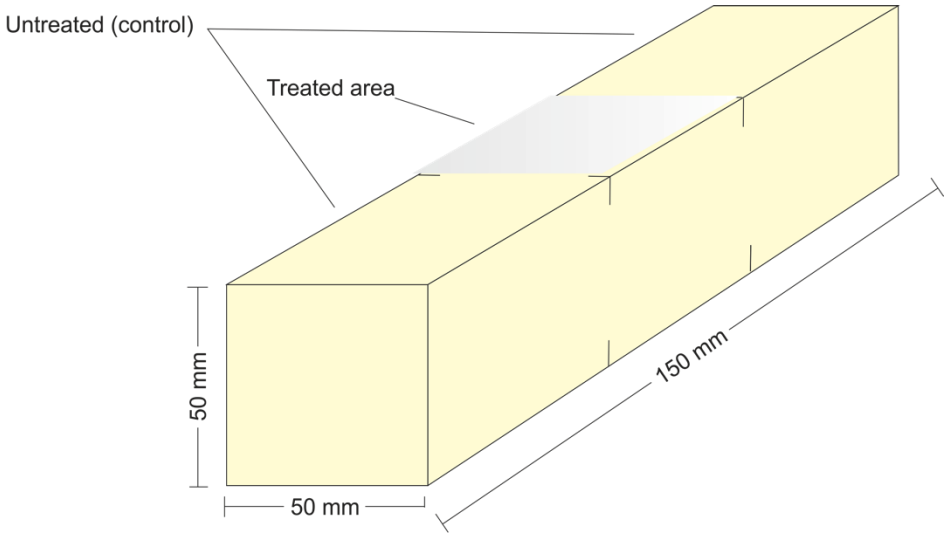



Figure 13: Replicate design

## Methods

Whilst there are a variety of analytical techniques that can be used to quantify the physical parameters of stone samples and how they respond to consolidant treatments for this initial investigation of number of

replicates and weathering status a few key ones were selected. Criteria for selection included those that were non-destructive, quick to perform and easy to interpret.

### Mechanical Properties

Mechanical properties were examined to assess the effect of each consolidation treatment on the surface and internal cohesion of the stone. Surface hardness was determined using a Proceq Equotip (Equotip 3); a dynamic hardness tester which uses a rebound technique to calculate *Leeb hardness* using change in velocity (Viles et al. 2010). 10 measurements were taken per 50x50mm area on the topmost surface of each replicate; including both the treated area and the control areas on either side. Readings were recorded before and after each application of consolidant.

The modulus of elasticity (Young's Modulus), as an indicator of internal strength of the stone, was calculated using GrindoSonic. The GrindoSonic system measures the elastic properties of materials using the "impulse excitation technique". The stone replicate is subjected to a light mechanical impulse and then produces a transient mechanical vibration. The frequency of this vibration depends on the mass of the object and its stiffness, which is determined by its shape and dimensions and the modulus of elasticity of the material. The modulus of elasticity for each replicate was calculated with the frequency values obtained by the GrindoSonic before and after both applications of consolidant. The GrindoSonic provides longitudinal, flexural and torsional measurements depending where the reading is taken from on the replicate. These measurements are then inputted into the accompanying software program *GeneMod* which calculates the modulus. Five repetitions per measurement per replicate were taken, giving a total of fifteen measurements for each replicate at each stage of the process. It is important to note that it is not possible to measure the central treated area without the outer areas due to the way in which the GrindoSonic operates.

### Colour Properties

To assess the effect of the 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 with a 10° observer and using colour data software *SpectraMagic xs*. 10 measurements were taken per 50x50mm area on the top surface to give a mean colour difference for each area. The CIE-Lab system expresses the difference between two colours as $\Delta E_{00}$ – the distance between the two colour locations:

$$\Delta E_{00} = \sqrt{\left(\frac{\Delta L'}{K_L S_L}\right) + \left(\frac{\Delta C'}{K_C S_C}\right)^2 + \left(\frac{\Delta H'}{K_H S_H}\right)^2 + R_T \left(\frac{\Delta C'}{K_C S_C}\right)\left(\frac{\Delta H'}{K_H S_H}\right)}$$

**Equation 3: CIE 2000 colour difference formula**

Based upon the lightness difference ΔL*, saturation difference ΔC*, and hue difference ΔH*, with correction using weighing coefficients (SL, SC, SH) and constants called parametric coefficients (kL, kC, and kH) (Konica Minolta 2007).

### Distribution of Consolidant

Distribution and penetration depth of consolidant were observed using variable pressure and high vacuum scanning electron microscopy (VP-SEM Hitachi S-3700). Replicates were first observed whole using variable pressure SEM (at 30Pa pressure) to look at surface distribution and appearance of the consolidant. Images were taken using back-scattered electrons (BSE); high energy electrons from the electron beam are reflected or 'back-scattered' due to elastic scattering interactions between the beam electrons and atoms in the sample. Elemental maps of the surface were taken using energy-dispersive X-ray spectroscopy (EDS). EDS uses quantitative analysis of the X-ray spectra emitted by the sample when under the electron beam to determine elements present in the sample, and their relative concentrations. After this, 10mm cubed samples were cut from the surface, vacuum impregnated with resin and mounted to provide a cross-section to look at depth of penetration of consolidant and the interface between the consolidant and stone substrate using the SEM under high vacuum (rather than in variable pressure mode).

### Water Penetration Capacity

Water penetration was measured before and after treatment using the Karsten Tube penetration test. The Karsten Tube test involves a glass tube with a base diameter of 25mm, bonded to the surface of the replicate with putty. Water is filled to the 0 level on a graduated scale on the side of the tube. 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. The mean amount of water absorbed over time was graphed for each sample.

## Results and Discussion

### Surface Hardness – Equotip

Measurements were taken at the start, and after 1st and 2nd applications of consolidant, on both untreated and treated areas of each replicate. 10 repetitions per 50x50mm area on the surface were taken each time and the mean and standard errors calculated from these. This provided the opportunity to compare the effectiveness of the consolidant but more importantly for this investigation, a chance to compare the variation over the number of replicates and between the fresh and old replicates.

Figure 3 shows the Equotip results as mean surface hardness for each replicate over time with the first values (▼) taken before any treatment was applied, the second values (●) after the first application of consolidant, and the third (■) taken after the second application of consolidant. Each pair of graphs in figure 13 shows the values taken from the same blocks, with the treated results measured on the central 50x50mm area and the untreated or control results from the untreated 50x50mm areas either side.

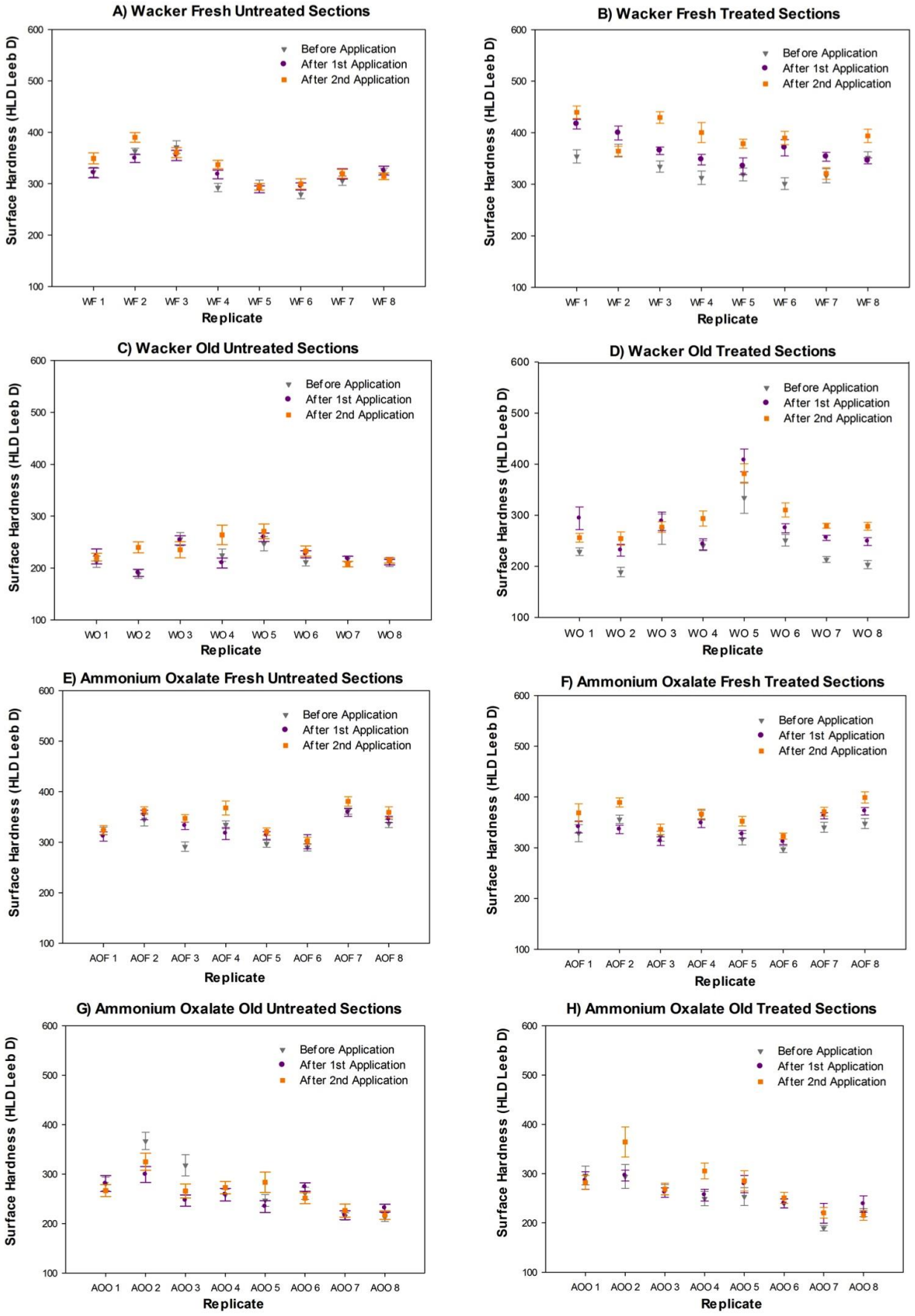



Figure 13: Graphs to show mean Equotip values with standard error bars a) Wacker Fresh untreated, b) Wacker Fresh treated, c) Wacker Old untreated, d) Wacker Old treated, e) AmOx Fresh untreated, f) AmOx Fresh treated, g) AmOx Old untreated, h) AmOx Old treated

There appears to be quite a large variability between all replicates. Research has shown that there is often variability between measurements taken on natural stone with an Equotip and that larger sample sizes are generally needed (Viles et al. 2010). Greater differences between replicates would perhaps be anticipated with the older stone than the fresh. Indeed for both the ammonium oxalate and Wacker treated replicates there is greater variability within the old replicates- demonstrated by larger error bars on the graphs, but it appears also to be that there is variability within the freshly quarried replicates. This variation presents itself in two ways. Firstly each individual replicate is slightly different to the others in its category even when they have been cut from the same block of stone, with Leeb values ranging across around 100 Leeb altogether. Secondly there is an inherent variability over time within each replicate as even the untreated areas provide slightly different results every time they are tested (on Fig. 13 Graphs A, C, E and F the ▼, ● and ■ rarely fall in exactly the same point on the graph). The inherent variability in individual replicates could be addressed by taking more Equotip values to obtain a truer estimate. The variability between the replicates perhaps indicates that a greater number need to be used than in past investigations.

Both the Wacker Fresh and Wacker Old replicates demonstrate a clear increase in surface hardness after treatment. This is visible on the graphs, by assessing the difference between the before (▼), the values after the first application of consolidant (●), and the values from after the second treatment (■). Many replicates, for example WF1 and WF3 (Figure 13 Graph B), WO2 and WO8 (Figure 13; Graph D) experienced an increase in surface hardness of over 100 Leeb. This is especially noticeable in comparison with the untreated areas on both sets of replicates (Figure 13; Graphs A and C respectively) and is backed up by t-tests for both, where the difference is statistically significant at the 95% confidence interval ($P = 0.002$ and $P = 0.038$ respectively). It is important to note however that not all the replicates (WF2, WF7 (Figure 13 Graph B) and WO1, WO3, WO5 (Figure 13 Graph D) experienced an increase in surface hardness. This further highlights the importance of a large number of replicates to be included in any testing of consolidants.

Figure 13 shows no clear trends in surface hardness after treatment on either fresh or old ammonium oxalate treated replicates, although there is a slight trend towards increased surface hardness on the fresh replicates (See figure 13, Graph F). Statistically, a t-test at the 95% confidence interval suggests that the difference in surface hardness on the ammonium oxalate fresh replicates was greater than would be expected by chance ($P = 0.029$), compared to the old replicates where the difference is not significant. A couple of the old replicates (AOO2 and AOO3 in figure 13 Graph H) do demonstrate a clear increase in surface hardness after treatment. This, coupled with the fact that the ammonium oxalate does seem to be having an effect on the fresh stone, suggests that perhaps more treatments of ammonium oxalate are needed to produce a more obvious impact upon surface hardness, particularly on the old stone.

With both treatments the difference in surface hardness appears to be more significant on the fresh replicates than the old. This suggests caution should be applied when assessing the effectiveness of consolidants that have only been tested on fresh stone replicates. It is also important to note that increasing surface hardness might not be directly comparable to the effectiveness of a consolidant. Whilst harder surfaces may be more resistant to deterioration, it is also important to assess the interaction between the surface and the substrate to check the increase in strength in the upper layers is not causing material to detach from the lower substrate.

## Internal Strength – GrindoSonic

An average Modulus of Elasticity for each replicate was calculated from the 15 measurements taken, as described in section 2.3.1. Then an overall mean was calculated for the fresh and weathered groups for both consolidants. The E Modulus for each group before and after application of consolidants is plotted in Figure 14.

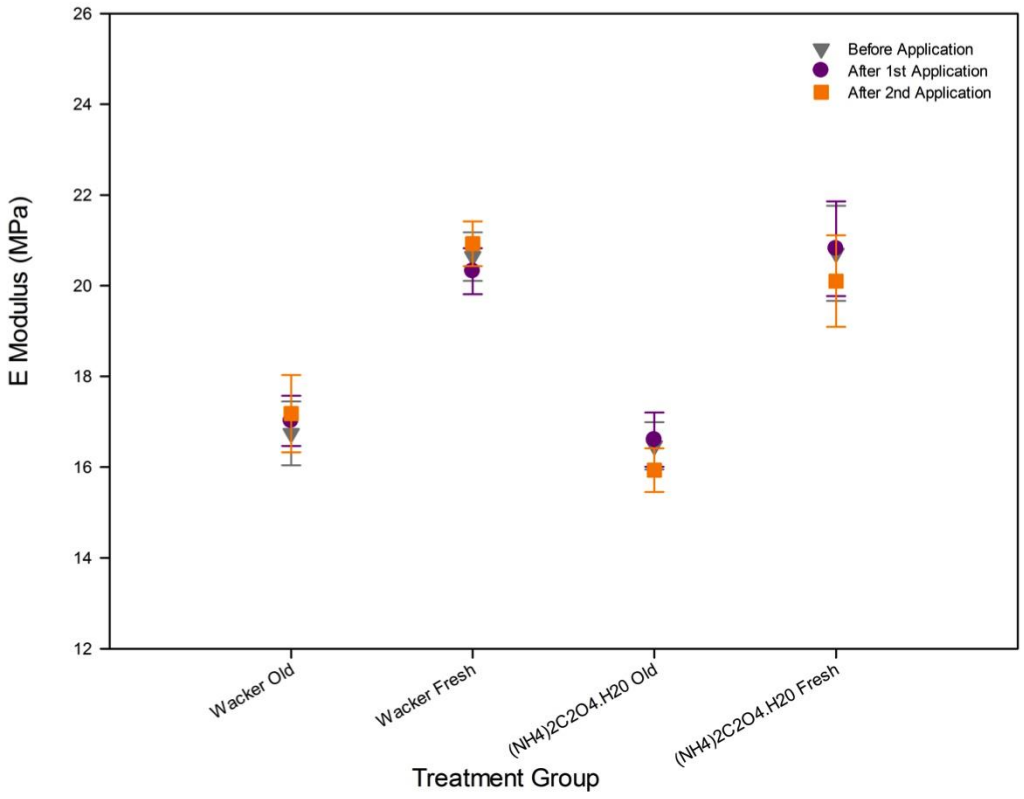



**Figure 14: Variation in E-Mod between fresh and weathered stone replicates before and after application of consolidants**

From Figure 14 it can be seen that there is an obvious difference in the EMOD values between the old stone and the fresh, with the old weathered stone having a much lower value (around 17 compared to around 21 for the fresh), and hence less internal strength, as would be expected. However, there does not appear to be any consistent trend in EMOD values with either consolidant on either stone type. And t-tests for each group of replicates, produced non-significant results. The reason for a lack of change in internal strength could potentially be due to the application method, the suitability of the GrindoSonic as a measurer for internal strength or may mean neither consolidant improves internal strength. Most likely it is due to the relatively small area of application; as only a small area on one surface was treated it is unlikely that this would have an effect on the overall internal strength of the stone. Treating one entire long face (or all faces) in future experiments would enable a better assessment of any changes in strength.

## Water Penetration (Karsten Tube)

Often consolidants also protect the stone by reducing the ingress of water, however it is important that any consolidant does not block pore spaces entirely so that water vapour can still be exchanged. A very easy and simple method to measure the penetration of water into stone uses the Karsten Tube penetration test. Amount of water penetrated was calculated for the replicates before and after application of consolidants. As this test brings water into direct contact with the treated surface, and this could impact upon subsequent testing, it was decided to just do this test after the 2nd and final application, rather than after the 1st and 2nd.

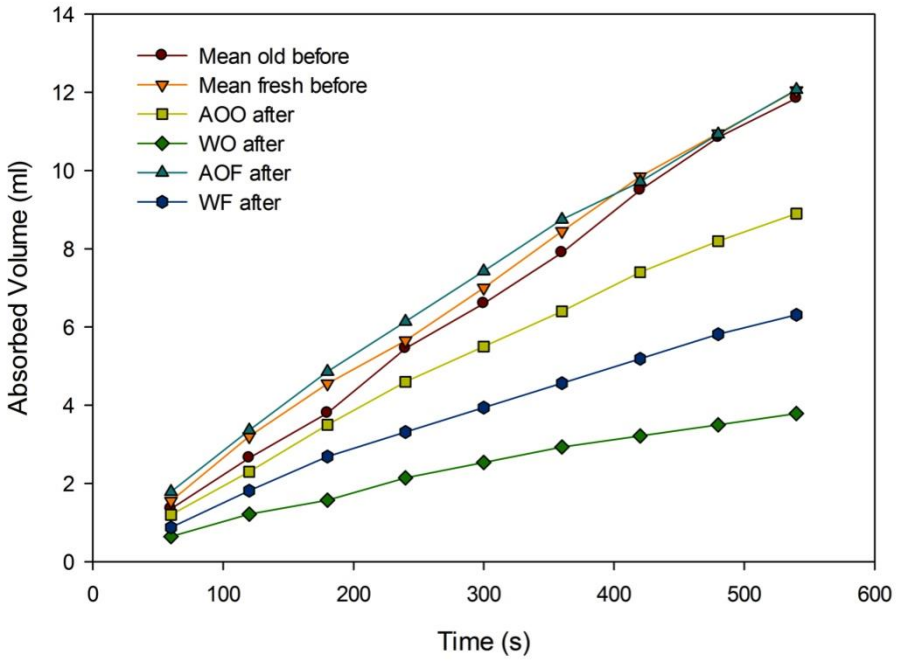



**Figure 15: Mean absorbed volume of water over time in old (AOO and WO) and fresh (AOF and WF) stone samples after treatment with Wacker SILRES BS OH 100 (WO and WF) and ammonium oxalate (AOO and AOF) in comparison with mean absorbed volume before treatment.**

The results from the ammonium oxalate treated replicates and the Wacker treated ones were very different. As illustrated in Figure 15, the Wacker had a noticeable effect on the absorbed volume of water, lowering it in all on both the fresh and the old stone. Before treatment, there did not appear to be a great difference between the amount of water absorbed by the fresh and the old stone. After treatment with the Wacker, the old replicates have a lower water penetration capacity than the fresh, suggesting the Wacker had a greater effect on the old stone. The older replicates were cut from a block of Hartham Park, which has a higher porosity than the Elm Park. It might be expected therefore that the older replicates would have a higher WPC than the fresh. However, the higher porosity could mean a greater amount of Wacker was absorbed, leading to the increased effect.

As indicated in Figure 15, the ammonium oxalate did not have such an obvious effect as the Wacker. The fresh stones treated with ammonium oxalate had the same water absorption as before treatment. The old stones had reduced water penetration however not to the extent of either the fresh or old stones treated with the Wacker.

The variability seen between replicates within the Karsten Tube experiments add weight to the idea that a greater number of replicates is needed to gain an accurate interpretation of the effects of consolidants. Furthermore, the difference between results on the old and fresh stone in the Wacker experiments, show the importance of considering the degree of weathering of replicates.

## Spectrophotometer

One of the more visually obvious effects of a consolidation treatment is how it can change the chromatic parameters of the stone.

| Sample group | ΔL* | Δa* | Δb* | ΔC* | ΔH* | $\Delta E_{00}$ | $\Delta E^*_{ab}$ |
|---|---|---|---|---|---|---|---|
| **AOF** | -6.11 | 1.77 | 4.43 | 4.70 | -0.79 | 5.25 | 7.77 |
| **AOO** | -4.30 | 1.21 | 2.53 | 2.72 | -0.71 | 3.71 | 5.44 |
| **WF** | -4.16 | 0.87 | 2.62 | 2.74 | -0.35 | 3.36 | 5.01 |
| **WO** | -4.20 | 0.78 | 2.63 | 2.73 | -0.32 | 3.40 | 5.06 |

**Table 3: Spectrophotometer results by sample group**

When considering the global colour variation $\Delta E_{00}$, a value < 1 is considered indistinguishable to the human eye. On average, both treatments, on the old and the fresh stone, gave $\Delta E_{00}$ values > 1 with only one replicate (WO7) recording $\Delta E_{00} < 1$.

As can be seen in Table 2, the AOF replicates demonstrated the most significant colour variation with the other three groups recording fairly similar values. One-way ANOVA testing shows that whilst the AOO replicates have a slightly higher $\Delta E_{00}$, the difference between these and the WO and WF replicates is not significant. All the colour changes recorded are in the same direction; the treated replicates became darker, the colour more saturated, more red, and more yellow.

It is difficult to conclude therefore whether the ammonium oxalate treatment causes greater colour changes on the stone than the Wacker silane treatment. The difference between the chromatic changes on the fresh stone treated with ammonium oxalate, compared to the changes on the old stone, is noticeable and statistically significant in the one-way ANOVA test. This clearly demonstrates a case where the consideration of whether to use fresh or old stone in future experiments is important. If only fresh stone had been used in this experiment, it would appear that the ammonium oxalate treatment had caused a much greater colour alteration and would perhaps be considered less desirable.

## SEM Observations

The surface of both fresh and old replicates treated with Wacker and ammonium oxalate were first observed with variable pressure Scanning Electron Microscopy (VP-SEM). This allowed for the whole replicate to be put in the vacuum chamber, with the advantage of being able to view the whole surface; far larger than the traditional sample size under high vacuum, without the need for destructive sampling or carbon coating. The whole replicate was put in the VP-SEM and the top surface viewed. On the surface of the Wacker treated replicates it was possible to see a difference in the morphology and identify the treated versus the non-treated areas, with the treated area (on the right hand side of figure 16) appearing much more smooth and with fewer loose fragments. This visible difference was confirmed by mapping Si present on the surface, which showed a higher concentration in the treated area (appearing as white, yellow to bright orange on the map).

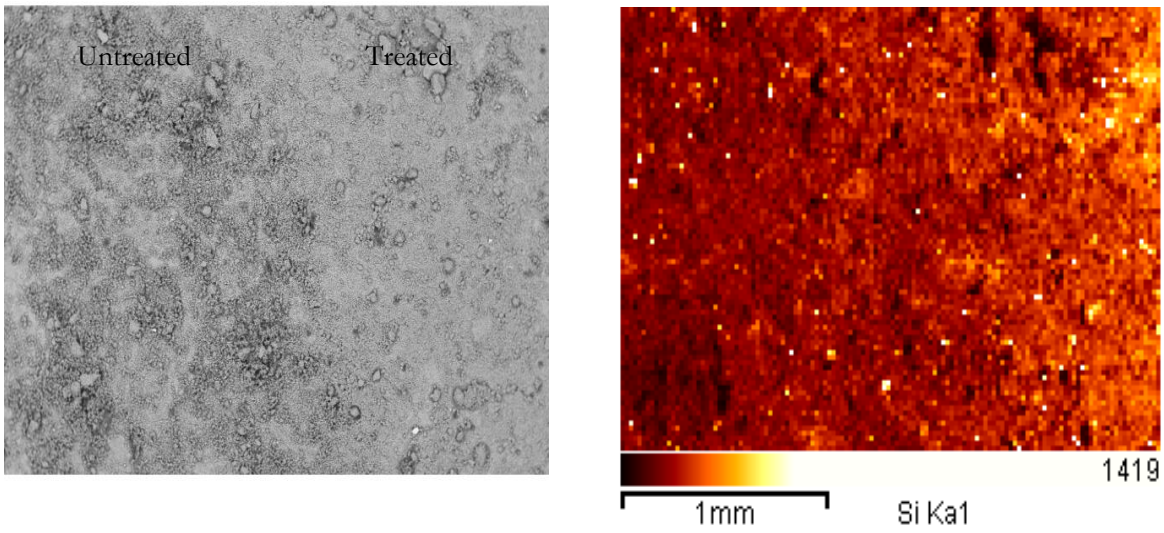



**Figure 16: BSE SEM surface view of WO2 (left) and Si energy dispersive X-ray mapping (Oxford Instruments INCA X-Max detector) of same surface (right) using 30Pa pressure, 20kv, working distance 10.0mm)**

It was not possible to see a difference on the surface of the replicate treated with ammonium oxalate when viewed under VP-SEM. This suggests the ammonium oxalate did not have such a great impact upon surface morphology.

A 1cm cube sample was then cut from each of the replicates and made into a cross section after vacuum impregnation. The aim was to look at the penetration depth of the consolidants and how it had filled the pore spaces. However it was not possible to see anything conclusive. More extensive examination at a higher resolution, staining of the consolidant, or another method such as thin section petrography, might prove more useful when assessing penetration depth visually.

## Conclusions

The experiments in this study were designed with several aims in mind:

- To develop a basic methodology to be applied to future investigations (this included assessing size and shape of replicates and analytical techniques to be used)
- To assess the impact of the initial degree of weathering of stone replicates on results
- To look at the number of replicates needed to produce a reliable interpretation of the effects of consolidants.
- A subsidiary aim was to gather initial ideas about the use and effectiveness of the two consolidation treatments tested.

Lessons were learnt from these experiments with reference to the size and shape of replicates for future experiments. The shape used here was dictated by the GrindoSonic, however the large size would make

sourcing future stone difficult. The large size was chosen to make it possible to observe large penetration depths, however it appears that the consolidants did not penetrate very deeply. In future experiments replicates could be smaller to allow for a larger quantity. Alternative methods to the GrindoSonic could be used to assess changes in internal strength which would not require the samples to the three times as long as wide.

Differences between the fresh and the old stone replicates were observed during testing of surface hardness, water penetration capacity and chromatic parameters. These differences suggest that the consideration of the degree of weathering of a test specimen or replicate is important. This is especially so where the difference is so significant that it could impact upon the choice of one consolidant over another. The most obvious example of this is with the colour difference observed on the fresh replicates treated with ammonium oxalate in comparison with the old. In this case, if only fresh replicates had been used in a comparison study of the consolidants, the Wacker would seem preferable with a much lower colour difference. With both consolidants the increase in surface strength appeared to be greater on the fresh replicates than the old. This could mean that if only fresh replicates were used then the consolidation effect of a treatment may appear greater than would actually be experienced by a weathered artefact. Combined, these observed differences suggest that to gain an accurate impression of the effect of consolidation treatments on stone, weathered stone needs to be used in the experiments. This could either be old stone that has been weathered naturally, or fresh stone artificially aged before treatment. In some of the experiments, for example when using the Equotip, there was a greater variability between individual measurements on the old stone (as evidenced by larger error bars on Graphs C and G Fig. 3) compared to the fresh. Artificially aged stone could have the advantage of controlled weathering to reduce the variability between replicates.

One of the main observations from these experiments is that there is a considerable variation between individual replicates within the replicate groups (given 8 replicates); this is demonstrated particularly with the Equotip and Karsten Tube measurements. This suggests that a large number of replicates are needed to

produce a statistically reliable result. Previous investigations into consolidants do not often specify the number of replicates used to trial the treatment, when they do, the number is often fairly small usually three or five. The variability seen in this study suggests that these numbers are too small and that a larger quantity of replicates should be used. The time taken to actually treat the replicates was not great so a larger quantity should not be a problem time-wise. However, the quantity would impact upon the amount of stone required and hence may hence have a secondary effect on the size of replicates used – if stone availability and cost is a limiting factor.

Part of the aim of this study was to gather initial ideas about the effectiveness of the two treatments. Further analytical tests such as those to look at penetration depth and effect on salts would be needed to accurately compare the two, however the results from the analytical tests used within this experiment could provide initial ideas. The Wacker silane treatment appears to have had a greater impact upon surface hardness than the ammonium oxalate. However, the ammonium oxalate treatment is still in its early stages of investigation and may need adaptation in terms of method of application. This is compared to the Wacker, which is a proven consolidant and was applied as directed by the manufacturer. The Wacker also had a noticeable effect on the amount of water absorbed during the Karsten tube penetration test, whereas the ammonium oxalate only did on the old stone and not to such a great extent.

The experiments detailed within this chapter looked at key factors such as sample shape, size and degree of weathering but before using the information gathered here to compare the consolidation treatments an investigation into CIPS treatment needed to be conducted. This was primarily due to the fact CIPS had not been used within the museum environment before. The investigation into the Calcite In-situ Precipitation System or CIPS can be found in the following Chapter 6.

# Chapter 6

*Calcite In-situ Precipitation System (CIPS) – A Potential New Inorganic Consolidant for Stone Museum Artefacts*

## Introduction

Stone has been used throughout human history to make tools, buildings, monuments and art. It is a material that forms a large part of our cultural heritage and preservation of stone is imperative for the current and future study of past societies. The British Museum has a large collection of stone artefacts, including limestone sculptures, from different geographic locations and cultural backgrounds. Many of these artefacts suffer a range of deterioration problems, varying in severity. In particular several Ancient Egyptian artefacts, formed from stone with a naturally high salt concentration, are degrading rapidly and have reached a state where consolidation to improve their internal cohesion is necessary. Current consolidation treatments available, such as silanes, have not always been successful when applied to these artefacts, and also have significant drawbacks in ease and safety of application and environmental sustainability. Inorganic consolidants are an alternative that could offer greater compatibility with carbonate stones, but they have been criticised in the past for their poor penetration depth and deposition within pores. New technological developments, particularly research into 'nano-limes', have led to a return to investigating the possibilities for inorganic consolidants (Dei & Salvadori 2006).

This chapter reports on one of these; the Calcite In-situ Precipitation System (CIPS), on three levels: producing and characterising the solution, treatment of a range of unconsolidated sands, and the treatment of weathered stone. The aims of the CIPS investigation were:

- To discover if the CIPS solution be reproduced on a small scale in the laboratory.
- To characterise the CIPS components to check what is being introduced to the stone.
- To assess the basic consolidation action of CIPS by applying it to loose sand.
- Gather initial ideas about the behaviour of CIPS on weathered stone.

Initial analysis of the treatment and its constituent solutions is followed by demonstrations of its consolidation effectiveness on both loose sand and weathered stone using X-Ray Diffraction, Ion Chromatography, Scanning Electron Microscopy and the Proceq Equotip 3 for surface hardness. Complete consolidation of the loose sand is shown along with an impressive increase in surface hardness on weathered stone, although testing of the CIPS solution also reveals a high salt concentration that has the potential to be problematic.

## Preservation

The origins of modern conservation can be traced to the middle of the 19th century, with Ruskin and Morris and the 'Anti-Restoration Movement' (Jokilehto & Jokilehto 1999). With the desire to preserve the original materials of an object or building, rather than replace with new, came the development of many new conservation methods and treatments. Over the last century within the stone conservation field, these new treatments usually consist of surface coatings and consolidants (Cnudde et al. 2004). Surface coatings can be used with a wide range of intentions - as water repellents, anti-graffiti coatings, salt inhibitors, biocides and sacrificial layers, plus many more (Doehne & Price 2010). Consolidants are a group of treatments, the use of which is intended to increase the structural strength of a deteriorating and disintegrating stone. Consolidants artificially repair the bonds between grains within a stone that hold it together. Effective treatments need to meet certain performance requirements concerning durability, depth of penetration, effect on stone porosity, effect on moisture transfer, compatibility with stone and effect on appearance (Cnudde et al. 2004). There are a wide variety of stone consolidants available and it can be difficult to select the most appropriate product to use out of these, as this will vary depending upon the

stone involved, its location, deterioration problems and history. Some research in the past focused on the attempt to find a treatment that both consolidated and provided surface protection, however it is now generally accepted that two treatments are required (Doehne & Price 2010).

## Treatment of Egyptian Artefacts at The British Museum

Since the 1940's a range of stone consolidants has been used at the British Museum to treat Ancient Egyptian stone artefacts. These treatments include soluble nylon, polyethylene glycol (PEG), and a variety of silanes. Whilst the latter have been used extensively in Europe over the last few decades they have not been used at the British Museum since the late 1980's. Whilst successful in many cases organic treatments are not always suitable and a major problem is the often lack of affinity with the stone substrate (Favaro et al. 2008). Inorganic treatments overcome this, and those involving calcite can boast a high compatibility with carbonate stone substrates. In the past, due predominantly to poor penetration and inconsistent deposition inorganic consolidants have not been regarded as feasible alternative to organic (Favaro et al. 2008). However, recent scientific developments have led to resurgence in interest and research into the potential of inorganic consolidants.

## CIPS

The 'Calcite In-situ Precipitation System' or CIPS is one such new possible inorganic consolidant under consideration by the British Museum. The CIPS method was developed in Australia by Commonwealth Scientific and Industrial Research Organisation (CSIRO) scientists Edward Kucharski and Graham Price. The product is now the proprietary technology of two companies: Lithic Technology Pty Ltd and CarboTech Fosroc GmbH who both market the product in Europe (Tatzki 2004). The product licence for the *Back to Nature* project was obtained by the British Museum from Lithic Technology Pty Ltd, and the Arts and Humanities Research Council (AHRC) funded a visit to Graham Price, now of Lithic Technology

Pty Ltd, in Australia. CIPS is not available as a 'ready made' product so this visit was particularly important for learning techniques associated with CIPS production and application.

CIPS is designed to improve the internal cohesion and mechanical strength of granular materials - from loose sand to disaggregated stone, through a calcite cementation process (Kucharski et al. 2000, Price 2010). The calcite is precipitated from two solutions that are mixed and then permeated or injected through the material to be consolidated. Through reactions within the mixed CIPS solution, calcite crystals are formed, and these then coat surfaces of grains within the material creating bridges between them (Ismail et al. 2002). There are two defining parameters associated with the increase in strength that will be achieved using CIPS; the maximum amount of calcite that could potentially be precipitated from a litre of CIPS solution, and the rate at which the reactions within take place (Ismail et al. 2002). Different factors affect the rate of the CIPS reaction, including temperature and the amount of different components added when making up the two original solutions prior to mixing. Repeat treatments are possible to increase the strength further (Price 2010) .

The CIPS treatment was originally developed for the oil and gas industry in Australia, to improve the ground around offshore foundations, and has since been used for a variety of consolidation purposes. This includes an investigation with London Underground; looking at the possibilities of shoring up railway embankments, building beach landing sites, and improving the strength of the limestone walls of the Whalers Tunnel in Perth (Soudain 2001, Kucharski et al. 2000, Geotechnical Consulting Group 2002, Price 2007). CIPS has several attractions for conservators caring for deteriorated limestones. Along with compatibility, particular advantages of CIPS are its ease of use and low toxicity. However, prior to the *Back to Nature* project, CIPS has only been used for large-scale applications, and other than on the Whalers Tunnel, never for heritage items. It was important therefore, when considering CIPS as a potential consolidant for British Museum artefacts, that a full investigation into CIPS was undertaken.

# Experimental

## CIPS Preparation

Preliminary investigations centred on first establishing that CIPS could be recreated in the lab in the British Museum based upon the directions given by Lithic Technology Pty Ltd. Secondly, CIPS solutions were used for basic consolidation of free flowing sand. This allowed for an initial look into the essential consolidation properties of CIPS and analysis of its constituent materials. Thirdly, CIPS was applied to weathered stone to assess its performance.

The CIPS fluid is formed from two solutions (designated Solution A and Solution B) that are mixed in equal proportions just prior to application. The exact composition of the two solutions, and their production methods, are proprietary to Lithic Technology Pty Ltd who can be contacted for more details. When solutions A and B are mixed a defined chain of processes is set into action, these stages can be observed and timed (see figure 17). Before mixing, Solution A is clear and Solution B an opaque light yellow colour. After combining them the mixed liquid is a translucent light yellow colour. The mixture gradually becomes whiter and thicker over approximately 20 minutes until it has formed a thick white gel. After approximately 45-60 minutes from the original combining of Solutions A and B the white gel begins to break down into a white precipitate and a yellowish clear liquid. Within a treated sample the precipitate is the calcite, which would form around the grains, and the yellowish clear liquid the spent CIPS fluid that would remain in pore spaces.

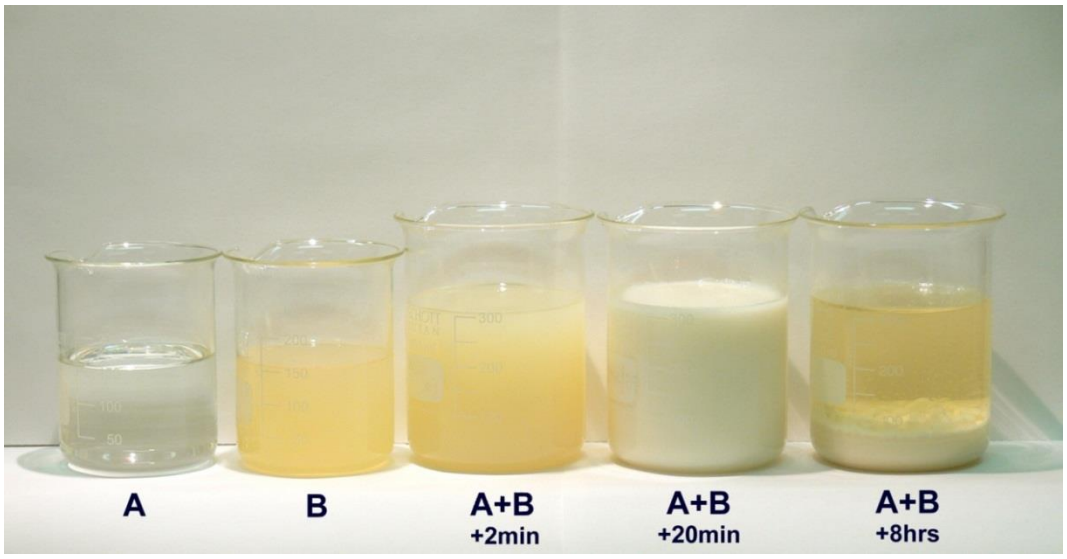



**Figure 17: CIPS solution stages: before mixing; 2 min post mixing; 20 min post mixing; 8 hrs. post mixing (Price 2010)**

## Sand samples Treated

Three types of loose sand were treated with the CIPS; acid washed silica sand, aragonite sand and a white conservation-grade acid washed silica sand. All were analysed using a Malvern Mastersizer 2000 laser diffraction granulometer and associated dispersion units to look at particle size distribution. The conservation-grade acid washed silica sand was the most uniform with a median diameter of 383.6μm, the acid washed silica sand had a median diameter of 253.3μm and the aragonite was the least uniform and had a median diameter of 242.4μm. All three were also observed using a Leica dissecting microscope and compared to the Powers scale of roundness (Powers 1953). The acid washed silica sand was sub angular with high sphericity, the conservation grade sand sub rounded with low sphericity and the aragonite well rounded with a mixture of low and high sphericity.

## Weathered stone samples treated

During a research trip to Lithic Technology Pty Ltd in Australia, CIPS solution was applied to six samples of weathered stone. Before treatment, each stone was photographed and then sawn in half and then one half treated whilst the other left untouched, to permit direct comparison to be drawn between treated and

non-treated areas. After treatment, the stone was shipped back to the UK. The CIPS was applied twice by pipette, following common practice for consolidant application in stone conservation.

At the British Museum CIPS was applied to loose sand. Before application it was important to check that it had been re-created correctly in the British Museum. To do this 5ml of Solution A and 5ml of Solution B were mixed and then observed to see if the mixture followed the pattern mentioned in the CIPS Preparation section.

After observing the expected sequence of events (described in 'CIPS Preparation') CIPS was applied to three types of free flowing sand; acid washed silica sand, aragonite sand and a white conservation-grade acid washed silica sand. The aragonite and the two types of silica sand were poured into silicone trays (25mm diameter, 20mm depth). Beforehand small holes were punctured into the silicone moulds to allow for free draining of the CIPS fluid. CIPS can be applied in a number of ways depending upon the requirements of the object or area to be treated. After the trial application on stone in Australia, and following discussions with Lithic Technology PTY and the stone conservators in the British Museum, it was decided that spraying would be the ideal technique to apply the CIPS to the sand.

According to the product description, a sample can be treated with CIPS multiple times, growing in strength with each application, and around 6 applications can be made before a colour change is noticeable (Price 2010). Groups of 6 samples of sand were treated an increasing number of times with the first in each group treated once, the second twice and so on up to 6 treatments (see figure 18). There were at least two groups per sand type. The treatments were applied at 24hr intervals. After the 6$^{th}$ and final treatment, the sand samples were left in the trays to cure under normal lab conditions for 8 weeks, and then removed for analysis.

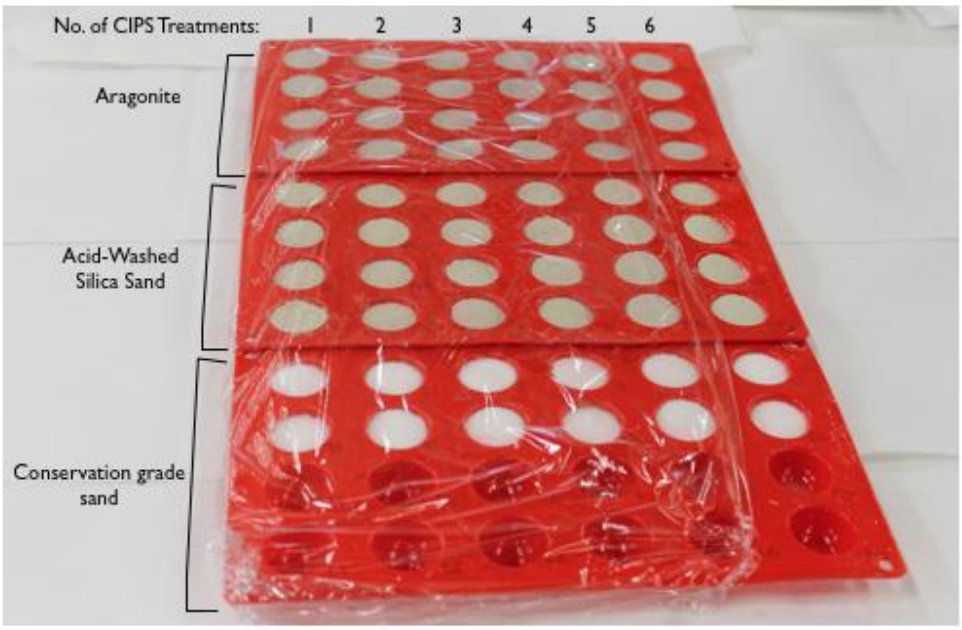



**Figure 18: Sand samples ready for 6th application of CIPS**

## Methods

Under the licence agreement with Lithic Technology Pty, the CIPS solution had to be produced within the British Museum and not at Oxford. For later experiments the two components CIPS solution would be made up in the British Museum and then transported to Oxford to treat the stone replicates. For this initial investigation into the CIPS treatment itself it was decided that the analytical methods used would be those available at the British Museum, or where equipment was easily portable to the British Museum (for example the Equotip was taken to the Museum from Oxford.

### Characterisation of CIPS Fluid

The first stage in analysis was the important step of confirming the composition of the spent CIPS fluid and the precipitate to see what was actually being applied to the samples; this is what could be potentially introduced in the future into real, deteriorating, artefacts. From the CIPS fluid initially created, the precipitate was filtered out, washed with deionised water, and dried at room temperature. Analysis using X-

Ray Diffraction (XRD) was then performed with a Phillips PW 1120/90 diffractometer using Cu Kα radiation. A sample of the precipitate was also applied to carbon tape and observed (Variable Pressure Scanning Electron Microscope (VP-SEM) Hitachi VP-SEM S-3700N).

The other resultant component (spent CIPS fluid) was retained for analysis using a Dionex DX500 Ion Chromatograph. The spent CIPS fluid was diluted 10000 times and analysed as follows:

To test for fluoride, chloride, nitrate, phosphate and sulphate anions, an Ionpac AS14A (3 x 150 mm) analytical column with a 8 mM Sodium carbonate / 1mM sodium hydrogen carbonate eluent, at a 0.5 ml $min^{-1}$ flow rate was used. The sample loop size was 125 µl and the temperature 30°C. ASRS Ultra II (2mm) was used as the suppressor, with a current of 50 mA. Each sample was run three times for 12 minutes. The standards used were 1:1, 10:1, 100:1, 1000:1 and 10000:1 dilutions of the stock solution containing fluoride (20 ppm), chloride (30 ppm), nitrite (100 ppm), bromide (100 ppm), nitrate (100 ppm), phosphate (150 ppm) and sulphate (150 ppm).

To test for formate, acetate and carbonate anions, an Ionpac ICE-AS1 (9 x 250 mm) analytical column with a 1.0 mM heptafluorobutylric acid eluent, at a 0.8 ml $min^{-1}$ flow rate was used. The sample loop size was 50 µl and the temperature 19°C. AMMS-ICE II (4 mm) was used as the suppressor, with a solution of 5 mM tetrabutylammonium hydroxide (TBAOH) at a 4 ml $min^{-1}$ flow rate. Each sample was run once for 19 minutes. The standards used were 10:1, 100:1, 1000:1 and 10000:1 dilutions of the stock solution containing 1000 ppm of acetate, formate and carbonate.

To test for lithium, sodium, ammonium, potassium, magnesium and calcium cations, an Ionpac CS12A (4 x 250 mm) analytical column with a 20 mN methansulphonic acid (MSA) eluent, at a 1.0 ml $min^{-1}$ flow rate was used. The sample loop size was 25 µl and the temperature 30°C. CSRS Ultra II (4 mm) was used as the suppressor, at a 50 mA current. Each sample was run three times for 12 minutes. The standards used were 1:1, 10:1, 100:1, 1000:1 and 10000:1 dilutions of the stock solution containing lithium (50 ppm), sodium (200 ppm), ammonium (250 ppm), potassium (500 ppm), magnesium (250 ppm) and calcium (500 ppm).

### Observation of the consolidated sand

To investigate the bonding between sand grains and distribution of the precipitate within the consolidated sand, and also to check for any unwanted materials from the CIPS, some of the samples were observed using high vacuum scanning electron microscopy (SEM) and environmental scanning electron microscopy (VP-SEM) with a Hitachi VP-SEM S-3700N. Whole consolidated sand samples were observed using VP-SEM , then some samples sawn in half, mounted via vacuum impregnation using a Struers CitoVac vacuum pump, and polished to provide a cross-section. These were then observed under vacuum using SEM with EDS for elemental analysis.

The surface hardness of a selection of the consolidated sand samples was assessed using a Proceq Equotip Piccolo 2 portable hardness tester. This uses the Leeb rebound method and calculates hardness values based upon the changing velocity between impact and rebound (Viles et al. 2010). Measurements of the consolidated sand were taken at 5 individual points on the top, or until the impact created major failure of the consolidated sample.

### Observation of treated weathered stone

Qualitative observations were made of how the CIPS behaved during treatment of weathered stone and the Proceq Equotip Piccolo 2 hardness tester used to compare the surface hardness of treated vs untreated portions. 10 individual measurements per surface were taken and averaged.

## Results and Discussion

The first aim of this investigation was to ensure reproducible production of CIPS according to the manufacturer's directions. This was successfully achieved by comparing observed reactions between the Solutions A and B created at the British Museum, with those observed at the developers in Australia and by

checking that the various stages in the reaction occurred at the expected times (outlined in 'CIPS Preparation').

## Characterisation of the CIPS spent fluid

Analysis of the spent CIPS fluid using Ion Chromatography showed high levels of both chloride and ammonium salts (Table 3). A high salt content in stone is often a cause for concern as it can be a major factor in deterioration (Price 1996, Goudie & Viles 1997). Introducing salts to an artefact would therefore be potentially dangerous and this aspect of the CIPS fluid requires further investigation in the future. When doing this it will be important to remember that the salts introduced with CIPS are chloride and ammonium based; as mentioned in the introduction, Egyptian stone with high chloride salts had been found to be relatively sound, it was the stone with a high concentration of nitrates that were experiencing the most problems.

| | Cl | $NH_4$ |
|---|---|---|
| Dilution | 10000 | 10000 |
| PPM | 100800 | 50900 |
| % | 10.08 | 5.09 |
| m g/L | 100.8 | 50.9 |
| n (Mol/L) | 2.839437 | 2.827778 |

**Table 4: Results from ion chromatography of spent CIPS fluid**

## Characterisation of the precipitate from CIPS fluid

The precipitate from the initial trial mixing of solutions A and B was filtered, dried and then washed with deionised water. A small portion of this was finely ground and then analysed using X-ray powder diffraction (XRD). The resulting diffraction pattern was measured and compared to known standards for forms of calcium carbonate. By comparing the pattern with the standards from the International Centre for

Diffraction Data (ICDD), it appeared the precipitate produced was in the form of Vaterite; an anhydrous crystalline polymorph of calcium carbonate with a hexagonal unit cell (Liu & Zhang 2010), that is usually found in spherical form (Olderoy et al. 2009). Vaterite is the least stable form of calcium carbonate often found when calcium carbonate precipitates at high levels of supersaturation, and usually transforms into a more stable compound over time (Olderoy et al. 2009, Andreassen 2005).

As the vaterite form of calcium carbonate was unexpected (CIPS is designed to produce calcite) the precipitate was investigated using the VP-SEM, to assess the crystal shape and to perform elemental analysis. Figure 19 shows the nature of the precipitate.

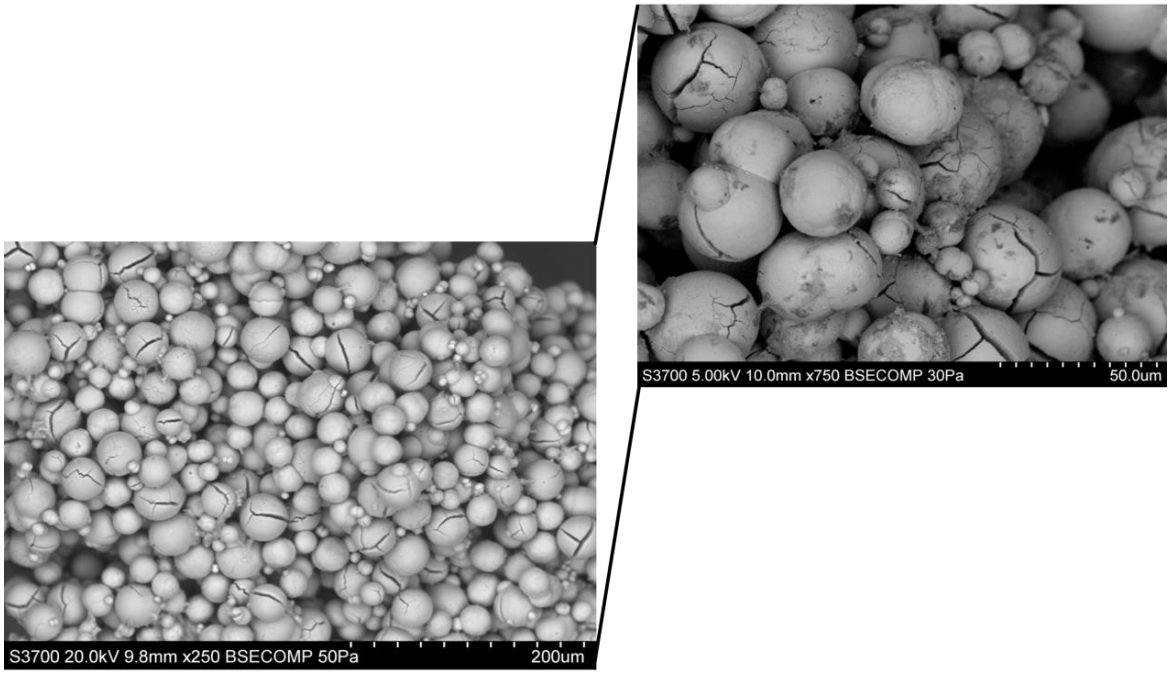



**Figure 19: VP-SEM micrographs of CIPS precipitate x250 and x750 magnification**

Visible in the micrographs in Figure 19 are cracked spheres that would be expected if the calcium carbonate was in the form of vaterite. Elemental analysis (table 4) confirms calcium carbonate with a small trace of phosphorous.

| Element | Weight (%) | Atomic (%) |
|---|---|---|
| **C** | 20.90 | 32.47 |
| **O** | 43.58 | 50.83 |
| **Si** | 0.09 | 0.06 |
| **P** | 0.77 | 0.46 |
| **S** | 0.26 | 0.15 |
| **Cl** | 0.13 | 0.07 |
| **Ca** | 34.28 | 15.96 |
| **Totals** | 100.00 | |

**Table 5: Elemental analysis of CIPS precipitate using SEM_EDS (Energy dispersive X-Ray analysis)**

## Analysis of the consolidated sand

The second aim of the research was to investigate the consolidation of silica and aragonite sands with CIPS. The consolidation effect of the CIPS was impressive. With just one treatment solid hemispheres of sand were created that could be handled without major disaggregation (Figure 20). From visual inspection it appeared that greater consolidation was achieved with a greater number of treatments; there were fewer loose particles of sand once the sample was removed from the tray. There seemed to be a difference in the consolidation effectiveness between the three different types of sand with the two types of silica sand less likely to break and fall apart than the aragonite. However, in all cases it was obvious that the CIPS solution penetrated all the way through the sand from the treated surface to the base of the mould (a depth of 20mm) since there was no sand left unconsolidated. Whilst the samples were originally loose sand with plenty of pore spaces, and thus good penetration might be expected, these findings also suggest that CIPS might overcome one of the major disadvantages of other inorganic consolidants; poor penetration depth.



**Figure 20: Hemisphere (25mm) of "CIPS rock" formed after treatment of loose sand with one application of CIPS fluid**

As mentioned in the methods section, cross-sections were cut, mounted in resin, polished and then observed using SEM. A cross-section of one of the acid washed silica sands, treated only once with CIPS, was investigated using SEM-EDS elemental mapping as shown in figure 21.

Figure 21 illustrates the deposition of CIPS precipitate within the silica sand sample. Using elemental mapping it is possible to distinguish between the silica grains (figure 21b) and calcium presence within the sample (figure 21c). As seen in figure 21d, the Ca has been deposited around the edge of the grains. This supports the claim that when the CIPS solution is applied to a granular material, calcium carbonate precipitates out, binding the grains together.

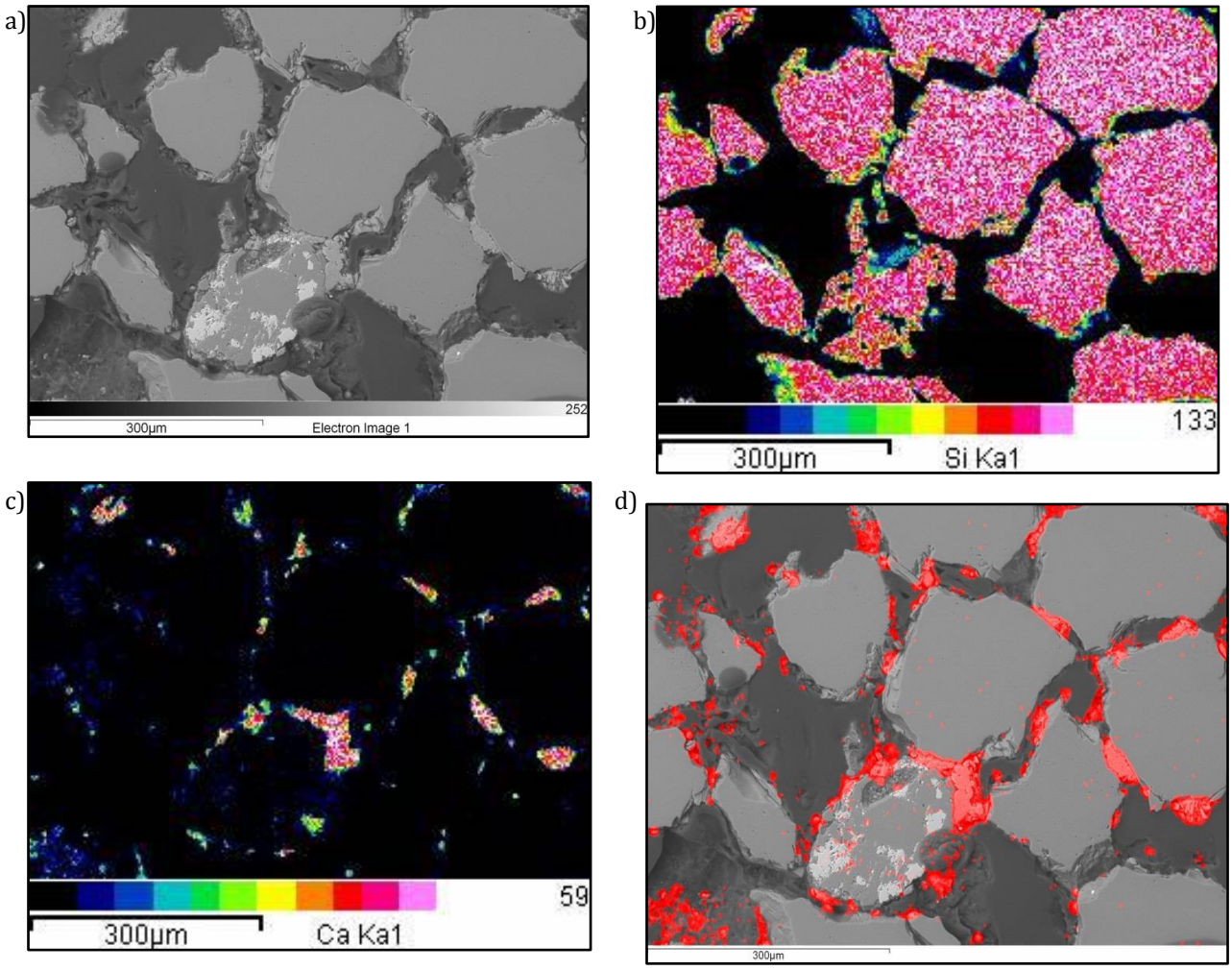



**Figure 21(a-d): a) SEM BSE image of consolidated silica sand treated once with CIPS; 30Pa, 10kv, 10.01mm b) SEM-EDS elemental map showing Si distribution; c) SEM-EDS elemental map of same sample showing Ca distribution; d) Overlay of Ca map on original BSE image**

The CIPS consolidation process is described as follows according to the manufacturer (Price 2010). Long, narrow, fibrous calcite crystals grow perpendicular to the grain surface. Crystals on neighbouring grains eventually interact forming 'calcite bridges' which bind the grains together. Variable Pressure SEM images at increasing magnitudes (Figure 22a-c), taken of whole consolidated aragonite hemispheres, show the aragonite grains bonded together by the expected narrow crystals.

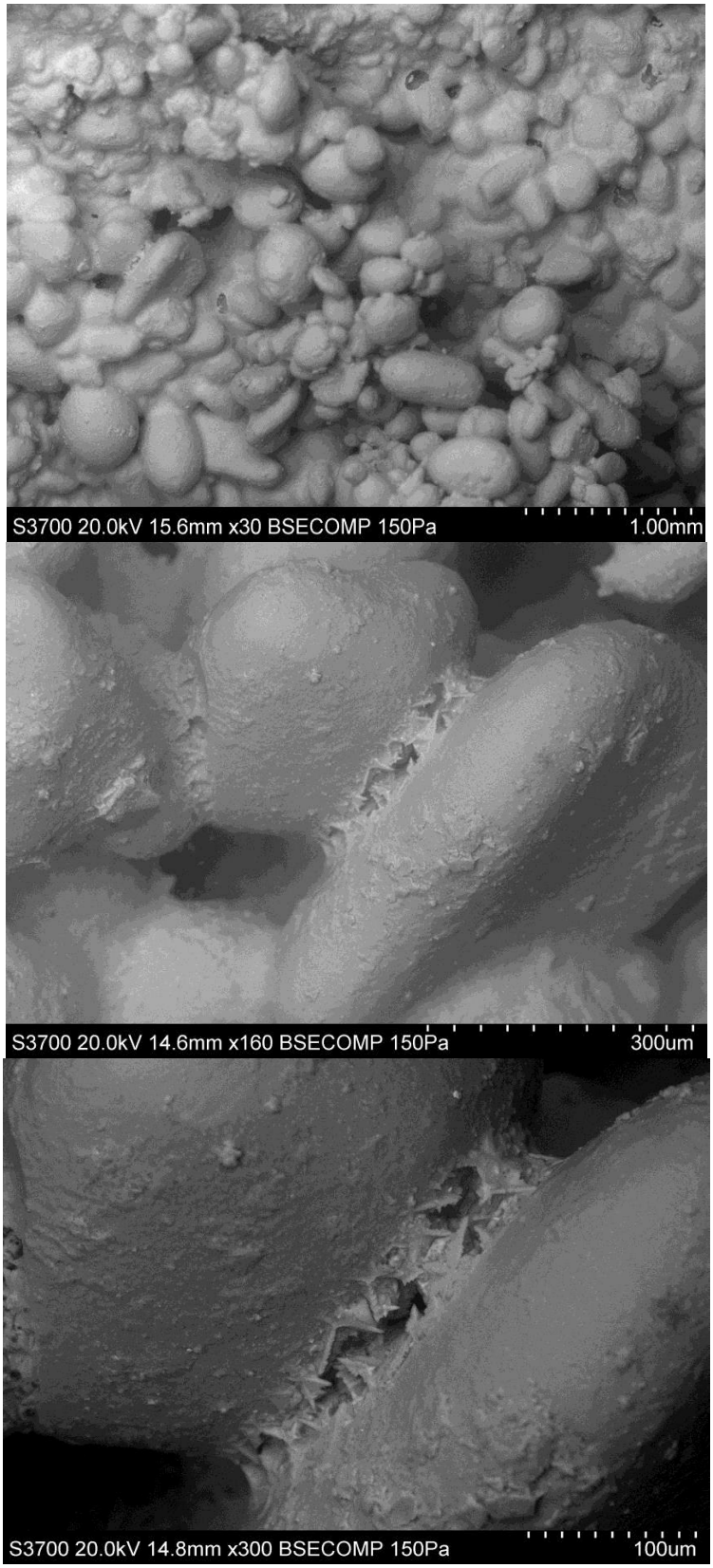



**Figure 22 (a-c): a) VP-SEM image showing $CaCO_3$, assumed to be calcite, bonding between aragonite grains x30 magnification. b) x160 magnification, c) x300 magnification**

The strength of the consolidated sand samples was investigated using the Proceq Equotip Piccolo 2 portable hardness tester with an impact energy of 11Nmm (Viles et al. 2010). This impact was too great for both the consolidated aragonite and white conservation sand samples. These tended to collapse when tested. The acid-washed silica sand samples however, withstood usually a minimum of 5 impacts before disintegration. This allowed surface hardness of CIPS consolidated silica sand to be calculated and this can be seen in Figure 23.

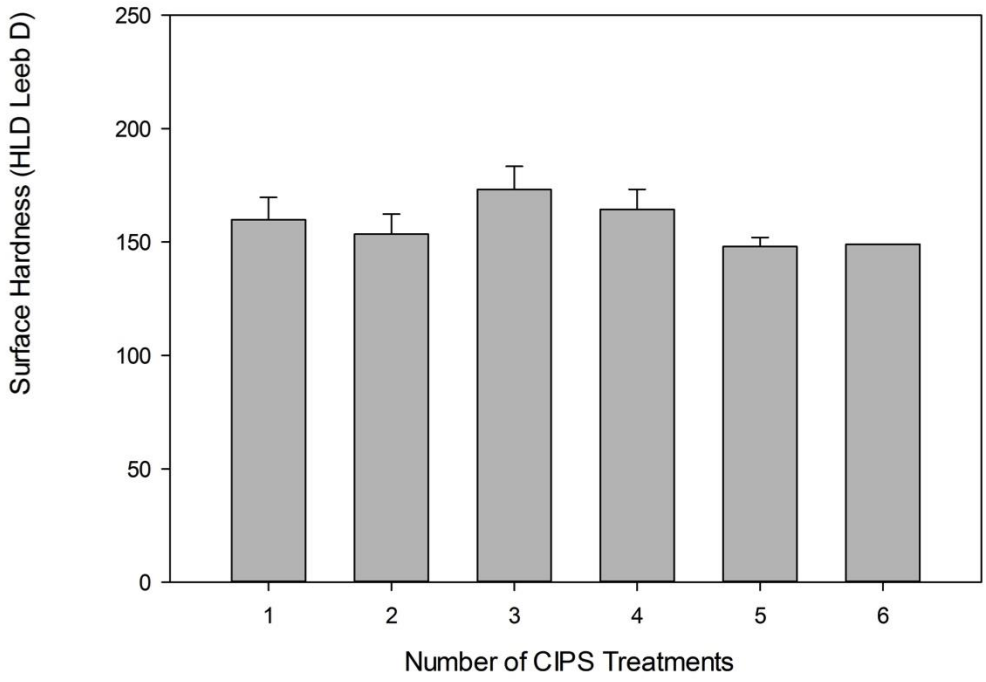



**Figure 23: Graph to show surface strength of consolidated sand samples with increasing numbers of treatments (means with error bars)**

Unexpectedly, the surface hardness did not appear to vary much with the increasing number of treatments. It is interesting to note that the surface hardness of the consolidated sand is comparable to some of the

untreated weathered stones used in the third part of this investigation (figure 24) - demonstrating the ability of CIPS to turn loose sand into stone.

## Investigation into CIPS on weathered stone

The third aim of the research was to investigate the performance of CIPS on weathered stone. Comparing the two halves of each of the 6 stones brought back from Australia, after two months it was not possible to visually discern the treated half from the untreated. This is promising as it suggests that the CIPS solution might not impact upon the appearance of an object.

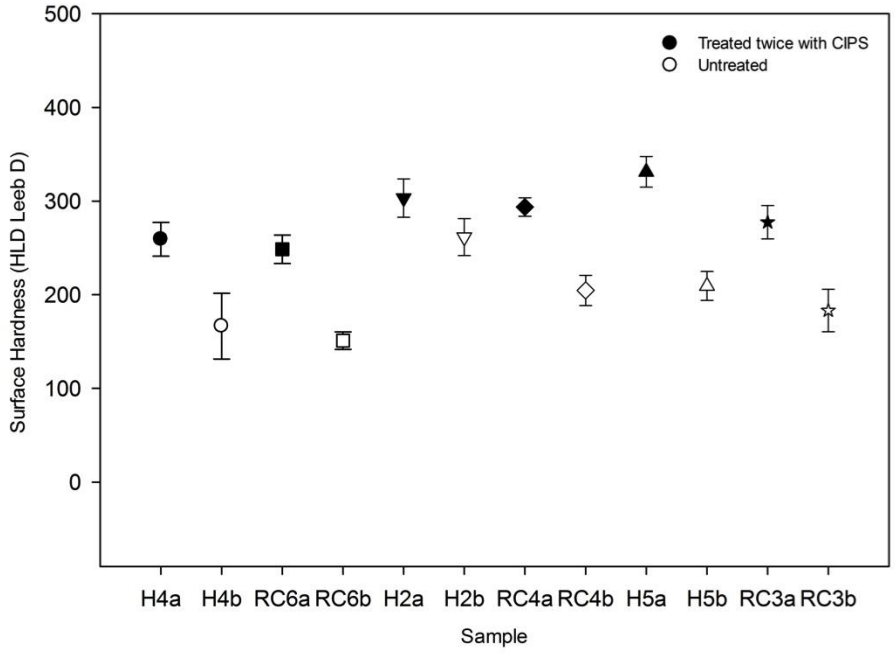



**Figure 24: Piccolo results to show difference in surface hardness between treated and non-treated areas of stone (mean and standard error bars)**

Figure 24 shows the Piccolo hardness results and as can be seen, there was an increase in surface hardness on every stone after treatment. Two way ANOVA testing including all stone samples shows that the CIPS treatment's effect upon stone hardness is statistically significant, and is greater than the inherent variability

between each stone. However, when analysing the two stone types separately the effect of the treatment is significant upon the RC stones, but not on the H stone type. There were only a few samples in this preliminary study, but this may suggest CIPS effectiveness varies with stone type.

## Discussion and conclusions

The Egyptian limestone collection at the British Museum presents a challenge to stone conservators with many items needing attention, and several reaching the stage of major deterioration. In the past these have been treated with a variety of stone consolidants, including silanes, however these have not always been successful and in some cases have worsened deterioration. Presented within this chapter are the initial investigations into the "Calcite In-situ Precipitation System" (CIPS), which it is hoped may be a future consolidant for such limestone museum artefacts.

There were four parts to these investigations:

- Producing the CIPS solution successfully in the lab at the British Museum
- Characterising the solution
- Treatment of a range of unconsolidated sands
- Treatment of weathered stone.

The CIPS solution was easy to manufacture reproducibly in the museum and safe enough to handle that all lab work could be done without the need for a fume cabinet. Due to the quick curing time of CIPS, 6 applications onto loose sand were accomplished within one week. The CIPS was quickly and easily applied

twice to the weathered stones by pipette, although other application methods such as spraying or immersion could be used if preferred.

Analysis of both the precipitate and the consolidated sand show calcium carbonate forming, this can be seen bonding grains of silica together. For limestone objects, or sandstones with $CaCO_3$ as a cementing agent, an effective consolidant with calcium carbonate as its bonding agent could be a potential solution to the ethical and chemical issue of compatibility between consolidant and artefact.

In treating the unconsolidated sands even just one application provided impressive consolidation, with loose sand forming a solid hemisphere. Upon testing for surface hardness, the consolidated sand samples showed the same strength as the weathered stone used in this investigation. The CIPS treatment appeared to be most effective upon the acid washed silica sand and least upon the aragonite, this may have been due to the shape of the sand particles - analysis under the microscope showed the acid washed silica sand particles to be sub-angular in comparison to the well-rounded aragonite.

Weathered stone showed a statistically significant increase in surface hardness of approximately 50-100 Leeb units upon treatment, indicating the potential of CIPS as a consolidant. This was without a noticeable change in surface appearance - an important factor for conservators to consider.

A concern is the high concentration of chloride and ammonium salts found in the analysis of the spent CIPS fluid. This is an aspect that needs further investigation, as many deterioration problems associated with limestone are a product of complications involving soluble salts. Indeed these are thought to be one of the main reasons past consolidation treatments have not been successful, and one of the hopes for CIPS would be that it would be good for artefacts with soluble salt problems.

The aim of these series of experiments was to gain a greater depth of information about CIPS and how it works due to the fact it had never before been used in the field of archaeological conservation. These preliminary investigations have demonstrated that CIPS is easily and safely reproducible and does indeed have a considerable consolidation effect, bonding grains with calcium carbonate. The success of the aims of

this part of the Back to Nature project; producing the CIPS in the lab and achieving consolidation action, meant the project could progress to a comparison of CIPS with ammonium oxalate, CaLoSil and Wacker OH. This experimental comparison can be seen in the next Chapter.

# Chapter 7

*Reconsidering Inorganic Consolidants: A Comparative Assessment of Three New Treatments for Carbonate Stones Using Pre-weathered Blocks*

## Introduction

Over the last few decades, emphasis in conservation has been on the importance of the reversibility of any treatments (Rodgers 2004). However, consolidation treatments for stone are rarely truly reversible. Therefore, stone conservation has started to focus more on compatibility of a conservation treatment with the stone substrate (Sasse & Snethladge 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).

Organo silanes are consolidants that have been fairly popular in the past, and indeed are still used by many stone conservators. Used in the British Museum in the 1980's, there are a number of treated artefacts in their collections that demonstrate the success of silanes as stone consolidants. However, there are some stone artefacts, mainly limestone objects, where deterioration has worsened since being treated with organo silanes (cf. Figure 4, Chapter 2) (Thickett, Lee & Bradley 2000) . 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 the possibility of inorganic consolidants (Chelazzi et al. 2013).

It was this resurgence of interest within the field of stone conservation that led to the development of the Back to Nature project by the British Museum, to investigate the potential of new inorganic consolidants to

be used on their stone collections, in particular on limestone. The focus of the project was on scientific assessment of the performance of the consolidants in comparison with an organic alternative. Close liaison with the conservators at the British Museum ensured that realistic application methods were used on samples representative of real artefacts. The first two stages within this project involved a series of experiments to develop a robust investigative methodology and to discover more about one of the new consolidants in particular that had been developed outside the heritage conservation field. The details and results from these experiments can be found in Chapters 5 and 6. Presented within this chapter are the results from the comparative experimental assessment of three potential new inorganic consolidants for use on the British Museum limestone collections: Calcite In-situ Precipitation System (CIPS); CaLoSil; and Ammonium Oxalate treatment, alongside a previously used and well-known silane: SILRES® BS OH 100 (Wacker OH). There were three objectives to this assessment:

- To experimentally compare the "effectiveness" of each consolidant with one another.
- To see if any of the three inorganic consolidant's holds potential for future use in the British Museum
- To treat both fresh and weathered stone to compare consolidation action on different stone substrates

There were several expected outcomes from this assessment:

1. Silane SILRES BS OH 100 (Wacker OH)
    I. The silane is a proven consolidant so increases in both surface hardness (Equotip) and internal strength (Pundit) were predicted.
    II. SILRES BS OH 100 does not contain hydrophobic additives, however it is known to reduce water permeability so it was predicted this would be shown on the Karsten Tube results.
    III. The silane is designed to penetrate deep into stone so it was expected this would be shown with SEM and DRMS.

IV. Some colour change was anticipated, however this would be expected to be low as it had not been raised as an issue when the silanes had been used previously.

2. Ammonium oxalate treatment (AmOx)

I. This treatment creates calcium oxalate; a proven protective layer. Therefore increases in surface hardness using Equotip were expected.

II. As its further properties as a consolidant are unproven it was predicted that this increase in strength would be limited to a superficial layer and SEM, DRMS and Pundit measurements would show this.

III. If there was a hard surface layer there might be a reduction in water penetration seen in the Karsten Tube results, but porosity would most likely remain the same which would be shown using MIP.

3. CaLoSil

I. This treatment has been specifically designed to consolidate heritage stone. It was therefore predicted increases in surface hardness using Equotip, and internal strength using Pundit, would be seen.

II. As a nanolime it was predicted this treatment would penetrate into the stone which would be seen using DRMS.

III. No influence on water permeability was predicted.

IV. There had been some mention of a white bloom that sometimes appeared with treatment so to was predicted that colour change using spectrophotometry might be high.

4. Calcite In-situ Precipitation System (CIPS)

I. The consolidation potential of CIPS had been demonstrated during a previous round of experiments (detailed in Chapter 6). As such, increases in both surface hardness using Equotip, and Internal strength using Pundit and DRMS, were anticipated.

II. Previous experiments had shown the potential for salts to remain in the stone so testing using ion chromatography was expected to show raised levels of chloride and ammonium salts.

Data from this experimental stage was included in the conference proceedings for the 12th International Congress on the Deterioration and Conservation of Stone. A copy of this can be found in Appendix B.

## Materials and Methods

Replicate samples from two stone types were prepared, pre-weathered, and then four consolidants applied. Differences in a number of key characteristics (including weight, colour, surface hardness, and water penetration) were evaluated both before and after pre-weathering and before and after consolidation.

### Stone Materials & Pre-Weathering

The stone types used in these experiments were Elm Park and Hartham Park (as described more fully in chapter 4). These 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. Forty, 50x50 mm cubic limestone samples were cut to give 10 samples per consolidant investigated, the stone type for each sample can be seen in Table 5 below. All 40 were artificially weathered using heating in a furnace followed by rapid quenching in cold water. The samples 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, based on pilot study results, which showed demonstrable reductions in both surface hardness and internal strength.

| Sample | 1* | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10* |
|---|---|---|---|---|---|---|---|---|---|---|
| **CIPS** | EP | EP | EP | EP | EP | EP | EP | EP | EP | EP |
| **AmOx** | HP | HP | HP | HP | EP | HP | HP | HP | EP | HP |
| **CaLoSil** | HP | HP | HP | EP | EP | EP | HP | EP | HP | HP |
| **Wacker** | EP | EP | EP | HP | EP | HP | EP | HP | HP | EP |

**Table 6: Stone type by sample**

*****: Control samples: left untreated

**EP**: Elm Park

**HP**: Hartham Park

## Consolidants

Four different consolidants were investigated in this experimental comparison; Calcite In-Situ Precipitation System, ammonium oxalate treatment, CaLoSil, and Wacker Silres BS OH 100. Detailed description of each consolidant's components and method of action can be found in Chapter 4. The four consolidants were applied as directed by the manufacturers with any necessary modifications arising after discussion with BM stone conservators. More information on the application methods is given below. Samples were tested for a range of characteristics (surface hardness, internal strength, water penetration, weight, effect on internal salt concentration and pore size) before and after weathering and before and after treatment, and results analysed to determine effectiveness and which (if any) consolidant had the potential to be used in the future in the museum. All samples were kept together throughout the experiment under laboratory conditions; temperature of 24°C, RH 62%.

### Calcite In-situ Precipitation System (CIPS)

The CIPS fluid is formed from two solutions mixed in equal proportions just prior to application. Once mixed, there is a limited time to apply the CIPS fluid before it forms a solid gel – usually this occurs

approximately 10 minutes after mixing. Multiple applications of CIPS can be undertaken to further strengthen the stone; six are recommended for sufficient consolidation without inducing a highly noticeable change in the surface appearance (Price 2010). Of the 10 samples for CIPS analysis, 8 were treated by spraying with the mixed solutions (as can be seen in Figure 25); two of the 10 samples were kept as controls. The samples were treated every 24hrs for 6 applications.

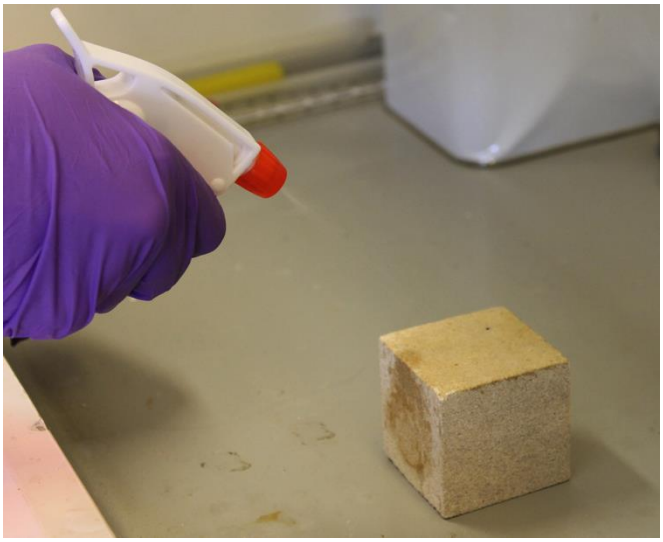


**Figure 25: Application of CIPS by spraying**

### Ammonium Oxalate (AmOx)

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). More details about the background of oxalate films and the reactions used to produce them can be found in Chapter 4. Within this study, a reaction involving ammonium oxalate to produce calcium oxalate was used. Ammonium oxalate monohydrate was mixed with water at 5%w/v and then applied to 8 of the ammonium oxalate samples using a cellulose poultice as recommended by Cezar (1998) and as shown in the treatment protocol in Figure 26. 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 24hrs before removal. After 3 weeks the process was repeated for a second time.

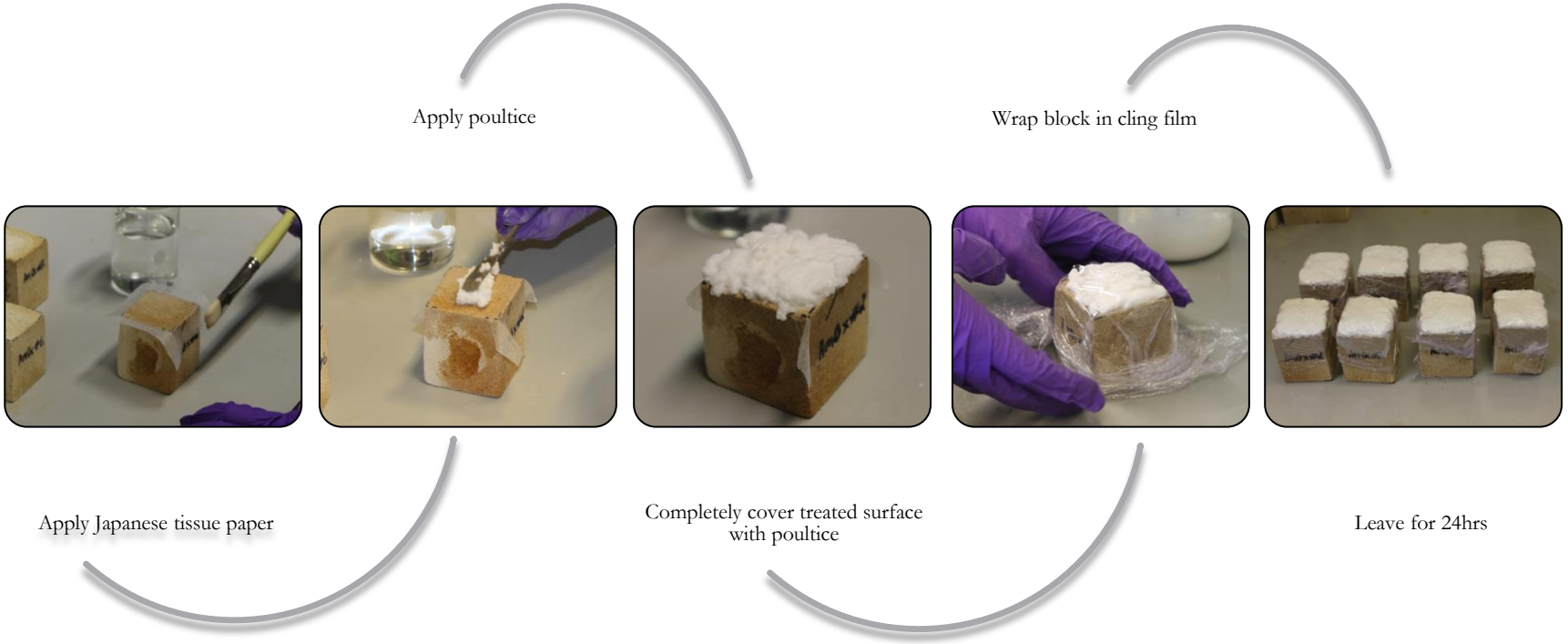



**Figure 26: Ammonium oxalate treatment protocol**

### CaLoSil

CaLoSil is a new, commercially available, nano-lime stone consolidant developed specifically for consolidating calcareous historic material (Campbell et al. 2011). Nano-particles of $Ca(OH)_2$ are suspended in different alcohols. After application, the alcohol evaporates to leave solid calcium hydroxide behind. This then reacts with atmospheric carbon dioxide to form calcium carbonate. Due to the small size of the particles, CaloSil is designed to penetrate deep into the stone. CaLoSil E25 (calcium hydroxide particles dispersed in ethanol at 25g/L) was applied by spraying (fig.27) to 8 of the 10 samples (with two remaining as untreated controls). After three weeks a second application was undertaken.

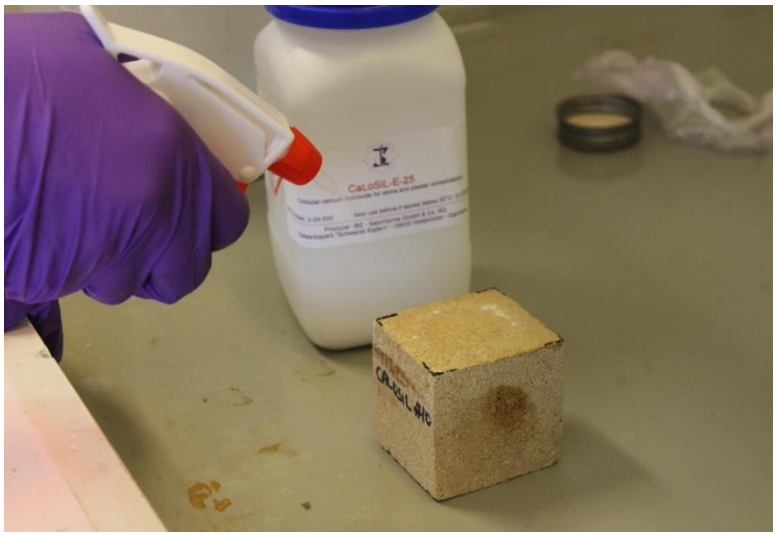



**Figure 27: Application of CaLoSil by spraying**

### Silres BS OH 100 (Wacker)

Silanes are a very popular group of consolidants within stone conservation (Price 2006). The silane selected for use in this experiment was SILRES® BS OH 100, also known as Wacker OH 100. Produced by Wacker Chemie AG, SILRES® BS OH 100 is a solventless ethyl-silicate that penetrates into the stone forming a glass-like silica gel binder ($SiO_2$·aq.)(Wacker Chemie AG MTDS). More information on chemical composition, and the history of the use of silanes, can be found in Chapter 4. The SILRES® BS OH 100

was applied by pipette (again to 8 of the 10 samples with 2 left as untreated controls) until saturation and left to cure (figure 28). After three weeks a second application was undertaken.

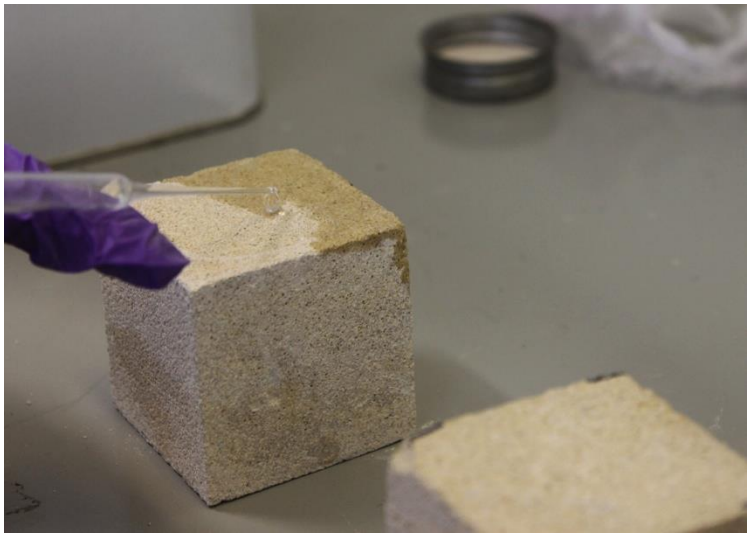


**Figure 28: Application of Wacker by pipette**

## Testing methods

To investigate, and compare the four different consolidants, a variety of analytical methods were used; some non - (or minimally) destructive, others destructive. As explained in Chapter 4, the project methodology involved combining a multitude of analytical tests to provide an overall picture of the effects of each consolidant to allow for comparison. More details on each testing method can also be found in Chapter 4. Within this experimental phase it was decided to use as many analytical tests as possible – those that were available at the British Museum or in the OxRBL lab (particularly those that had been shown to provide useful data in previous experimental phases) and some when the opportunity arose to include them. The Pundit Lab, Mercury Intrusion Porosimetry and DRMS all were either offered on loan, or time was made available on equipment at other universities at the time the experiment was ongoing. Where possible, simple statistical analysis was used to test for significance in any change induced by the consolidation

treatments. Results were tested for normality using a Shapiro-Wilk test and then paired t-tests were performed at the 95% confidence interval.

### Weight

All samples were weighed three times, i.e. before artificial weathering, after artificial weathering/before treatment, and after treatment. Dimensions were measured repeatedly to enable calculation of volume and thus density. From these measurements any changes in weight and density after both the pre-weathering and the consolidant treatments could be identified.

### Equotip

Surface hardness was determined using a Proceq Equotip (Equotip 3). Ten measurements were taken per 50x50mm area on the topmost surface of each sample. This number was chosen as the maximum number of measurements possible without overlapping. Measurements were taken before artificial weathering, after artificial weathering/before treatment, and after treatment.

### Pundit

The Pundit Lab is an ultrasonic pulse velocity (UPV) test instrument, which when used with 250kHz Shear Wave Transducers can be used to calculate the Elastic Modulus of a material (Young's modulus of elasticity). Changes in elasticity can be used to detect a stones susceptibility to deterioration (Committee on Conservation of Historic Stone Buildings, Monuments, National Materials Advisory Board, National Research Council 1982). The control, untreated, samples were measured along with the treated samples post-treatment. Each sample was measured five times and an average calculated as recommended by the equipment manufacturer Proceq (pers comm 2012). The equipment was only available post treatment so it was not possible to measure the samples before and after treatment, hence the use of a control group.

### Spectrophotometer

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*) were measured using a spectrophotometer (Konica Minolta CM 700d/600d) under illuminant D65 with 10 degree observer and using colour data software *SpectraMagic xs*.

Ten measurements were taken on the 50x50mm area on the top treated surface before and after treatment to give a mean colour difference. Using the medium aperture with a diameter of 8mm, ten measurements were selected as the maximum possible without taking overlapping measurements.

### Karsten Tubes

Water penetration was measured before and after treatment using Proceq Karstenröhrchen Wassereindringprüfer (Karsten Tubes). A glass tube with a larger open vessel at one end (25mm in diameter) containing water is bonded vertically to the surface of the sample with putty (plastic fermit). The drop in water level is measured over time. Water level within the tube is maintained to ensure consistent pressure at the surface. Measurements were taken every minute for 10 minutes and graphed to show amount of water absorbed. A EN standard is still in the progress of being created so the procedure according to TQC was followed (Thermimport Quality Control 2013, Hendrickx 2012).

### Drilling Resistance Measurement System (DRMS)

Drilling resistance measurements were taken to look at penetration depth of the various treatments, and to quantify any consolidation action they provided. The Drilling Resistance Measurement System (DRMS) is a portable system, highly useful in direct evaluation of consolidation of carbonate stones(Pamplona et al. 2007, Ferreira Pinto & Rodrigues 2012, Ferreira Pinto & Rodrigues 2008). DRMS measures the force necessary to drill to a certain depth with constant rotational speed and penetration rate (Pamplona et al. 2007). For this investigation a SINT Technology DRMS was used with a 3mm Diaber (Polycrystalline Diamond) drill bit also from SINT Technology. Rotation speed was set at 600rpm with a penetration rate of 10mm $min^{-1}$. Measurements were taken before and after sampling using a homogenous artificial reference sample (ARS) to monitor drill bit wear.

### Scanning Electron Microscopy (SEM)

Cubes approximately 10mm in size were taken from stone samples treated with each consolidant. These were vacuum impregnated with resin and set into cross sections. After polishing, the cross sections were examined using scanning electron microscopy (SEM). The cross sections were observed uncoated in a

Hitachi S3700 SEM with EDS. Subsequently the cross-sections were carbon coated and examined using a high resolution Hitachi S4800 field emission SEM.

### Mercury Intrusion Porosimetry

Chippings were taken from stone samples treated with each of the different consolidants and analysed using Mercury Intrusion Porosimetry (MIP). A Micromeritics AutoPore IV 9500 V1.09 with (09-0582) 5ml Bulb, 1.131 Stem, penetrometer was used. Porosity and pore structure was analysed by evaluating cumulative intrusion, pressure, and pore diameter.

### Ion Chromatography

Ion chromatography to analyse salt content was performed using a Dionex IC DX500 Chromatograph. Drillings were taken from samples at 0.8mm and 1.5mm depth and processed as outlined in the flowchart in Chapter 4. A particular concern about whether CIPS would introduce salts had been raised due to the components within the CIPS fluid, as demonstrated during the investigation into this treatment outlined in Chapter 6. One block per sample group was assessed. It was originally thought that there would be a separate, much wider, investigation into the interaction of each of these treatments with salts in the stone, so for this experiment samples were just taken from one sample block per treatment group. This would give a brief indication of the possible effects of the treatments upon salt levels within the stone.

## Results

### Weight

All sample groups decreased in weight and density after the artificial weathering pre-treatment, these changes were all statistically significant. The changes in mean weight and density after the artificial weathering, seen in the table below, show that there was variation in the degree of weathering experienced between the different sample groups and between each individual replicate. This does add complexity to the interpretation of subsequent analytical tests however, this is the difficulty with needing to compare

consolidants on weathered stone samples. Artificial weathering of replicates, in comparison with testing on very variable naturally weathered stone, limits the variation in weathering as much as feasibly possible.

As can be seen from table 6, the CIPS treatment showed the greatest increase in weight (and hence density) out of the four treatments, at nearly double the next highest weight increase; the Wacker OH sample group. This in turn was more than double the next highest increase, which was the sample group treated with ammonium oxalate. The lowest weight and density increase was seen with the CaLoSil samples which was almost the same as the natural fluctuations shown by the control samples. Dimensions of the blocks did not significantly change so these fluctuations are thought to be due to moisture absorption. All treatments induced a statistically significant weight increase.

| | **Before/After Weathering** | | | **After Weathering/After Treatment** | | | |
|---|---|---|---|---|---|---|---|
| **Sample Group** | Mean ΔM (g) | | Mean Δρ (kg/m³) | Mean Δ M (g) | | Δ M as % Original M | Mean Δρ (kg/m³) |
| **Control** | -0.35 | (σ 0.13) | -2.53 | 0.23 | (σ 0.07) | 0.09 | 2.52 |
| **CIPS** | -0.22 | (σ 0.09) | -1.71 | 3.14 | (σ 0.46) | 1.15 | 24.54 |
| **CaLoSil** | -0.57 | (σ 0.24) | -4.66 | 0.32 | (σ 0.12) | 0.13 | 2.63 |
| **Wacker** | -0.43 | (σ 0.12) | -3.35 | 1.56 | (σ 0.33) | 0.62 | 12.22 |
| **AmOx** | -0.52 | (σ 0.11) | -4.34 | 0.61 | (σ 0.09) | 0.26 | 5.07 |

**Table 7: Mean change in weight (ΔM) with standard deviation (σ) and density (Δρ) after artificial weathering and after consolidation treatment**

## Surface Hardness - Equotip

Figure 29 shows before weathering (▼), after weathering/before treatment (●) and after treatment (■) Equotip values for each sample, divided into consolidant groups. Looking at all graphs (a-e) it can be seen that there was a high variability in original surface hardness between blocks.

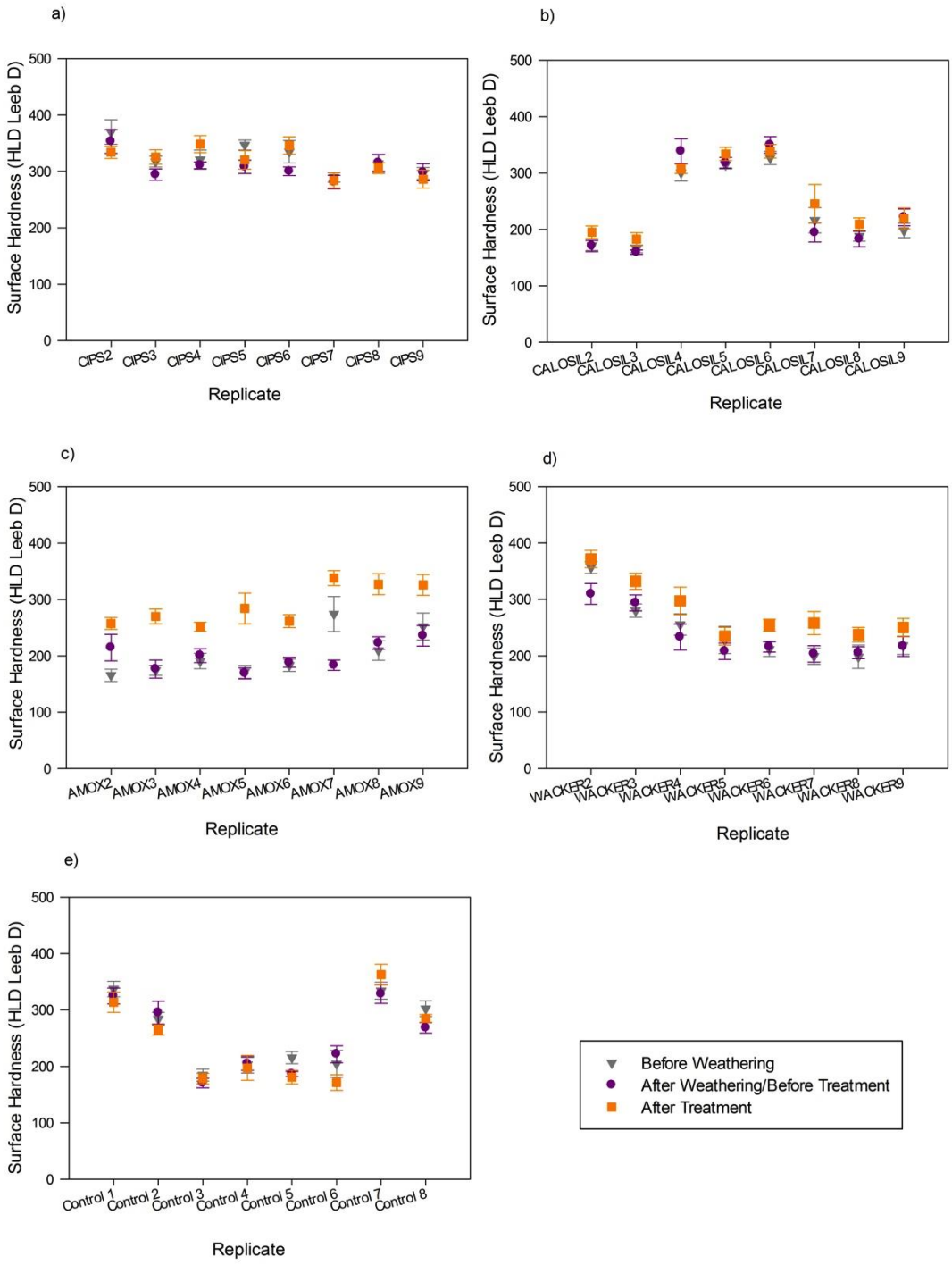



**Figure 29: Graphs (a-e) to show change in surface hardness as measured by Equotip: a) CIPS samples; b) CaLoSil samples; c) AmOx samples; d) Wacker samples; e) Control samples. Points are means with standard error bars.**

Equotip values for the CIPS samples show that the artificial weathering pre-treatment caused a statistically significant drop in surface hardness (P = 0.030), however for all other sample groups the difference caused was not statistically significant.

Figure 29 (a) shows that some CIPS samples demonstrated a noticeable increase in surface hardness after consolidation, however, some did not and overall there is no statistically significant difference (P = 0.237). Similarly, some CaLoSil samples increased in hardness, as shown in figure 29 (b) but overall there is no statistically significant difference (P= 0.519). All ammonium oxalate figure 29 (c) and Wacker figure 29 (d) samples showed a clear increase in surface hardness that was shown to be statistically significant using paired t-tests (P=<0.001 for both AmOx and Wacker). The increase in surface hardness demonstrated by the ammonium oxalate samples was not only statistically significant but was quite large with many experiencing an increase of more than 90 HLD Leeb. All four graphs within figure 29 show the inherent variability between the stone samples. Particularly there is a large difference between the initial surface hardness of those treated with CIPS in comparison to those treated with ammonium oxalate despite a significant drop in hardness after pre-weathering in CIPS blocks.

## Internal Strength – Pundit

Figure 30 shows Pundit Lab results. The only observable difference in the E Modulus between the control and the treated samples was the variability between the individual samples. Whilst the control samples possess variety in E-Mod, the CaLoSil, Wacker, and AmOx samples are far more variable. The CIPS samples showed a similar distribution of results to the control samples.

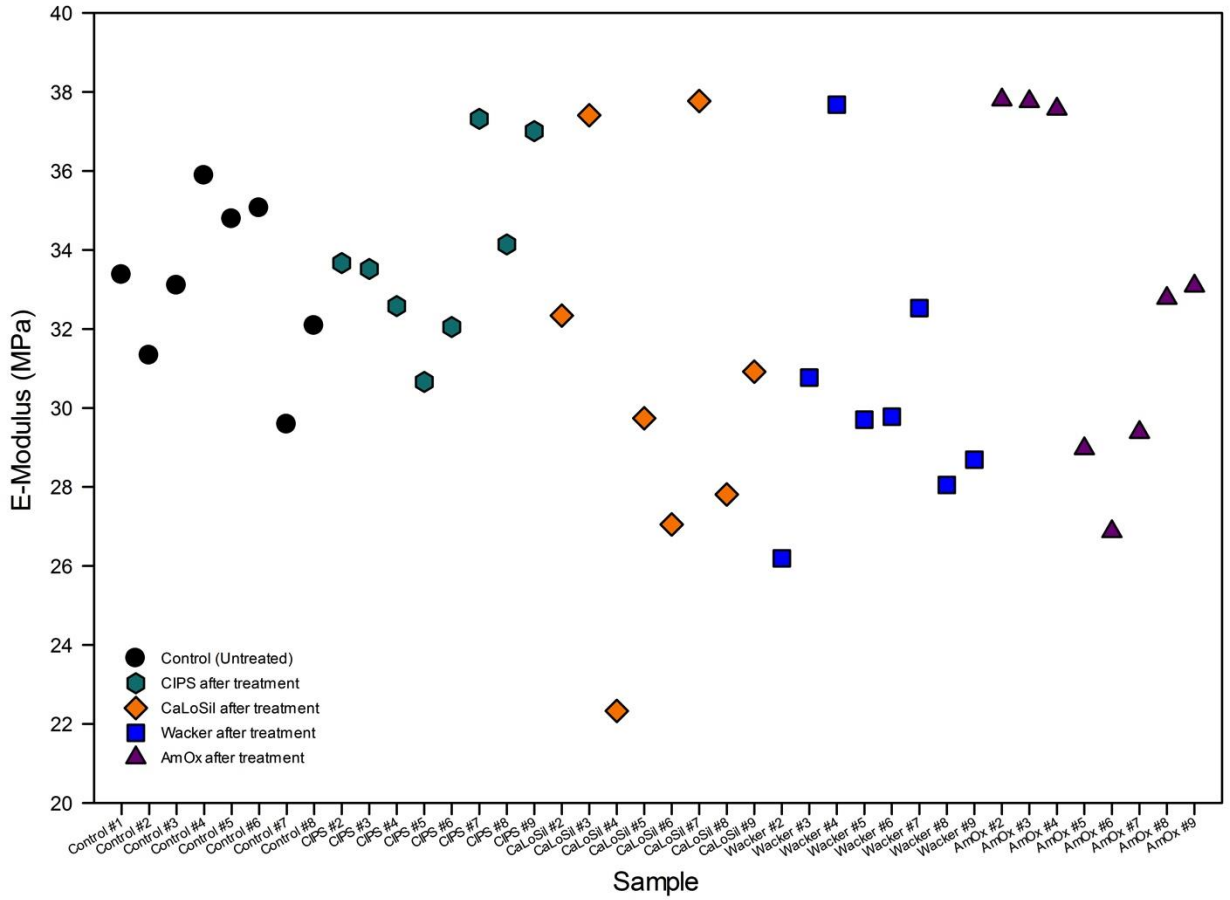



**Figure 30: Graph to show E-Modulus for samples after treatment in comparison to untreated controls**

## Colour Change - Spectrophotometer

Before analysis, samples were observed qualitatively by eye. A $\Delta E_{00}$ value greater than 1 is generally accepted to be noticeable by the naked eye. However, this can depend upon the colours involved and the observation conditions. Figure 31 is a photograph showing a representative of the treated surface of samples treated with each consolidant in comparison to an untreated control. Colour change between CIPS samples and untreated blocks was difficult to detect visually, however, the surface had changed in appearance with treated samples acquiring a sheen. Colour difference between the ammonium oxalate

blocks and the untreated blocks was also difficult to detect by eye. The Wacker samples were slightly darker in appearance, but only on very close inspection. The biggest change was seen with the CaLoSil samples. A white haze or 'bloom' was visible on nearly all treated samples.



CIPS AmOx CaLoSil Wacker Untreated Control

**Figure 31: Photos to show comparison of treated colour vs. untreated control**

As can be seen from table 7, all samples demonstrated an overall colour change ($\mathbf{\Delta}E_{00}$) greater than 1. The samples that demonstrated the lowest overall colour change were ones treated with CIPS; $\Delta E_{00}$ of 2.72 SCI (Specular Component Included) and 2.85 SCE (Specular Component Excluded). The Ammonium Oxalate samples had the next lowest colour change with $\Delta E_{00}$ of 3.58 SCI and 3.57 SCE. Wacker samples had an even greater overall colour change and the greatest colour change was seen with the CaLoSil samples, which had a $\mathbf{\Delta}E_{00}$ of 9.50 SCI/SCE. This CaLoSil result was to be expected with the significant white haze that appeared on the surface. Shiny or glossy surfaces can cause variances in the colour seen, SCE (specular component excluded) values that exclude spectral reflectance can help to produce a colour evaluation that is representative of visual observation of an object (Konica Minolta 2007). Differences between SCE and SCI (Specular Component Included) can show a difference in the gloss on the surface. For all groups except the CIPS these two values are almost identical. The CIPS samples showing a difference is likely due to the sheen can now be identified on the surface.

| Sample Group | Group Traits | ΔL* | Δa* | Δb* | ΔC* | $\Delta E_{00}$ |
|---|---|---|---|---|---|---|
| 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 8: Summary of mean colour changes before and after treatment per sample group**

## Water Penetration - Karsten Tubes

As can be seen in Figure 32, all samples treated with CIPS, Ammonium Oxalate, and Wacker OH showed a decrease in the average water penetration as measured with Karsten tubes. These differences were found to be statistically significant (P= <0.001). The Wacker samples showed the largest decrease with hardly any water penetrating after treatment. The CIPS and Ammonium Oxalate samples demonstrated a fairly similar decrease; after treatment water penetration was low, but still measurable. Some individual CaLoSil samples demonstrate a slight decrease in water penetration, but overall the differences are not statistically significant (P=0.055).

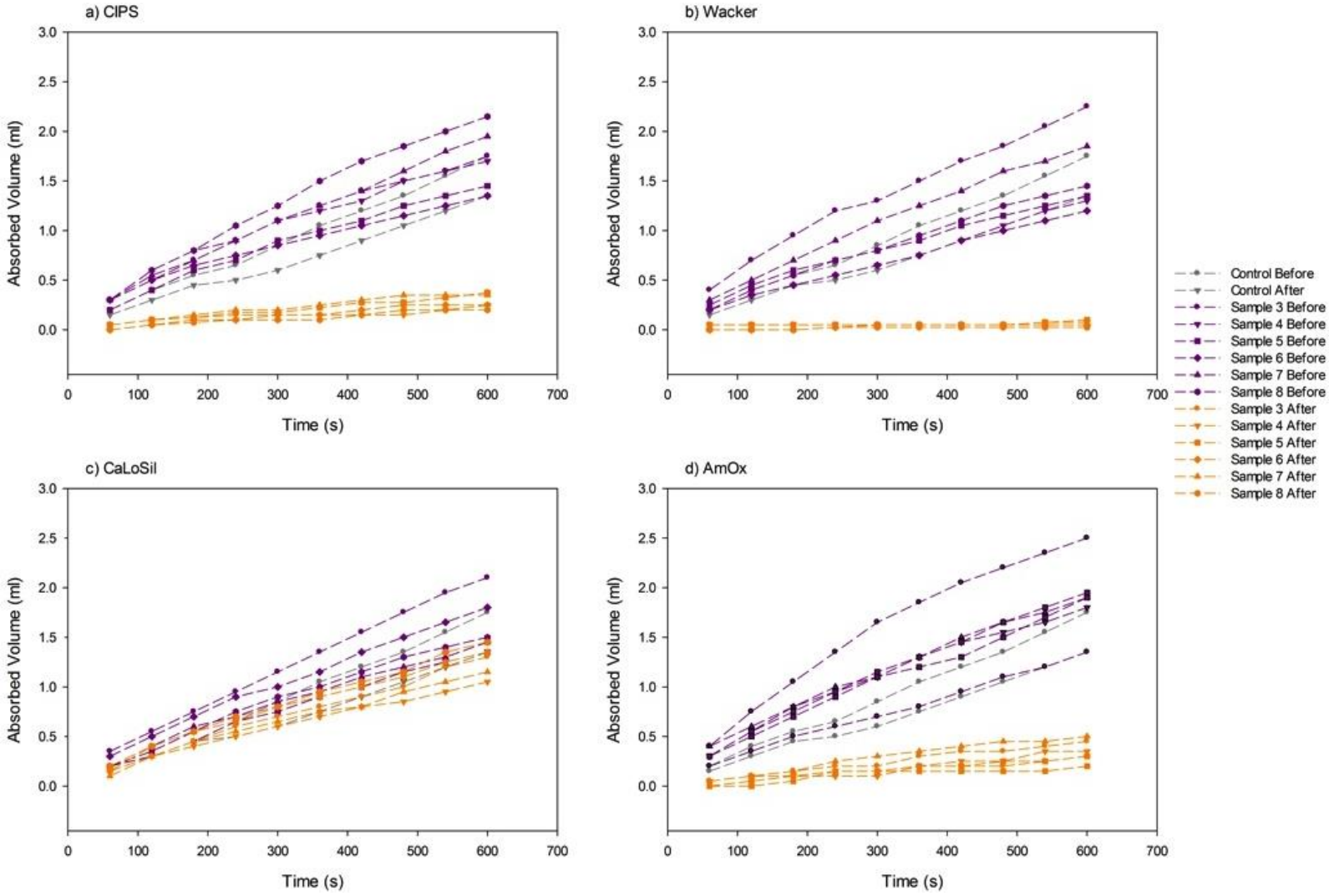



**Figure 32: Graphs to show water penetration (ml) over time, for samples before and after treatment. a) CIPS samples; b) Wacker samples; c) CaLoSil samples; d) AmOx samples**

## DRMS

Figure 33 shows the drilling resistance measurement profiles for samples #3 from each consolidant group, in comparison with the control CIPS#10 (Control #2). The black shaded area represents positive difference in force required to drill into the stone; i.e. greater internal strength.

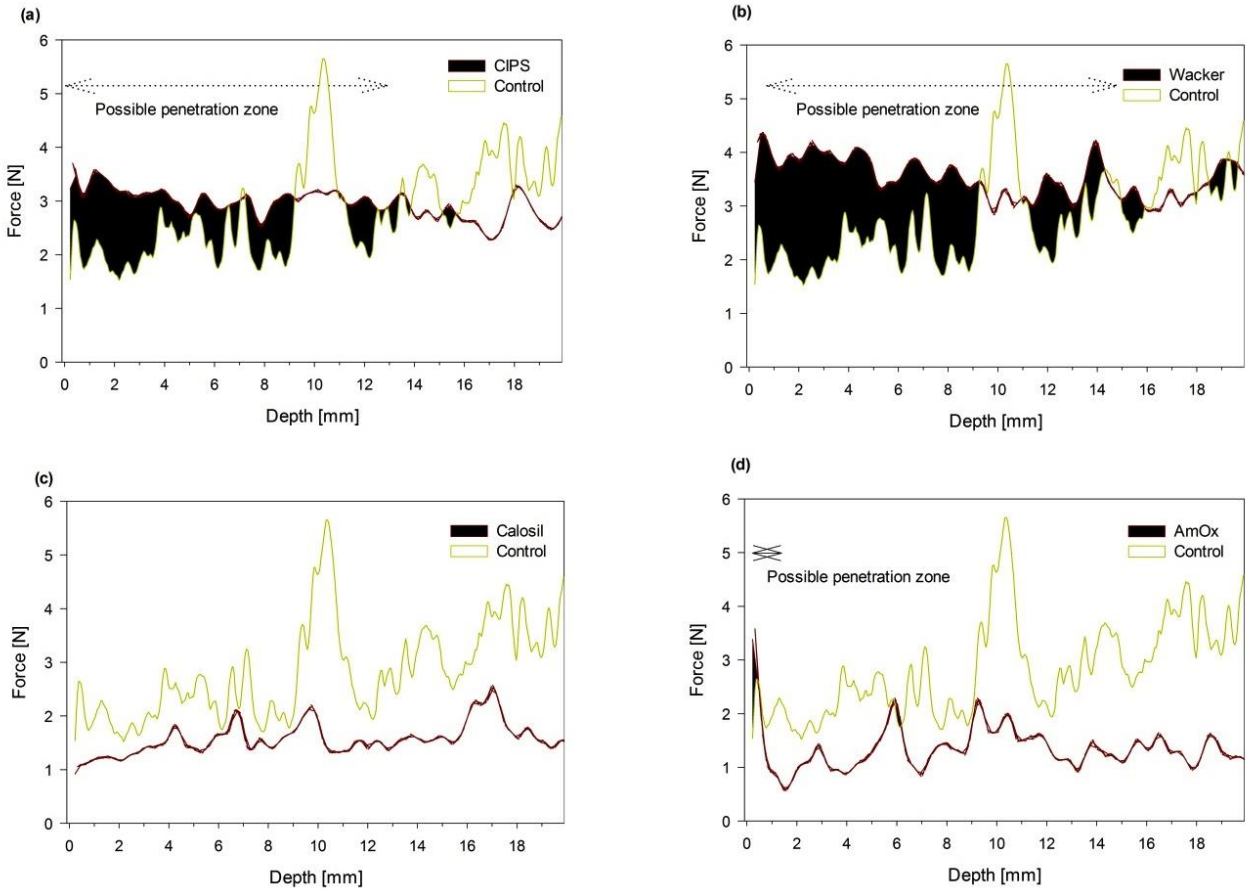



**Figure 33: Average drilling resistance profiles for stones treated with different consolidants. a) CIPS treated stone vs. untreated control; b) Wacker OH 100 vs. untreated control; c) CaLoSil vs. untreated control; d) AmOx vs. untreated control.**

Figures 33a and 33b clearly show that both the CIPS treatment and the Wacker OH demonstrated consolidation action over a depth between 12 and 15mm. The profiles are similar in shape showing a comparable gradual change, implying a diffuse interface between treated and non-treated substrate, however the Wacker OH appears to provide a slightly greater increase in strength than the CIPS. There did

not appear to be any demonstrable effect of the CaLoSil treatment, the resistance profile is lower than that of the control for the whole of the analysed depth and there is no evidence of elevated levels of drilling resistance near the surface. The resistance measurements for stone treated with ammonium oxalate indicated a strength increase limited to a very superficial layer. This is consistent with naturally occurring calcium oxalate films. For both the CaLoSil and AmOx (figure 33c and 33d) the overall profiles show lower drilling resistance of the blocks cf control, Wacker, and CIPS. These two blocks were Hartham Park, in comparison to the others which were all Elm Park (cf Table 5). This could show the Hartham Park blocks had a lower internal strength than the Elm Park.

## SEM

Figure 34 shows two backscattered electron (BSE) images of the cross-section of a CIPS sample with the treated edge at the top. The CIPS deposition is clearly visible in a layer along the treated edge. In the higher magnification image it can be seen that the calcite from the CIPS treatment is deposited as small amorphous crystals. DRMS results suggest penetration of the CIPS at least 12mm into the stone. It was difficult to identify the CIPS deposited calcite further within the stone on this cross section. Elemental mapping did not show a difference between the calcite within the stone and the calcite deposited by the CIPS.

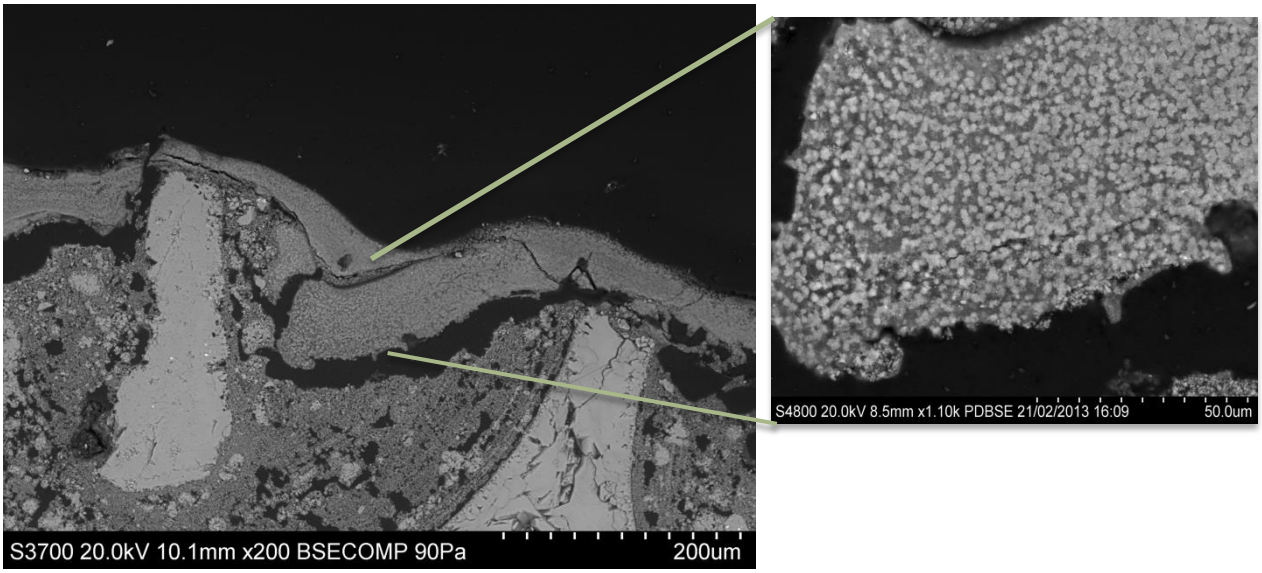



**Figure 34: Cross-section of stone treated with CIPS x200 magnification with x1.1k magnification image of CIPS precipitate deposition**

Figure 35 shows the elemental map of the Wacker cross-section. Presence of silicon is highlighted in red. Due to the lack of silica within the stone samples and the resin used to make the cross sections, the silicon within the Wacker sample can be attributed to deposition from the Wacker OH treatment. Silicon was found all the way through the 10mm sample re-enforcing the DRMS results that suggested a penetration depth of at least 12-15mm for the Wacker OH treatment.

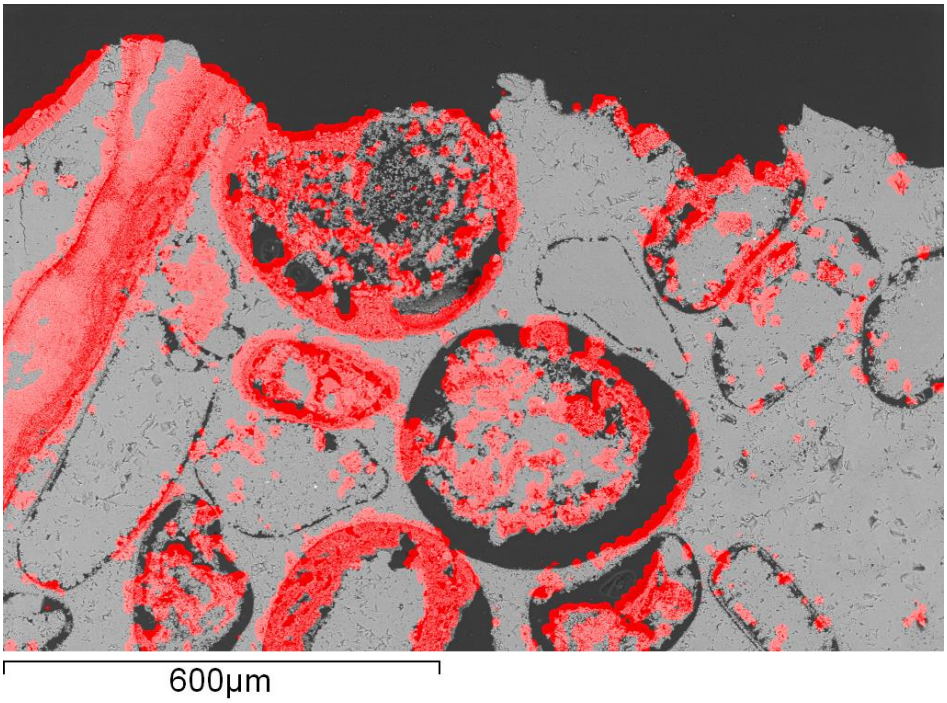



**Figure 35: (SEM EDS) Elemental map of sample treated with Wacker OH showing distribution of silicon in red (90Pa, 20kv, 10.1mm operating depth).**

Cross sections of stone treated with both the ammonium oxalate treatment and CaLoSil were also examined using SEM. It was not possible to identify the presence of the treatments visually or elementally.

## MIP

The graph in figure 36 plots the log of cumulative intrusion (ml/g) of mercury into each sample (one sample for each consolidant), against the pore diameter (µm). Each curve has been normalised to account for the different porosity of the stone samples.

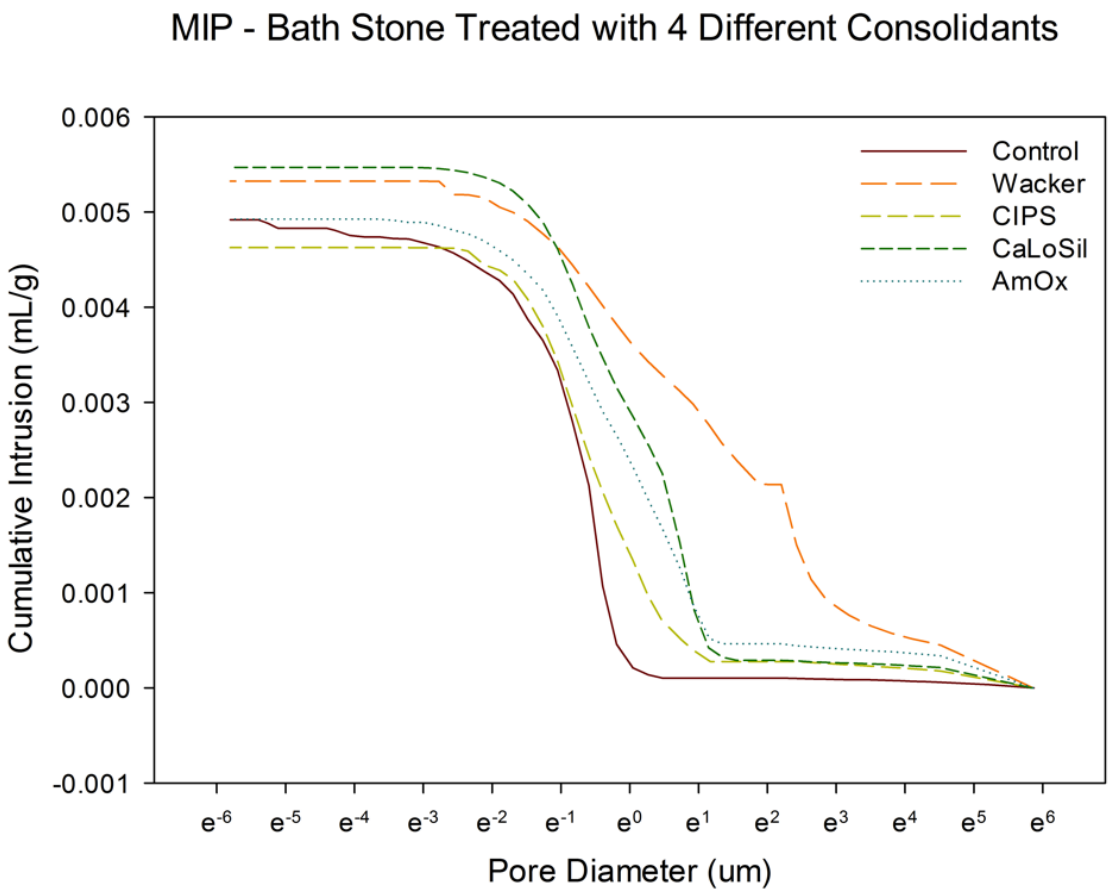



**Figure 36: Cumulative intrusion vs. pore diameter (intrusion normalised to take porosity of each stone sample into account) where $e^{-6} = 10^{-6}$ – in this case $1x10^{-6}$ microns; $e^{0} = 1 \times 10^{0}$ microns = 1 micron**

It can be seen that all the stone samples have predominantly small pores. The samples treated with CIPS and ammonium oxalate have very similar profiles to the control sample in comparison to the Wacker and CaLoSil samples. The results were normalised for porosity so this perhaps indicates the differences can be attributed to changes due to the two treatments.

## Ion Chromatography

As can be seen in Table 4, the CIPS block tested (CIPS#8) was found to have much higher chloride ($Cl^-$) concentrations in samples taken from 0.8mm and 1.5mm depths than any of the other blocks. The CaLoSil block had raised nitrate ($NO_3^-$) levels in comparison to the other blocks and both the CIPS and AmOx

blocks had ammonium ions ($NH_4^+$) present, whereas the other three blocks did not. The CaLoSil block also showed a higher sulphate ($SO_4^{2-}$) concentration than the other blocks. This was more evident in the 8 - 15mm sample than the 0-8mm sample suggesting this was an internal presence of salts, not due to treatment or weathering.

| Sample | F% | Cl% | NO3% | SO4% | Na% | NH4% | K% | Mg% | Ca% |
|---|---|---|---|---|---|---|---|---|---|
| 0-8mm Depth | | | | | | | | | |
| Control 8 | 0.004 | 0.007 | 0.002 | 0.013 | 0.004 | 0.000 | 0.006 | 0.005 | 0.095 |
| CaLoSil 8 | 0.001 | 0.081 | 0.036 | 0.082 | 0.015 | 0.000 | 0.007 | 0.006 | 0.184 |
| CIPS 8 | 0.000 | 0.412 | 0.000 | 0.025 | 0.006 | 0.013 | 0.004 | 0.005 | 0.432 |
| Wacker 8 | 0.001 | 0.014 | 0.000 | 0.006 | 0.003 | 0.000 | 0.004 | 0.005 | 0.232 |
| AmOx 8 | 0.001 | 0.004 | 0.000 | 0.004 | 0.003 | 0.002 | 0.003 | 0.004 | 0.086 |
| 8mm-15mm Depth | | | | | | | | | |
| Control 8 | 0.003 | 0.026 | 0.000 | 0.009 | 0.017 | 0.000 | 0.004 | 0.004 | 0.065 |
| CaLoSil 8 | 0.000 | 0.067 | 0.033 | 0.102 | 0.016 | 0.000 | 0.006 | 0.006 | 0.198 |
| CIPS 8 | 0.002 | 0.345 | 0.000 | 0.005 | 0.008 | 0.019 | 0.008 | 0.008 | 0.411 |
| Wacker 8 | 0.001 | 0.006 | 0.000 | 0.004 | 0.002 | 0.000 | 0.002 | 0.002 | 0.080 |
| AmOx 8 | 0.000 | 0.032 | 0.000 | 0.004 | 0.024 | 0.001 | 0.004 | 0.005 | 0.088 |

**Table 9: Anion and cation ion chromatography results in mass percent**

## Discussion

A large number of different analytical methods have been employed in this investigation. 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. However, by combining the results it may be possible to compare the consolidants. Below in table 9 is a summary of results versus expected outcomes. Most results confirmed the original hypotheses, however there were some unexpected outcomes.

| Consolidant | Expected Outcome | Result |
|---|---|---|
| **Silane SILRES BS OH 100 (Wacker)** | - Increase in surface hardness<br>- Increase in internal strength<br>- Reduction in water permeability<br>- Deep penetration<br>- Low but noticeable colour change. | - Statistically significant increase (Equotip)<br>- Apparent increase in internal strength (DRMS)<br>- Clear reduction in water penetration (Karsten)<br>- ≈14mm penetration<br>- Colour change ΔE00 4.47/4.46 |
| **Ammonium Oxalate** | - Increase in surface hardness<br>- Limited penetration<br>- Reduction in water penetration | - Statistically significant increase (Equotip)<br>- Penetration ≈ 1mm (DRMS)<br>- Reduction in water penetration |
| **CaLoSil** | - Increase in surface hardness<br>- Increase in internal strength<br>- Deep penetration | - No significant increase in surface hardness (Equotip)<br>- No apparent increase in internal strength (DRMS)<br>- No penetration detected |

| | | |
|---|---|---|
| | | (DRMS) |
| | - No change in water penetration<br>- Possible white bloom on surface | - No reduction in water penetration<br>- Very noticeable white bloom - $\Delta E_{00}$ 9.50 |
| **Calcite In-situ Precipitation System** | - Increase in surface hardness<br>- Increase in internal strength<br>- Raised chloride and ammonium salts | - Overall no statistically significant increase in surface hardness<br>- Potential increase in internal strength to ≈12/13mm depth<br>- Slightly raised levels of chloride and ammonium salts |

**Table 10: Summary of expected outcomes vs. results**

.

## Consolidation effect

Surface hardness testing using an Equotip 3 showed the ammonium oxalate treatment provided the greatest increase in surface strength, far larger than that demonstrated by the organic consolidant Wacker OH, although the increase shown with the Wacker was statistically significant. Further testing of strength using DRMS showed that the increase in hardness from the ammonium oxalate treatment was restricted to a very superficial layer. This was in comparison to the Wacker OH sample where the drilling resistance profile shows an increase in strength for at least 12mm into the stone. Both the CIPS and the CaLoSil had some individual samples that demonstrated an increase in surface hardness, but overall neither of these treatments provided a statistically significant increase in surface hardness. DRMS of a CIPS sample appears to suggest an increase in internal strength for around 12mm with a similar profile to the sample treated with

Wacker OH. The most effective consolidant in terms of surface hardness would seem at first glance to be the ammonium oxalate treatment. However, when combining these results with analysis of depth of penetration and the interface between consolidated areas and inner stone substrate using DRMS, it appears this is just a very solid surface crust, which could pose many problems for an artefact. The Wacker OH would therefore be the most successful consolidant with regards to strength increase. CIPS does show some promise for both surface and internal strength, perhaps application methods need to be investigated to discover how to maximise its effectiveness. The CaLoSil did not appear to be successful in increasing internal strength when analysed using DRMS.

The only observable difference in the E Modulus between the control and the treated samples was that the results for all samples other than CIPS seemed to have more variability than the control replicates. It was not possible to see if the treatments had increased the E Modulus. This could be due to only one surface being treated, the consolidant may not have penetrated far enough into the sample to affect the overall UPV. Future experiments looking at the change in UPV and E Modulus when all sides of a sample are treated could look into this factor

### Impact on water permeability/ porosity

Karsten Tube tests to analyse water penetration showed samples 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 samples. Some individual CaLoSil samples had a decrease in water penetration, however overall there was not a statistically significant difference. None of the treatments used were designed with hydrophobic properties in mind, however some decrease in water penetration capacity is to be expected as the consolidant forms new bonds in the spaces between the individual grains of the stone. Completely reducing the water penetration can be undesirable however as this can prevent the stone from dealing with changes in relative humidity, and can cause stress between the untreated substrate and the treated zone near the surface of the stone.

### Colour and salts change

Overall colour change for all samples 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 samples treated with ammonium oxalate, which were below the values for the samples treated with Wacker OH. The samples treated with CaLoSil developed a very obvious white bloom on the surface; shown by the extremely high $\Delta E_{00}$ 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.

## Conclusions

There are many consolidants available to treat deteriorated stone artefacts and the best one to use will depend upon a variety of factors including the stone itself, its location, deterioration problems and history. Preliminary testing looking at treatment effectiveness, compatibility with the stone and how it changes the stone appearance (along with other parameters), can help identify which consolidant would be best suited to the artefact.

Presented within this chapter are the results from the analysis of three inorganic consolidants being considered for use on British Museum limestone artefacts, in comparison with a previously used organic treatment, Wacker OH (SILRES® BS OH 100). The aims of this analysis were:

- To experimentally compare the "effectiveness" of each consolidant with one another.
- To see if any of the three inorganic consolidant's holds potential for future use in the British Museum
- To treat both fresh and weathered stone to compare consolidation action on different stone substrates

In this experiment, the Wacker OH appears to have provided the best consolidation action; statistically significant increase in surface strength with deep penetration complemented by an increase in internal strength. However, the DRMS results suggest the CIPS treatment may have provided an almost as effective increase in internal strength (even if this is not shown in surface hardness results). This is accompanied by a less drastic reduction in water penetration, and a much lower colour change. The original aim of the project was to look for an inorganic consolidant that would provide a similar consolidation action to the silane, with a greater compatibility with the substrate, and with fewer health and safety implications. The CIPS has shown great potential for this and so would be recommended for further testing for use on stone museum artefacts. The ammonium oxalate had a significant effect on surface hardness but this was limited to a superficial layer. Due to this, and to the conservators at the British Museum indicating they would not be happy with the recommended application method, it has been decided that there will be no further investigation into the possibilities for using ammonium oxalate treatment in the British Museum. The lack of consolidation effect from the CaLoSil was unexpected and disappointing. Much further work would be needed to perfect this treatment.

The amount of samples needed for this experiment necessitated the use of stone from two sources. These were distributed a bit unevenly throughout the different treatment groups and control samples tested did not always match the treated stone sample type. Future experiments should have an even distribution of stone types per consolidant group and ensure controls are directly comparable to tested samples.

Differences between the weathered and fresh stone used within this stage of the project were noted. However, after much discussion between OxRBL and the conservation department within the British Museum, it was decided that whilst some of the weathered samples used here came from stone that had been exposed to the external environment for over 100 years, all had been freshly cut into cubic replicates before the experiment began, and the artificial weathering conducted after cutting may not have sufficiently weathered the surface to achieve a realistic comparison to naturally weathered stone. There were also debates over the behaviour of consolidants on cubic replicates versus carved limestone – likely to be in a

variety of shapes and not just with flat surfaces to treat. The next and final stage of the project, detailed in the following Chapter 8, was designed to address these issues by comparing the consolidants on naturally weathered stone samples of a variety of shape and size.

# Chapter 8

*Reconsidering Inorganic Consolidants: Experiments Using Deteriorated Stone*

## Introduction

Evaluating the performance of consolidation treatments can be highly complex; a wide variety of parameters are usually measured and then combined to assess effectiveness, and there are many factors that can affect consolidant performance. These factors can include aspects of application protocol, environment, the type of material treated and its state of degradation (Ferreira Pinto & Rodrigues 2012, Pamplona, Melo & Aires-Barros 2008). The principle aim of consolidants is to increase cohesion between grains within a stone, the amount to which this can be achieved is obviously partially dependent upon the amount of decay a stone has experienced (Franzoni et al. 2011). If consolidants are to be applied to decayed stone, then it follows that any testing of consolidation effectiveness should be undertaken upon decayed, and not sound, stone (Theoulakis, Karatasios & Stefanis 2008, Franzoni et al. 2011).

Naturally weathered stones can possess great variability of characteristics and furthermore, often have unknown histories. It can be difficult to gain enough to produce the number of replicates required for experimental testing. Because of this, laboratory investigations into consolidants frequently make use of freshly quarried stone. As condition of this stone is not usually comparable to that requiring consolidation, these stones are usually artificially weathered (Laurenzi Tabasso & Simon 2006). In line with this, investigations into the potential held by new stone consolidants within this project detailed in the previous chapter, centred on evaluating the effectiveness of consolidants using freshly cut, artificially weathered, stone cubes. Before making an ultimate decision about whether to try any of the inorganic consolidants tested on actual museum artefacts, the British Museum conservators suggested a trial upon naturally weathered samples of a variety of shapes and sizes. The results of this investigation are presented within

this chapter. Ammonium oxalate treatment was not used within this experiment after consultation with the British Museum conservators, as explained below.

The aims of this stage of investigation were:

- To use naturally weathered stone to compare the effectiveness of three consolidants (two inorganic, one organic)
- To assess if the effectiveness demonstrated differs from results on artificially weathered stone used in previous experiments
- To see if analytical methods used on cubic samples with flat surfaces are equally as useful on weathered and rough surfaces.

Based upon the results from the comparative assessment on artificially weathered blocks, there were several hypotheses made about the performance of the various treatments on the deteriorated stones:

I. Consolidation effect
    a. Wacker treated stones would most likely show the greatest increase in surface hardness and internal strength, with the greatest depth of penetration. These samples would be closely followed by the CIPS treated stones.
    b. CaLoSil treated samples had not previously shown significant increases in surface hardness or internal strength. This could be due to the surfaces of the artificially weathered stone not being deteriorated to an extent that the CaLoSil would provide a noticeable effect. It would be interesting to see if more of a consolidation effect would be seen on the naturally weathered stones as they were in a greater state of decay.

II. Impact upon water permeability
    a. Wacker and CIPS treated samples were likely to show a significant drop in water penetration.

b. Previously the water penetration into CaLoSil samples had not changed upon treatment. It was hoped that on these very deteriorated stones more of a consolidation effect would be seen. If consolidation did occur, it would be interesting to note if this was accompanied by a reduction in water penetration.

III. Change in colour or salt level

a. Experiments detailed in Chapter 5 had shown colour change was less noticeable on weathered stone than fresh. It was therefore expected that colour change values for treatments on very deteriorated stone would be less than those seen on the freshly cut, artificially weathered, samples. However, it was expected that the order of change would be likely to remain the same with CIPS treated samples showing the lowest change in colour, then the Wacker treated samples, with the greatest change demonstrated by samples treated with CaLoSil. The CaLoSil samples in the previous experiment had a white bloom on the treated surface. It would be important to see if this was still an issue demonstrated by the highly deteriorated samples.

b. CIPS treated samples had shown raised levels of chloride and ammonium salts. It was expected that the samples within this series of experiments would also show this, however, it was also expected that the background salt level would be higher.

## Materials and Methods

### Stone Materials

For this part of the *Back to Nature* project the stone materials were naturally weathered limestones. Samples were cut from two larger blocks of stone; one removed from the south pavilion of Basildon Park, a

National Trust property in Berkshire with a relatively well-known history, and one provided by stone conservators at the British Museum that had been outside for the last few years. More details on these stones can be found in Chapter 4. The two larger stones were cut to give the maximum number of samples whilst maintaining at least one naturally weathered face per sample. There were five samples per consolidant group and three controls, each consolidant group had a mixture of samples from the two original stones. The samples were a selection of shapes and sizes as can be seen in figure 37. All samples were kept together throughout the experiment under laboratory conditions; temperature of 23°C, RH 62%.




**Figure 37: Samples before treatment in a variety of shapes and sizes a) CIPS; b) CaLoSil; c) Wacker; d) Control**

## Consolidants

Of the four different consolidants included in the Back to Nature project, the Calcite In-Situ Precipitation System (CIPS), CaLoSil, and Wacker Silres BS OH 100 were tested in this experiment. After the first assessment on the artificially weathered limestone cubes (see Chapter 7), a decision was taken not to include the ammonium oxalate treatment in any further investigations. This was predominantly because of the opinion of the British Museum stone conservators that the application method for this treatment was not considered feasible for large-scale stone artefacts. Further information on the three consolidants that were investigated can be found in Chapter 4. The three consolidants were applied according to information

from the manufacturers and after discussion with BM stone conservators – particularly with reference to previous experiments. More information on the application methods can be found in the following paragraphs. Samples were tested before and after treatment. Results were analysed to determine effectiveness and to see if any consolidant had the potential to be used in the future in the museum. These results were combined with ones from previous experiments to give a clearer indication of effectiveness and consolidant performance; this is discussed further in Chapter 9.

### Calcite In-Situ Precipitation System (CIPS)

The CIPS fluid was formed from two solutions mixed in equal proportions just prior to application. As described in previous chapters (4,6,7), 6 applications of CIPS are recommended for sufficient consolidation action without causing a noticeable change in the surface appearance (Price 2010). All 5 samples designated for treatment using CIPS, were sprayed with the mixed solutions, as can be seen in Figure 38. The samples were treated every 24hrs for 6 applications and then left with the other replicates whilst their treatments cured.

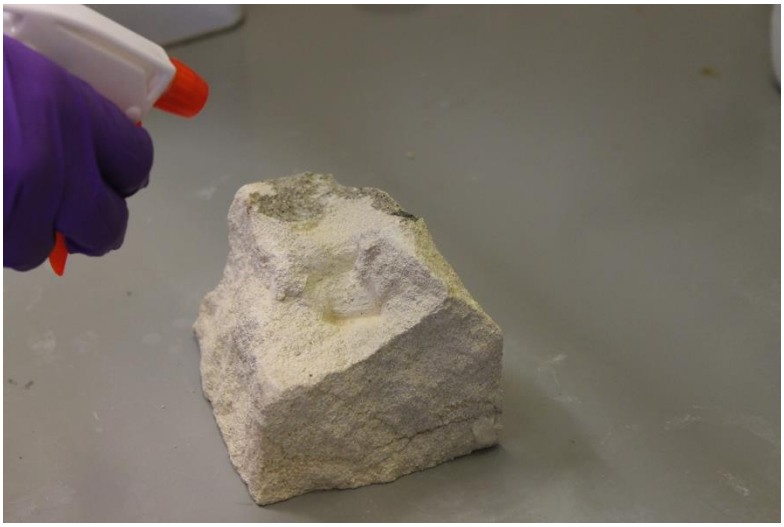


**Figure 38: Application of CIPS by spraying**

### CaLoSil

CaLoSil is a new nano-lime stone consolidant developed specifically for consolidating calcareous historic material (Campbell et al. 2011). Nano-particles of $Ca(OH)_2$ are suspended in different alcohols and react with carbon dioxide after application to produce calcium carbonate. More information on the reactions involved can be found in Chapter 4. CaLoSil E25 (calcium hydroxide particles dispersed in ethanol at 25g/L) was applied to all designated CaLoSil samples by pipette (figure 39), until surface saturation was achieved. After 3 weeks curing time, a second application was undertaken. Samples were then left for a further 3 weeks to cure before post-treatment measurements were taken.

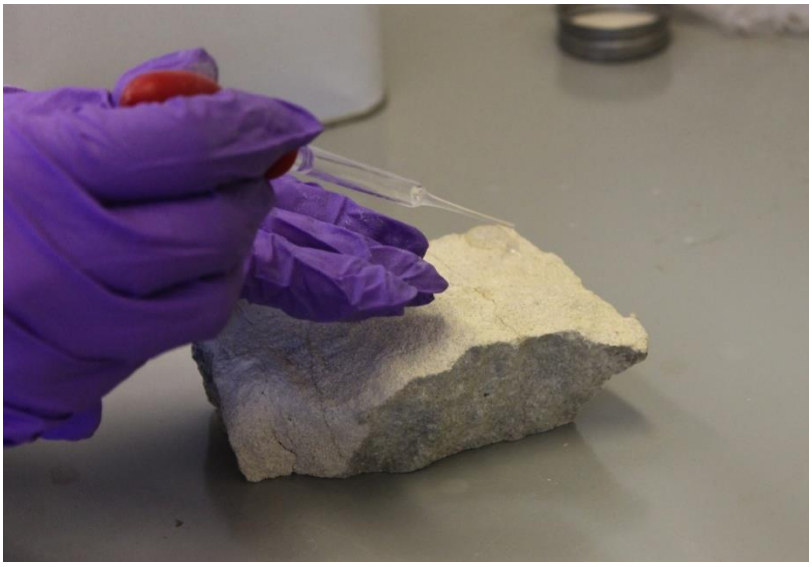


**Figure 39: Application of CaLoSil by pipette**

### SILRES BS OH 100 (Wacker)

Within each experiment designed to assess the potential of the new inorganic consolidants, an organic silane was used for comparison. The silane selected use within the entire *Back to Nature* project was SILRES® BS OH 100, also known as Wacker OH 100. More information on this silane can be found in Chapter 4. The SILRES® BS OH 100 was applied by pipette to all designated Wacker samples (figure 40), until saturation, and left to cure. After 3 weeks a second application was undertaken and then left to cure for another 3 weeks before any post-treatment measurements were taken.



**Figure 40: Application of Wacker by pipette**

## Testing Methods

To investigate, and compare the three different consolidants, a variety of analytical methods were used both non (or minimally) destructive, and destructive. As explained in Chapter 4, the project methodology involved combining a multitude of analytical tests to provide an overall picture of the effects of each consolidant to allow for comparison. In the previous set of experiments (Chapter 7) a large number of different methods were used. For this set of experiments a more slim-line approach was taken; some methods such as Pundit Lab and Mercury Intrusion Porosimetry had been used in the previous experiments as they were on loan to OxRBL or the opportunity arose to make use of equipment at other universities. Some methods such as thin section petrography had not provided useable data so were omitted from this experimental phase. Some samples had an obvious hardened surface layer, for example the Basildon Park samples looked to have a sulphate crust on some of the weathered surfaces. In these instances, readings were taken from those areas without a surface crust to try and minimise any skewing of results. More details on each testing method can also be found in Chapter 4. Where possible, simple statistical analysis was used to test for significance in any change induced by the consolidation treatments.

Results were tested for normality using a Shapiro-Wilk test and then paired t-tests were performed at the 95% confidence interval.

# Results

## Weight

Samples were weighed before and after treatment. Measurements for each sample group were averaged and the results can be seen in Table 10.

| Sample Group | Mean ΔM(g) before/after treatment |
|---|---|
| **Control** | 0.53 |
| **CIPS** | 6.09 |
| **CaLoSil** | 1.32 |
| **Wacker** | 2.47 |

**Table 11: Mean change in mass (g) before and after treatment**

As can clearly be seen from Table 10, the CIPS samples increased in mass the most in comparison to the other sample groups. The CaLoSil treated samples had the lowest increase in mass.

## Surface Hardness – Equotip

Surface hardness was measured using a Proceq Equotip (Equotip 3). Ten readings were taken per treated surface of each sample. This was in line with the measurement protocol used in the previous set of experiments. Measurements were taken before and after treatment.

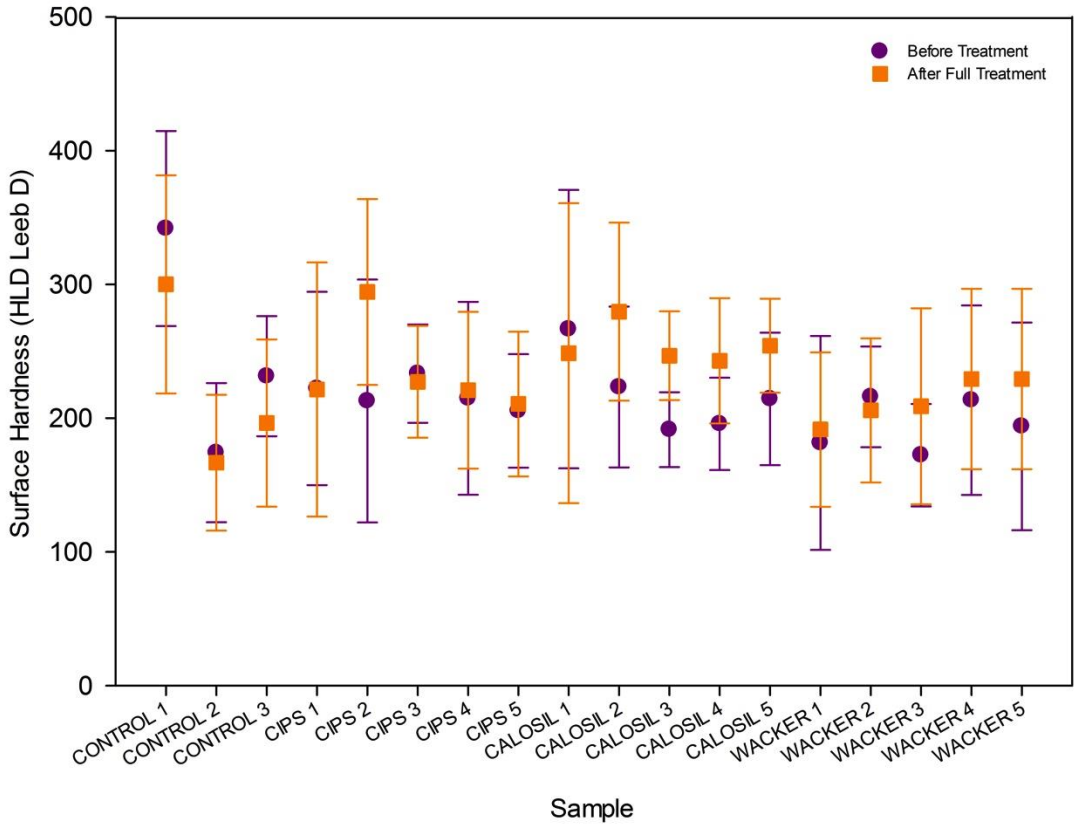



**Figure 41: Graph to show surface hardness measurements taken using Equotip 3 before and after treatment; means with standard error bars**

Looking at the graph in Figure 41 it is possible to see the variability between samples, even within each consolidant group. The large error bars show that this variability is present even within measurements on individual samples. None of the consolidant groups demonstrated a statistically significant change in surface hardness upon treatment.

## Colour Change – Spectrophotometer

To assess the aesthetic effects of each consolidation treatment on the stone, change in the colour parameters (CIE L*a*b*) were measured using a spectrophotometer (Konica Minolta CM 700d/600d) under illuminant D65 with a 10 degree observer, with the medium aperture diameter 8mm, and using colour data software *SpectraMagic xs*. Ten measurements were taken on each treated surface to give a mean colour difference. This was following the measurement protocol from the previous set of experiments. Overall change in colour ($\Delta E_{00}$) was examined, along with a more detailed look at change in colour, hue and saturation.

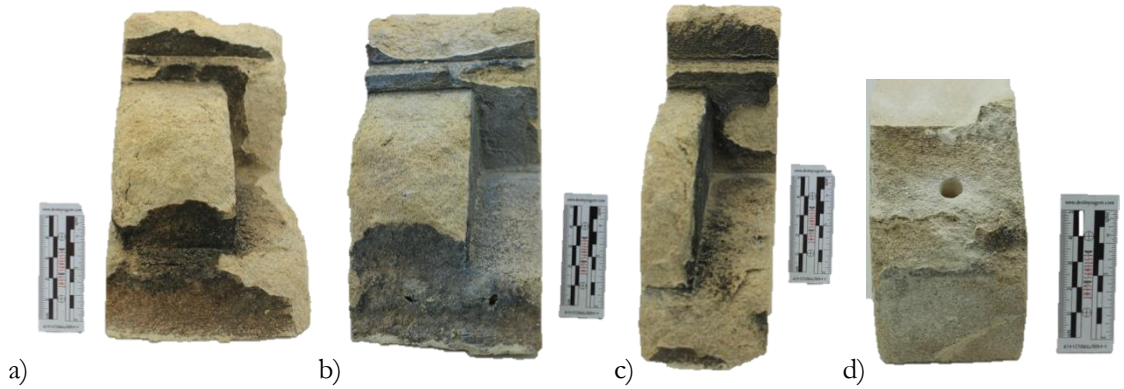



**Figure 42 (a-d): Photos of samples post treatment to show comparison of the colour of treated surfaces a) CIPS; b) CaLoSil; c) Wacker; d) Control**

As in previous experiments, samples were observed by eye to see if any colour change could be detected visually, prior to analysis with the spectrophotometer. Photos to show the difference can be seen in Figure 42. It was difficult to identify colour change on both the CIPS and Wacker samples. There was a noticeable white bloom on all CaLoSil samples.

| Sample Group | Group Traits | Δ L* | Δ a* | Δ b* | Δ C* | Δ $E_{00}$ |
|---|---|---|---|---|---|---|
| Control | SCI | 1.21 | 0.15 | 0.77 | 0.78 | 1.19 |
| Control | SCE | 1.14 | 0.15 | 0.76 | 0.77 | 1.20 |
| CIPS | SCI | -0.50 | 0.52 | 3.28 | 3.32 | 2.12 |
| CIPS | SCE | -0.50 | 0.51 | 3.29 | 3.33 | 2.13 |
| CaLoSil | SCI | 3.90 | -0.05 | -4.30 | -4.18 | 4.11 |
| CaLoSil | SCE | 4.02 | -0.05 | -4.29 | -4.17 | 4.17 |
| Wacker | SCI | -0.78 | 0.63 | 2.49 | 2.56 | 2.30 |
| Wacker | SCE | -0.68 | 0.64 | 2.49 | 2.57 | 2.26 |

**Table 12: Spectrophotometer results per consolidant group**

As mentioned in Chapter 7, a commonly accepted figure for a colour change visible to the naked eye is a $\Delta E_{00}$ value of 1. However, it can be see from Table 11 that the natural colour variation of the stone is such that the $\Delta E_{00}$ for the untreated controls is 1.19 SCI (specular component included) or 1.20 SCE (specular component excluded). The results for the CIPS and Wacker samples are around double this value at 2.12/2.13 $\Delta E_{00}$ and 2.30/2.26 $\Delta E_{00}$ respectively – these results are fairly close to one another. The colour change for the CaLoSil group was nearly double this again at a $\Delta E_{00}$ of 4.11/4.17.

## Water Penetration – Karsten Tubes

The original intention had been to assess water penetration before and after treatment using Karsten tubes. However, when attempting this, it was found that the putty (Plastic Fermit) used to bond the Karsten tube to the surface of the sample was too adhesive and was causing grains, and in some cases larger pieces of stone, to be removed with the tube. Other types of putty caused a similar reaction. It was decided that the surface was too weak and the Karsten tests were abandoned.

## Drilling Resistance Measurement System (DRMS)

The Drilling Resistance Measurement System (DRMS) is a portable system, often used in experiments designed to evaluate consolidation action within carbonate stones (Pamplona et al. 2007, Ferreira Pinto & Rodrigues 2012, Pinto & Rodrigues 2008). This system measures force necessary to drill to a certain depth with constant rotational speed and penetration rate (Pamplona et al. 2007). Drilling resistance measurements were taken for during this investigation to look at penetration depth of the various treatments, and to quantify any consolidation action they provided. A SINT Technology DRMS was used with a 3mm Diaber (Polycrystalline Diamond) drill bit also from SINT Technology. Rotation speed was set at 600rpm with a penetration rate of 10mm $min^{-1}$. Measurements were taken before and after sampling using a homogenous artificial reference sample (ARS) to monitor drill bit wear. One sample from each consolidant group, along with the control was measured, each sample was measured three times. Figure 43 (a – c) shows the average drilling resistance profiles for stones treated with each consolidant, in comparison to the average profile from measurements taken on an untreated control sample.

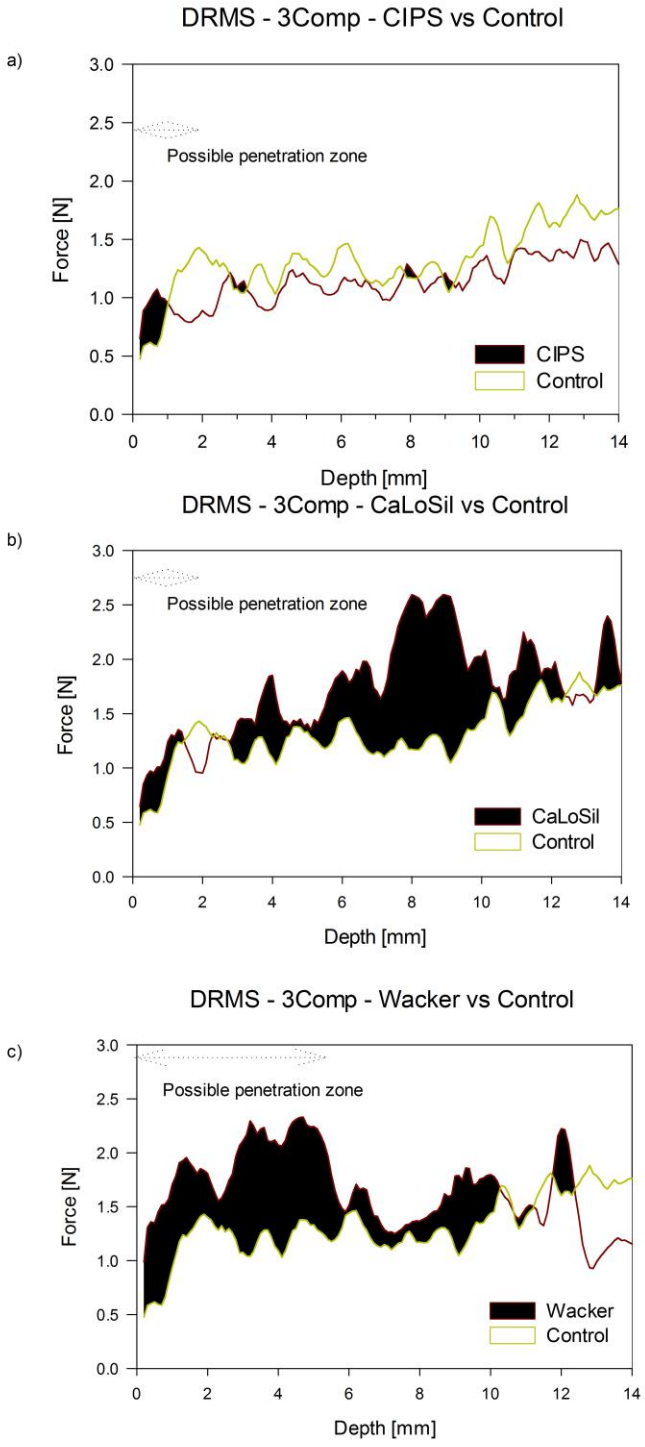



**Figure 43 (a-c): DRMS drilling profiles a) CIPS; b) CaLoSil; c) Wacker OH**

From the drilling resistance profiles in Figure 44, it can be seen that the Wacker treated sample had around double the strength of the untreated control for the first 6mm into the stone, and still had slightly greater strength between 6 and 10mm depth. The CaLoSil replicate had double the strength of the control for the first 1-2mm into the stone, after this whilst it presented a stronger resistance profile than the control it is suspected that this is just due to a stronger stone sample. The CIPS sample showed an increase in strength for the first millimetre, after this it presented a very similar drilling resistance profile to the control.

## Scanning Electron Microscopy (SEM)

Chippings approximately $10mm^3$ in size were taken from stone samples treated with every consolidant. One chipping for each consolidant was gold coated using an Edwards S150B sputtercoat, and examined using scanning electron microscopy (SEM) in a Hitachi S4800 FE-SEM. Another set of chippings were vacuum impregnated with resin and set into cross sections as outlined in Chapter 4. After polishing, the cross sections were carbon coated and examined using the Hitachi S4800 FE-SEM.

a)




b)

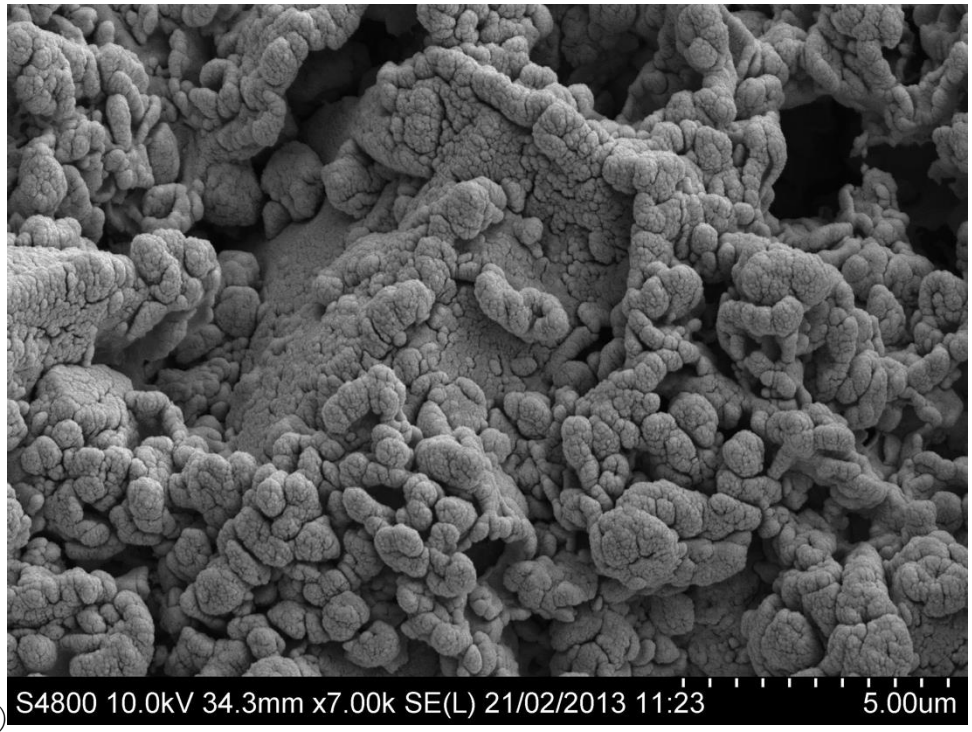



**Figure 44 (a and b): SEM micrographs of CIPS treated stone a) internal view of stone chipping x1k magnification; b) x7k magnification.**

It was possible to identify the CIPS precipitate coating grains throughout the whole of the gold-coated, chipped, sample (Figure 44(a)). As can be seen clearer in Figure 44(b), the precipitate appeared to take an amorphous form rather than the crystalline, granular or rhombohedral habit that might be expected of calcite.

a)




b)

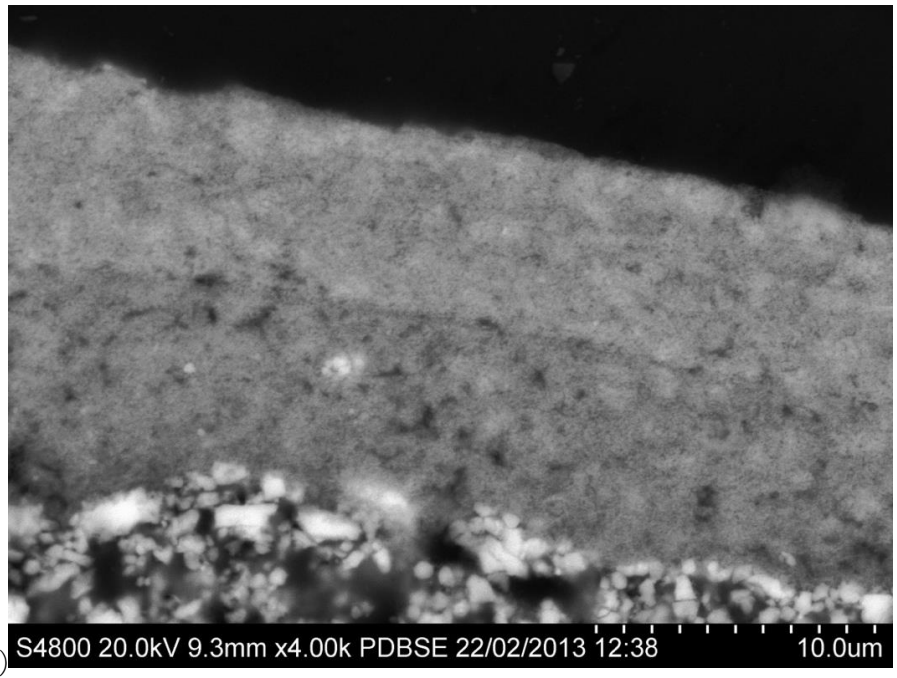



**Figure 45 (a and b): SEM micrographs of CaLoSil treated stone cross-sections a) treated surface x500; b) x4k**

From Figure 45(a) it is possible to see the CaLoSil treatment as a layer on top of the treated surface. Upon closer inspection in Figure 45(b) it is possible to see this layer is divided into two – this could correspond to the two separate applications of the CaLoSil treatment.

## Ion Chromatography

Ion chromatography to analyse salt content was performed using a Dionex IC DX500 Chromatograph. Drillings were taken from samples at 0-8mm and 8-15mm depth and processed as outlined in the flowchart in Chapter 4. As the samples were cut from limestones that had been exposed to the external environment for a number of years it was thought that they would likely have salts within. This analysis would help to show how these intrinsic salts might be affected by the treatments. Drillings were taken from samples from both stone types; the Basildon Park stone and the stone provided by the British Museum.

| Sample | Stone Provenance | F % | Cl % | NO3 % | SO4 % | Na % | NH4 % | K % | Mg % | Ca % |
|---|---|---|---|---|---|---|---|---|---|---|
| Depth 8mm | | | | | | | | | | |
| control 1 | Basildon Park | 0.002 | 0.015 | 0.000 | 6.153 | 0.010 | 0.002 | 0.013 | 0.004 | 1.279 |
| control 2 | British Museum | 0.004 | 0.057 | 0.012 | 0.053 | 0.005 | 0.001 | 0.005 | 0.004 | 0.104 |
| calosil1 | Basildon Park | 0.000 | 0.099 | 0.122 | 2.331 | 0.049 | 0.000 | 0.019 | 0.012 | 0.755 |
| calosil4 | British Museum | 0.003 | 0.023 | 0.010 | 0.027 | 0.004 | 0.001 | 0.006 | 0.002 | 0.095 |
| CIPS2 | Basildon Park | 0.000 | 0.574 | 0.028 | 0.493 | 0.024 | 0.008 | 0.011 | 0.006 | 0.433 |
| CIPS5 | British Museum | 0.002 | 0.351 | 0.000 | 0.008 | 0.002 | 0.009 | 0.002 | 0.002 | 0.136 |
| Wacker1 | Basildon Park | 0.002 | 0.012 | 0.000 | 14.444 | 0.006 | 0.002 | 0.005 | 0.004 | 3.160 |
| Wacker5 | British Museum | 0.002 | 0.010 | 0.005 | 0.012 | 0.003 | 0.000 | 0.002 | 0.003 | 0.185 |
| Depth 15mm | | | | | | | | | | |
| control 1 | Basildon Park | 0.003 | 0.029 | 0.000 | 0.377 | 0.001 | 0.002 | 0.006 | 0.007 | 0.207 |
| control 2 | British Museum | 0.003 | 0.017 | 0.000 | 0.027 | 0.006 | 0.001 | 0.004 | 0.004 | 0.140 |
| calosil1 | Basildon Park | 0.002 | 0.069 | 0.075 | 0.265 | 0.026 | 0.000 | 0.017 | 0.010 | 0.180 |
| calosil4 | British Museum | 0.004 | 0.034 | 0.005 | 0.015 | 0.002 | 0.005 | 0.005 | 0.003 | 0.085 |
| CIPS2 | Basildon Park | 0.000 | 0.440 | 0.079 | 0.245 | 0.027 | 0.004 | 0.014 | 0.011 | 0.278 |
| CIPS5 | British Museum | 0.003 | 0.064 | 0.000 | 0.009 | 0.006 | 0.002 | 0.003 | 0.003 | 0.114 |
| Wacker1 | Basildon Park | 0.002 | 0.015 | 0.000 | 0.362 | 0.004 | 0.001 | 0.004 | 0.003 | 0.229 |
| Wacker5 | British Museum | 0.003 | 0.013 | 0.001 | 0.054 | 0.003 | 0.005 | 0.003 | 0.004 | 0.117 |

**Table 13: Ion chromatography results in mass percent: values above 0.5% highlighted**

Looking at the results from the ion chromatography analysis in Table 12, the most obvious result is the high sulphate concentration for all the Basildon Park samples. This was expected as there was a hard crust covering part of these samples, which was thought to be a sulphate crust. It can also be seen that the CIPS samples had a higher chloride presence than any of the others; for example a concentration of 0.574mass% for the Basildon Park sample at 0.8mm in comparison to the Control1 sample which had a chloride concentration of 0.015%. As mentioned in Chapter 7, the British Museum considers a high chloride salt content in stone to be greater than 0.5 mass% (Walker & Bradley 1989).

## Discussion

This experiment was an extension of the previous comparative assessment of the new consolidants on artificially weathered stone samples. As such, there was a high degree of confidence in the expected outcomes. Not all of the results however confirmed the original hypotheses.

| Parameter | Expected Outcome | Result |
|---|---|---|
| **Consolidation effect** | - Wacker treated stones would show the greatest increase in surface hardness and internal strength, with the greatest depth of penetration. The results from the CIPS treated stones would be close to the Wacker results.<br>- CaLoSil treated samples might show a consolidation effect on the naturally weathered stones unlike the lack of effect seen in | - Wacker stones did show greatest increase in internal strength using DRMS, however, none of the groups of replicates showed a statistically significant increase in surface hardness.<br>- Mixed results on depth of penetration but Wacker looked to have penetrated the furthest, CIPS also possibly penetrated 10mm. |

| | | |
|---|---|---|
| | the previous experiment. | - CaLoSil treatment appears to be sat on surface, not penetrated through the stone. |
| **Impact upon water permeability** | - Wacker and CIPS treated samples likely to show a significant drop in water penetration.<br>- Previously the water penetration into CaLoSil samples had not changed upon treatment. in water penetration. | - Water penetration not possible to measure using Karsten Tubes due to severely deteriorated surface detachment. |
| **Change in colour or salt level** | - Colour change values for treatments on very deteriorated stone would be less than those seen on the freshly cut, artificially weathered, samples<br>- CIPS treated samples would show the lowest change in colour, then the Wacker treated samples, with the greatest change demonstrated by samples treated with CaLoSil.<br>- The CaLoSil samples in the previous experiment might show a white bloom on the treated | - Colour change definitely lower on naturally weathered stones<br>- Order of colour change remains the same with CIPS at the lower end, CaLoSil at the higher and silane in between<br>- White bloom still evident.<br>- CIPS samples have the highest chloride salts<br>- Background salts present – particularly sulphate crust |

| | |
|---|---|
| | surface.<br>- CIPS treated samples would show raised levels of chloride and ammonium salts.<br>- Background salt level would be higher than previous experiments. |

**Table 14: Summary of expected outcomes vs. results for Chapter 8**

### Consolidation Effect

From the difference in weight, and the fact the CIPS could be seen on the SEM it was clear the treatment had penetrated the CIPS sample, and perhaps up to 10mm deep, yet this was not shown on the DRMS results. This was particularly surprising in comparison to the DRMS results shown in Chapter 7. Initially when analysing the CaLoSil DRMS result it looks like the CaLoSil has increased internal strength. However, as can be seen in SEM images, the products of the CaLoSil treatment are present as two distinct surface layers – with no deep penetration. Perhaps the DRMS result for CaLoSil is just due to the sample tested being inherently stronger? This highlights the problem with comparing a treated sample to control rather than before and after testing on same sample, although that this was possible with DRMS.

There was a high variability with the Equotip results and no clear indication of surface strength increase, even with the Wacker treated samples. Previously, experiments applying CIPS onto weathered stone had shown statistically significant changes in surface hardness when using the Equotip (Chapter 6). However, it is known that sometimes on extremely rough surfaces the Equotip does not provide useful data (Viles, pers comm). This is something to consider if testing effectiveness on highly deteriorated surfaces in the future.

### Impact upon water penetration

The lack of data from Karsten Tube tests is frustrating, however it highlights the issue of the amount that can be tested on very deteriorated stone. This leads to the debate of which is preferable; a larger variety of tests that are easier to compare and statistically compare, or, fewer tests on material that is more applicable?

### Change in colour or salt content

As predicted, colour change before and after treatment was lower on the naturally deteriorated stone than the artificially weathered cubes in the previous experiment (Chapter 7). This is likely to be due to the less homogenous colour of the more deteriorated stone. Colour change might have been lower, however a definite white bloom was still evident on all CaLoSil samples.

Salts analysis shows confirmation that the black surface crust on Basildon park replicates is most likely sulphate as suspected. CIPS blocks show higher chloride concentration than all others tested – around the British Museum limit for high salts, however still at the lower end of the scale in terms of soluble salts present within the Egyptian statuary within the British Museum.

## Conclusions

There were three aims for this experimental stage of the Back to Nature project:

- To use naturally weathered stone to compare the effectiveness of the consolidants
- To assess if the effectiveness demonstrated differs from that expected based upon results on artificially weathered stone used in previous experiments
- To see if analytical methods used on cubic samples with flat surfaces are equally as useful on weathered and rough surfaces.

In terms of the consolidants investigated, the Wacker OH appeared to be working based upon DRMS results. The CIPS seemed to have penetrated deeply according to the SEM investigation, but was perhaps not as effective in increasing strength according to the DRMS results. IC results did show the increase in chloride salts resulting from CIPS treatment – more work would need to be done on this in the future to assess the impact of this increase. To check validity of any of these results future experiments would need to include testing of more than one sample.

Whilst some of the expectations of results for this experiment were fulfilled, some results varied considerably from those anticipated. For example, it was expected that the DRMS would show CIPS penetrating into the stone with a similar profile to the Wacker; this was what was seen on the previous experiment (Chapter 7) with the artificially weathered cubes. In actual fact, the DRMS seemed to suggest the CIPS was only present in the first mm or so. This contrasted with SEM results that appeared to show the CIPS penetrating at least 10mm. This shows the importance of using multiple methods to analyse effectiveness. The difference in expectations and results from this experiment does emphasise the importance of conducting such experiments upon very deteriorated samples rather than purely relying upon results from those conducted on less weathered stone replicates.

It was shown within this experiment that some of the analytical methods could either not be used (such as the Karsten Tubes) or did not provide clear data (for example the Equotip). This highlights the need for careful consideration of analytical methods to use if one is developing an experiment on very deteriorated stone. Potentially, work needs to be done with the Equotip to see if there are ways to improve its use on very rough surfaces – for example investigating if an increased number of measurements could reduce the standard error, or if there are attachments that could be used to greater effect.

# Chapter 9

*Discussion*

This chapter brings together results from the four main experimental phases that were designed to fulfil the aim of the *Back to Nature* project; to examine the possibilities of using new inorganic consolidants on stone artefacts in the British Museum. By combining the quantitative results with qualitative analysis, archival research, and specifications given by the museum's stone conservators, guidelines are presented for the future use of stone consolidants within a museum setting. Different ways in which the project could be developed in the future are also discussed.

## Experimental summary

Table 14 shows an overview of the four experimental phases within this project. These experiments were designed to be part of a developmental sequence and this can be seen with some of the differences between the phases. For example in the first phase ammonium oxalate treatment was applied by pipette. Subsequent research revealed that the suggested method was to apply it by poulticing, so in the third phase this was the application method used. CIPS was also first applied by pipette (in the second phase), however following discussions with the British Museum conservators it was decided this would be applied by spraying in future experiments. In the first phase stone blocks were 5x5x15cm so that the GrindoSonic could be used (the GrindoSonic requires sample length to be at least three times the width). This used a large amount of stone so in phase three, cubes 5x5cm were used.

| Experimental phase | Material | Shapes | Consolidant/ Application | Analysis |
|---|---|---|---|---|
| **1** | Elm Park (Fresh)<br>Hartham Park (weathered – 100 years) | 5 x 5 x 15cm | Wacker (pipette x 2)<br>AmOx (pipette x 2) | Equotip, GrindoSonic, Spectrophotometer, Karsten, SEM |
| **2** | Sand (3 types)<br>Sandstone (2 types- weathered at least 100 years) | Misc | CIPS (spray x 6)<br>CIPS (Pipette x 2) | Equotip, SEM, IC, XRD |
| **3** | Elm Park (fresh) and HP (weathered) – Both pre-weathered experimentally - 5 cycles | 5 x 5 x 5 cm | CIPS – spray x 6<br>CaLoSil – spray x 2<br>AmOx – poultice x 2<br>Wacker – pipette x 2 | Equotip, Pundit, MIP, IC, Spectrophotometer, Karsten, DRMS, SEM |
| **4** | Basildon Park Bath stone – weathered for 100+ years,<br>British Museum oolitic stone – weathered outside at least 5 years | Misc | CIPS – spray x 6<br>CaLoSil – pipette x 2<br>Wacker – pipette x 2 | Equotip, Spectrophotometer, (Karsten), DRMS, SEM, IC |

**Table 15: Overview of Back to Nature experimental phases**

Before the experimental comparison of the inorganic consolidants could begin, a methodology needed to be set. The investigation into this focused on two primary factors; variability between stone samples and the impact of weathering on comparative tests. For the first phase one inorganic consolidant (ammonium oxalate treatment) was compared to an organic silane (Wacker SILRES BS OH 100).

| | **Fresh – Elm Park** | | **Weathered – Hartham Park** | |
|---|---|---|---|---|
| | EP Before Treatment | EP After Treatment | HP Before Treatment | HP After Treatment |
| Equotip (Leeb) | | | | |
| Wacker | 300-375 | 400+ | 175-275 | 175-400 |
| AmOx | 300-375 | 300-400 | 200-375 | 200-375 |
| GrindoSonic (MPa) | 20-22 | | 16-18 | |
| Karsten (total ml) | | | | |
| Wacker | 12 | 6 | 12 | 3.5 |
| AmOx | 12 | 12 | 12 | 8.5 |
| Spectrophotometer ($\Delta E_{00}$) | | | | |
| Wacker | | 3.36 | | 3.40 |
| AmOx | | 3.71 | | 5.25 |

**Table 16: Summary of first phase of experiments (Chapter 5)**

It is known that stone can be highly variable – even between blocks cut from the same quarry. These experiments discovered however that variability is high between individual samples – even ones cut from the same block of stone, indicating that to ensure statistically reliable data, as many samples as possible per variable should be used. It is noted that there are factors that may affect the number of samples to be used

in any experiment including stone availability and amount of time to treat and test samples. The differences seen in results from analytical tests between freshly cut and weathered stone highlight the importance of considering the degree of weathering of the samples consolidants are being tested upon. An example of this is the colour change resulting from treatment was far less noticeable on weathered samples, than fresh, as can be seen in Table 15 above, something that was also noticed in later experiments (Chapters 7 and 8). Another analytical method that demonstrated the difference between fresh and weathered stone was the Karsten tube test. This indicates that testing of consolidants should be undertaken on both fresh and weathered stone.

The Calcite In-Situ Precipitation system was developed in Australia for the oil and gas industry and although it has been used for a variety of purposes since, it had not been trialled in the museum environment for stone conservation. The stone conservators within the British Museum had suggested the potential for its use as a stone consolidant for museum artefacts, and the possibilities of CIPS was one of the instigating factors in the decision to re-examine the potential of inorganic consolidants in general, and the development of the *Back to Nature* project. As it was untested in museums, and did not come as a ready-mixed solution, the manufacturing of CIPS, and an investigation into its basic components, needed to be undertaken prior to including it in any comparison of consolidants.

| | Silica sand | Aragonite sand | Conservation sand | Stones (H and RC) |
|---|---|---|---|---|
| Equotip (Leeb) | | | | |
| Untreated | n/d | n/d | n/d | 150-250 |
| Treated | 150 | n/d | n/d | 250-350 |
| IC – salt concentration in CIPS fluid | | | $Cl^-$ 10.8% (100.8mg/L)<br>$NH_4^+$ 5.09% (50.9mg/L) | |

**Table 17: Summary of second phase of experiments (Chapter 6)**

The evaluation of CIPS (Chapter 6) showed that it was easy and safe to manufacture within the museum. Results from these experiments were promising; the consolidation ability of CIPS was demonstrated with treated samples of loose silica and aragonite sand, and weathered stone samples exhibited statistically significant increases in surface hardness. One concern within the experiments to evaluate CIPS was the high concentration of chloride and ammonium salts in the CIPS fluid (as shown in Table 16 above) that would remain in pore spaces – this could be potentially very dangerous if a treatment is introducing salts.

The comparison of three inorganic consolidants (Chapter 7), to each other and to an organic silane, involved experimental assessment using a variety of analytical methods to characterise artificially weathered stone cubes before and after treatment. Methods included those to assess the consolidation action, ones to study the impact of the treatment on stone characteristics that may affect the longer-term success of the consolidant, and those examine the impact upon the aesthetics of the stone.

| Consolidant | Stone type | Before pre-weathering | After pre-weathering | After treatment |
|---|---|---|---|---|
| Wacker | HP | 200-250 | 200-250 | 225-250 |
| CaLoSil | HP | 175-225 | 175-200 | 200-250 |
| CIPS | HP | n/d | n/d | n/d |
| AmOx | HP | 175-275 | 175-225 | 250-350 |
| Wacker | EP | 200-350 | 200-300 | 250-375 |

| | | | | |
|---|---|---|---|---|
| CaLoSil | EP | 300-350 | 300-350 | 300-350 |
| CIPS | EP | 300-375 | 300-375 | 300-375 |
| AmOx | EP | 200-225 | 200-225 | 300-350 |

**Table 18: Summary of equotip results (Leeb values) from third experimental phase Chapter 7**

| | Control EP | Treated EP | Control HP | Treated HP |
|---|---|---|---|---|
| Pundit (MPa) | | | | |
| CIPS | 30-36 | 30-38 | 33-36 | n/d |
| CaLoSil | 30-36 | 22-29 | 33-36 | 30-38 |
| Wacker | 30-36 | 26-33 | 33-36 | 28-38 |
| AmOx | 30-36 | 28-33 | 33-36 | 26-38 |
| Spectrophotometer ($\Delta E_{00}$) | | | | |
| Calosil | | | 9.5 | |
| Wacker | | | 4.5 | |
| AmOx | | | 3.5 | |

| | | | | |
|---|---|---|---|---|
| CIPS | | | 2.8 | |
| Karsten | | | | |
| CIPS | 1.75 | 0-0.25 | 1.2 | 0-0.25 |
| Wacker | 1-2.25 | 0 | 1-2.25 | 0 |
| Calosil | 1.5-2 | 1-1.5 | 1.5-2 | 1-1.5 |
| AmOx | 1.25-2.5 | 0-0.4 | 1.25-2.5 | 0-0.4 |
| DRMS (mm penetration) | Wacker ≈ 14 > CIPS ≈ 12 > AmOx ≈ 1 > CaLoSil ≈ 0 | | | |
| Weight gain | CIPS >> Wacker > AmOx > CaLoSil | | | |

**Table 19: Summary of other results from third experimental phase (Chapter 7)**

The third phase; comparison of three inorganic consolidants to each other and with an organic consolidant (Chapter 7 and summarised in Tables 17 and 18 above) was conducted using artificially weathered stone cubes. Following this, it was extended into the fourth phase; comparing the consolidants on naturally weathered stones of a variety of shapes (Chapter 8). The main results from this phase can be seen in Table 19 below.

| | Control | CIPS | CaLoSil | Wacker |
|---|---|---|---|---|
| Equotip (Leeb) | | | | |
| Before | 175-350 | 200-225 | 200-275 | 175-225 |

| | | | | |
|---|---|---|---|---|
| After | n/d | 200-300 | 250-275 | 200-225 |
| Spectrophotometer (ΔE00) | 1.2 | 2.1 | 4.2 | 2.3 |
| DRMS (mm) | | 1 | 1-2 | > 6 |

**Table 20: Results summary for fourth phase of experiments (Chapter 8)**

## Surface hardness using Equotip

Consolidation action at its most basic is the increase of cohesion and strength. Looking at the Equotip results for all experiments several things can be noted:

- In the first experiment both weathered (HP) and fresh (EP) Wacker OH treated stones showed an increase in surface hardness (up to ≈400 Leeb units on both), AmOx treated stones did not.
- In the second phase of experiments CIPS treated stones showed an increase of up to 350 Leeb units. Consolidated silica sand showed surface hardness of around 150 Leeb – comparable to the results from some of the weathered stones.
- In the third phase of experiments, both ammonium oxalate and Wacker treated stones showed an increase on both HP and EP stone after pre-weathering (up to 350 Leeb units).
- In the fourth experiment all stones gave Equotip values within a 175-350 Leeb range, both the controls and treated areas. None of the stones showed a statistically significant increase in surface hardness.

Wacker treated samples most consistently showed increases in surface hardness, although not according to Equotip values in the fourth experiment. Whilst the ammonium oxalate samples in the first experiment did not show any increase in surface hardness, the ones in the third experiment showed the greatest increase in

surface hardness overall. The stone was the same in both experiments so perhaps this change is due to the differing application methods. Weathered stone samples treated in the original evaluation of CIPS (second phase of experiments, Chapter 6) demonstrated statistically significant increases in surface hardness (Table 16). This was not repeated in the third round of experiments. A reason for this could be that the artificial weathering did not cause the stone cubes to deteriorate to a level that would show the full impact of the CIPS treatment. The differing values for the original surface hardness of the stones can make it difficult to compare treatment efficacy. For example, perhaps some treatments would only show a statistically significant increase on stone with a particularly low original surface hardness. All Equotip values were variable, particularly in the fourth round of experiments as can be seen by the standard error bars in Figure 44, Chapter 8. Equotip data also only gives information about increases in hardness at the surface. For these reasons, whilst Equotip values could give useful information about consolidant performance, it is suggested that they be used in conjunction with other analytical tests.

### Internal Strength – GrindoSonic and Pundit Lab

Internal strength was assessed using the GrindoSonic in the first experiment and the Pundit Lab in the third. Summarising the results we can see:

- In the first experiment there were no significant differences before and after treatment on either the fresh stone 20-22(E Mod MPa) and weathered stone 16-18(E Mod MPa)
- In the third experiment there were no clear differences between controls and treated, E Mod 22-39 MPa.

The two points above show that there is quite a spectrum of values for E Modulus, especially when one tries to compare results in from the two different pieces of equipment. This illustrates the problems of trying to compare two very different methods. It also shows that there was a lack of clear evidence of the influence of the treatments upon internal strength. This could potentially be because only one side of the samples was treated which may not have allowed enough consolidant to penetrate the stone to have a significant influence on surface hardness.

## Water penetration – Karsten Tubes

Karsten tube results from the first phase of experiments show the Wacker drastically reduced the water penetration on both the fresh and the weathered stone. The ammonium oxalate treatment reduced the water penetration slightly on the weathered stone but not at all on the fresh. In the third experiment all treatments caused a reduction in water penetration except the CaLoSil. This was particularly apparent for the samples treated with Wacker OH. None of the treatments were designed to be hydrophobic, yet Wacker, ammonium oxalate and CIPS have obviously limited water intake to great extent. This could not be repeated on the weathered blocks in the fourth phase of experiments because the water and putty caused the surface to disaggregate. This is important to consider when thinking about future testing of consolidants and what is possible to test on very weathered samples. Another thing to note is the difference in Karsten results between the first stage of experiments and the third. The two experiments involved the same stone yet more water appeared to be absorbed post treatment in the first stage of experiments. The putty used with the Karsten tubes changed between the two stages; perhaps this affected the results. Ideally treatments would maintain stone characteristics, such as permeability, to reduce difficulties caused by the interaction between treated and untreated substrate. In this case, a consolidant that did not reduce water penetration would be preferred.

## Colour changes – spectrophotometer

Colour change of the treated surface of stone samples was measured using a spectrophotometer before, and at least three weeks post, application of consolidant. Colour changes seen in each experiment can be summarised as follows:

- In the first experiment Wacker samples (fresh and old) had a mean $\Delta E_{00}$ value of 3.4. Ammonium oxalate fresh samples had a mean $\Delta E_{00}$ value of 3.7 and the weathered samples 5.3.
- In the third experiment CIPS treated samples had a mean $\Delta E_{00}$ value of 2.8, ammonium oxalate samples 3.5, Wacker samples 4.5, and CaLoSil samples 9.5.

- In the fourth experiment control samples that remained untreated had a difference in colour values of 1.2 $\Delta E_{00}$, CIPS treated samples had a mean $\Delta E_{00}$ value of 2.1, Wacker samples 2.3, and CaLoSil samples 4.2.

All the consolidation treatments altered the colour of the replicates, however they changed the colour in different ways - the Wacker OH made the surface darker, the CIPS more yellow and more saturated, and the CaLoSil the most obviously caused a white bloom to appear on surface. Taking all of the different aspects of colour space into account with the $\Delta E_{00}$ values, the CIPS treatment changed the colour the least and the CaLoSil the most. Colour change was far less noticeable on the naturally weathered samples in the last round of experiments in comparison to the artificially weathered cubes. This was also seen in the early stages of the project on weathered blocks in comparison to freshly cut blocks. This is probably due to the surface of the naturally weathered stones being less homogenous in colour than the artificially weathered samples.

## Depth and nature of penetration

Depth of penetration of consolidation treatments was analysed using DRMS and SEM. Results from these can be summarised as follows:

- In the third experiment (Chapter 7) depth profiles from DRMS showed Wacker penetration into samples of approximately 14mm, CIPS approximately 12mm, ammonium oxalate around 1mm and there was no evidence of CaLoSil penetration. SEM confirmed the presence of Wacker at least 10mm into a stone sample. CIPS was identified at the treated edge of a cross section but not internally. Ammonium oxalate and CaLoSil was not identified using SEM.
- In the fourth experiment (Chapter 8) depth profiles using DRMS showed Wacker penetration of approximately 6mm, CaLoSil of 1-2mm and CIPS of approximately 1mm. CIPS was found using SEM all the way through a 10mm sample. CaLoSil was shown to be present only as a superficial layer on top of the treated surface.

Ideally a consolidation treatment would penetrate deep into stone, through a deteriorated region into the sound substrate. Poor penetration depth has been a criticism of past inorganic treatments so it was an important parameter to measure within the *Back to Nature* project. The potential for CIPS to penetrate into stone to a similar depth as the Wacker silane, demonstrated by the results summarised above, suggests that this inorganic consolidant may hold great promise for future use within stone conservation. That CaLoSil was discovered only at the surface suggests that there is still much work to be done to maximise the penetration of this consolidant.

Both the DRMS and SEM provided useful data concerning depth of penetration however in comparing results between the two it is possible to see there are some discrepancies. For example, on the weathered stones in the fourth experiment the DRMS results did not show the presence of CIPS past the first 1mm, yet using SEM, CIPS could be seen throughout a 10mm sample. This was further supported by the ion chromatography results that suggested CIPS had penetrated at least 8mm into the stone. Singularly both techniques can provide interesting data on penetration depth but combining results seems to allow for a more complete overview.

It might be expected that naturally weathered stones, deteriorated to a greater extent than the artificially weathered, might provide more scope for consolidation and hence show greater increases in strength or deeper penetration. However, in comparing the results between the third and fourth experiments this does not seem to be the case. There are several possible factors that affect this result. One could be that the two experiments involved different stone types; differences in porosity and pore structure could have affected depth of penetration. Differences in stone chemistry might have affected how the consolidant cured and bonded to the stone. Another factor to consider is that whilst each DRMS result is the mean of several holes drilled into the sample, it is only the result from one sample. Testing of more samples might provide clearer results. Another issue, one that is also important for SEM results, is that each sample is compared with an untreated control. The nature of destructive testing means that before and after testing is not possible, however this does mean it is difficult to define the exact results of a consolidation treatment.

## Salts analysis – Ion Chromatography (IC)

Salts analysis using ion chromatography showed higher levels of chloride ions in CIPS samples in both artificially weathered cubes and naturally weathered samples. Values were higher in the 0-8mm drillings than the 8-15mm drillings reinforcing the likelihood that these salts are a result of treatment. The results were close to the value of 0.5%mass that the British Museum considers to be a high salt content. However, when looking at a study of the Egyptian stone sculptures in the British Museum collection, the average chloride concentration was 0.69%mass with a range of <0.1 to 5.6%mass. This could put the results from the CIPS treated samples in perspective. If a sculpture has a very low chloride concentration, treatment with CIPS might not contribute to a dangerous increase, however, if a sculpture already has a concentration close to the higher end of the range then adding extra chloride salts could pose a problem. High salt levels are not a deteriorating factor on their own. Their potential to cause decay should be examined in conjunction with an assessment of the environmental conditions an artefact is going to be stored in. If the conditions are going to remain constant then the damage due to deliquescence and crystallization of the salts could be prevented. Aside from the higher levels of chloride salts in CIPS samples, there were also increased levels of nitrates in CaLoSil cubes and ammonium in CIPS cubes however this was not seen in the naturally weathered samples. An explanation for this could be that this was due to natural variation and not due to treatment. This theory is supported by the fact that salt levels were higher internally in the 8-15mm drillings, suggesting these salts were present in the stone before treatment.

Drillings were taken for salts analysis on only one sample per consolidant group, and at only one spot on each sample. This gives a brief overview of the salts potentially induced by the new inorganic treatments however, more in-depth analysis would be needed to confirm the levels of salts induced, particularly by the CIPS treatment. Salts are not necessarily distributed evenly throughout a stone sample. Only drilling in one spot might provide a very high or low result depending upon the salts within that small area.

## Evaluation of analytical methods

For each experimental phase within the Back to Nature project, different analytical techniques were used to assess a range of stone characteristics in order to compare the effectiveness of each consolidation treatment. This is in line with current practice in the conservation science field as outlined by Sasse and Snethlage (1996) and Laurenzi Tabasso and Simon (2006). Multiple methods were used where available, often to look at the same characteristic in a different way. The previous pages compare the results from the assessment of different stone characteristics to combine results from all experimental phases. The following table looks at the different analytical methods themselves to provide an evaluation of each technique, its limitations as shown within these experiments, and suggestions for when it could be used in future investigations into consolidation effectiveness or stone deterioration.

| Analytical Technique | Property Investigated | Method of Analysis | Experiments | Overall Evaluation | Limitations/ When to use? |
|---|---|---|---|---|---|
| **Drilling Resistance Measurement System - DRMS** | Internal strength and, depth of penetration of consolidants | Calculates force (N) needed to drill into stone at constant rotational speed and penetration rate | Stages 3 & 4: Comparison on artificially weathered stone (Chapter 7); naturally weathered stone (Chapter 8) | • One of the quickest and easiest methods used to show depth of penetration of consolidant and difference in internal strength – more successful in this (within these experiments) than thin section petrography, grindosonic and scanning electron microscopy<br>• Provides instant numerical and visual data | • Destructive but only 3mm hole drilled so could potentially be used on artefacts to monitor deterioration or treatment success – particularly when considering depth of penetration<br>• Not possible to do exact before and after treatment measurements so cannot do direct comparison – multiple drillings on multiple replicates treated with the same consolidant advisable |
| **Equotip** | Surface hardness of stone | Leeb hardness based upon change in velocity between impact and rebound | All | • Quick and easy, minimally destructive, technique to look at surface hardness<br>• Provides numerical data that is easy to plot.<br>• Data can be very variable even on one replicate – many measurements and replicates needed to counteract this variability | • Use if deterioration/consolidation action at the surface is of particular interest<br>• Could be useful as a minimally destructive method to look at artefact deterioration; minimal destruction means method can be used before and after consolidation treatment<br>• Variability increases with surface roughness and if surface is very weathered or irregular in shape it can be difficult to get a reading. Due to this it might be difficult to use on deteriorated artefacts. |

| Analytical Technique | Property Investigated | Method of Analysis | Experiments | Overall Evaluation | Limitations/ When to use? |
|---|---|---|---|---|---|
| **GrindoSonic** | Internal strength via E Modulus | Impulse excitation Technique. Results translated into E-Mod using GeneMod software | Stage 1: Basic Methodology (Chapter 5) | • Simple technique but appears to be lots of scope for operator bias<br>• Did show clear difference between fresh and weathered stone | • Main limitation was the sample size requirement – that the replicate length needed to be ≥ 3 x replicate width<br>• Use if sufficient stone source for requisite number of replicates with length 3 x width<br>• Could be used as cheaper alternative to DRMS if no DRMS equipment is available<br>• Non-destructive technique that can be used before and after treatment |
| **Ion Chromatography** | Presence and concentration of salts | Separation of ions and polar molecules based upon charge | Stages 2, 3 & 4: Investigation into CIPS (Chapter 6); Comparison on artificially weathered stone (Chapter 7); naturally weathered stone (Chapter 8) | • Highly technical procedure with multiple steps but each step itself is simple; take time to learn procedure<br>• Good technique to analyse which salts are present in the stone (inherent and due to treatment) and their concentration | • Drillings taken from stone are destructive although smaller size of drill bit can minimise this; already accepted technique for use on artefacts.<br>• Destructive nature of the technique means direct comparison before and after treatment is not possible<br>• Drillings are taken from and until a certain point (e.g. from 0 - 8mm depth) so results do not provide an exact depth of penetration of salts due to treatment |

| Analytical Technique | Property Investigated | Method of Analysis | Experiments | Overall Evaluation | Limitations/ When to use? |
|---|---|---|---|---|---|
| **Karsten Tubes** | Water Penetration Capacity (WPC) | Drop in water level in graduated, glass tube bonded to sample surface, measured over time | Stages 1, 2 & 3: Basic Methodology (Chapter 5); Investigation into CIPS (Chapter 6); Comparison on artificially weathered stone (Chapter 7) | • Relatively simple technique to look at water penetration through treated surface; data provided is easy to graph and interpret<br>• Achieving a good seal between the glass tube and stone surface is paramount and can be difficult. This varies with bonding material used - of several tested within this project, German *Plastic Fermit* provided the best seal | • Attempted use on naturally weathered stone with very deteriorated and irregular surface without success – putty used to bond tube to stone removed part of the surface and it was difficult to get a good seal to carry out the test without water leaking.<br>• Can provide interesting data in the lab but use on an actual artefact might be risky if surface is fragile |
| **Mercury Intrusion Porosimetry - MIP** | Pore size and distribution | Mercury intruded measured through changes in capacitance. | Stage 3: Comparison on artificially weathered stone (Chapter 7) | • Technically difficult and expensive procedure<br>• Provided some interesting initial information but more in-depth results would need more training in the technique and a larger sample size | • Sampling is destructive so can only be done after treatment; comparison is with a control area not direct<br>• Careful interpretation of results is needed - Washburn equation assumes cylindrical pore geometry and does not account for closed pores; use in conjunction with other analytical techniques |

| Analytical Technique | Property Investigated | Method of Analysis | Experiments | Overall Evaluation | Limitations/ When to use? |
|---|---|---|---|---|---|
| **Pundit** | Internal strength via E Modulus | Ultrasonic Pulse Velocity measurements converted into E-Mod. | Stage 3: Comparison on artificially weathered stone (Chapter 7) | • Results indicated a variability between replicates but little else<br>• Equipment takes practice to use and couplant for transducers is incredibly sticky and messy to use | • Lack of useful results from this technique could be due to only one face of replicates being treated with consolidant - perhaps only use in future experiments if whole replicate treated<br>• Couplant (required between transducer and replicate surface) leaves a very sticky and greasy residue; unlikely to be suitable for use on artefacts<br>• Minimally destructive and can be used before and after treatment |
| **Scanning Electron Microscopy - SEM/VP-SEM** | Depth of penetration, deposition within pores. Elemental mapping of consolidant distribution | Images acquired using secondary electrons (SE) or back-scattered electrons (BSE) | All | • Highly useful technique, one of the most useful within the whole project - particularly when used in conjunction with other data, allowing for visual investigation at high magnification and elemental characterisation<br>• Much practice needed with equipment to achieve good results<br>• An idea of what to look for is needed when gathering visual data | • Sample prep is usually destructive and can take significant time, resources and practice - use if results will add valuable data<br>• Whole replicates can be examined using VP-SEM to look at surface changes |

| Analytical Technique | Property Investigated | Method of Analysis | Experiments | Overall Evaluation | Limitations/ When to use? |
|---|---|---|---|---|---|
| **Spectrophotometry** | Colour change | Change in colour space defined using CIE L*a*b* $\Delta E_{00}$ | All | • Useful method to quantify colour change rather than relying on naked eye interpretation<br>• Quick and easy to use<br>• Can detect not only overall change in colour but also change in colour space - helps to compare just how a treatment changes surface colour, hue, saturation and gloss | • Use whenever the aesthetic effect of a treatment is important<br>• Assess how many measurements are needed to give an overall interpretation of surface colour change<br>• Can be more difficult to use on rough surfaces – if there are gaps between aperture and surface external light could alter readings |
| **Thin Section Petrography** | Distribution of consolidant, depth of penetration and how pore spaces affected | 30µm thin sections analysed using optical light microscopy | Stage 3: Comparison on artificially weathered stone (Chapter 7) | • Allowed for a detailed characterisation of the stone used<br>• Did not provide data on depth of penetration or deposition of consolidant within pore spaces even when thin section slides stained | • Destructive technique – does not allow direct comparison before and after treatment<br>• Significant time and skill involved in sample preparation – perhaps trial with one sample to assess if useful data might be produced |
| **XRD** | Mineralogical composition | X-rays diffracted from sample in characteristic pattern to demonstrate crystal types present | Stage 2: Investigation into CIPS (Chapter 6); | • Older equipment used takes time and requires user to have an idea of what the composition is likely to be to aid interpretation of results.<br>• XRD analysis demonstrated the unexpected formation of vaterite when calcite was expected, this was valuable as it was unable to be detected by other analytical techniques used | • Technique is destructive – after treatment samples can be compared to controls<br>• Can be used to provide information on mineralogical composition and crystallography when data not available/not detected by SEM |

| Analytical Technique | Property Investigated | Method of Analysis | Experiments | Overall Evaluation | Limitations/ When to use? |
|---|---|---|---|---|---|
| **Other** | Dimensions, weight, density, photos etc | N/A | All | • Basic measurements that were used in conjunction with many of the other techniques.<br>• Useful for comparison between replicates within the same treatment group | • Should be used for all laboratory tests and should also be taken before, during and after treatment programmes within museums |

**Table 21: Assessment of methods; their limitations and implications for future experimental investigations**

## Guidelines for conservators

The primary aim of this project was to investigate the potential of inorganic consolidants for use on limestone artefacts in the British Museum. Three inorganic consolidants were studied: Calcite In-situ Precipitation System (CIPS), CaLoSil and ammonium oxalate, along with a silane Wacker SILRES BS OH100 for comparison. The expected output of this project would be guidelines for the stone conservators about the feasibility of use of these consolidants and also suggestions for how stone consolidants could be tested in the future.

### Ammonium oxalate treatment

During the first major comparison experiments ammonium oxalate was applied by poultice, as recommended by Cezar (2011). Impressive surface hardening was noted however DRMS results indicated this was just a superficial hardening and that the consolidant was not effective at depth. Subsequently, ammonium oxalate was ruled out of the investigation as the application method was thought to be unsuitable by the conservators within the British Museum. Future conservators should bear this in mind, however perhaps ammonium oxalate could be considered in the future if an object had deterioration just at the very surface.

### CaLoSil

CaLoSil surprisingly did not show good increase in cohesion or strength and had a very noticeable white bloom. This was surprising because it was developed specifically for stone heritage so it had been anticipated that results would be promising. However, the treatment was applied straight from the pre-prepared solution. Whilst this is what the manufacturer recommends, many people have recently adapted the solution – mixing it with TEOS or diluting the solution down for example (Ziegenbalg & Piaszczynski 2012, Costa & Delgado Rodrigues 2012). In the materials and methods chapter (Chapter 4), it was mentioned that time taken for the carbonation reaction at the base of the CaLoSil treatment to occur would be important. Tests to look at characteristics altered by this process would need to be conducted

after the calcium hydroxide had converted to calcium carbonate to fully examine the effectiveness of CaLoSil. The three weeks minimum curing time used within this project was longer than the recommended time of at least 7 days so it was thought there would have been plenty of time for the reaction to take place, however maybe this was not the situation. Future investigations into CaLoSil could use a phenolphthalein indicator test to assess if conversion to calcium carbonate had occurred as described by Daehne and Herm (2013). The rate of conversion of calcium hydroxide to calcium carbonate could also be increased by the addition of a carbonisation agent such as DiLoCarb-E as suggested by Campbell et al (2011). The number of different research groups that are currently working with this treatment suggests that it perhaps should not be completely ruled out as a potential consolidant for use within the British Museum, however much more work would be needed to maximise effectiveness and prevent drastic colour change.

### Calcite In-situ Precipitation System (CIPS)

In some results the Calcite In-situ Precipitation System looked like it could be very promising, certainly the most promising out of the three inorganic consolidants tested. Consolidation action was shown with the loose sand and some stone samples – both artificially weathered and naturally, showed an increase in surface hardness and internal strength. One set of DRMS results showed a similar profile to the Wacker OH. Further testing could show if the second, less impressive, set of DRMS results is an accurate representation or an anomaly. This treatment had a reduced change in colour and water penetration in comparison to the previously used silane Wacker OH. A major drawback with CIPS could be the chloride salts introduced to the stone but this is not necessarily something that should prevent all use of the treatment in the future – an assessment of the level of salts introduced, and the environmental conditions the object was to be kept in, could show the extent to which these salts might pose a problem. Perhaps the next stage in the investigation into CIPS would be to test it on a severely deteriorated artefact. Or to do accelerated ageing/weathering experiments to see how the specific levels of chloride salts involved would affect stone. It was expected that the calcium carbonate created during the CIPS process would exist in the form of calcite. However, during the investigation of CIPS (Chapter 6) both XRD and SEM analysis suggested that initially vaterite was being produced. As vaterite is known to be unstable it is likely the

vaterite would transform into more stable calcite. The rate at which this occurs could be important for the interpretation of post-treatment analyses. Spanos and Koutsoukos (1998) show that at temperatures similar to those in lab conditions for these experiments, the conversion of vaterite to calcite is independent of temperature and pH but very dependant upon the level of supersaturation. They also show how when in solution the transformation of vaterite to calcite can happen in a matter of hours, however this process takes much longer in the solid state (Spanos and Koutsoukos 1998). For the CIPS treatment this could mean that initially the vaterite, precipitated out within the stone, could be converting fairly rapidly, however as the treated block drys out post-treatment the rate of conversion could slow down. Future investigations could examine this by post-treatment analysis over a longer period of time.

In the process of the investigation into inorganic consolidants a major issue was highlighted: What do conservators want? Is the most important consideration the physical, chemical and ideological compatibility of a treatment with an artefact? Or, is the most important factor the treatment that will provide the greatest consolidation action – primarily in terms of imparting strength and cohesion? Ideally one would find a consolidant that would fit both of these criteria, but this might be an unattainable goal. Overall, looking at results from all the experiments within this project, the consolidant that provided the greatest, and most consistent, increase in strength was the silane Wacker OH. New inorganic consolidants might not be AS good but could get close, particularly with more refining, and could be much better in terms of health and safety, environmental footprint along with providing greater compatibility.

## Future directions

There are several ways in which this project could be developed in the future. The first would be to continue with the investigation into CIPS and CaLoSil. This could include a more in-depth look at salts, accelerated ageing experiments, and an exploration of the best application methods to maximise

consolidation action and minimise effects such as the white bloom seen with CaLoSil. This might be expanded to studying modifications to the treatments such as developing a combined nano-lime/ silicic acid ester combination. Another extension to this could be to look at the other inorganic consolidants that are starting to appear as potential treatments including microbially induced carbonate precipitation or biogenic carbonate treatment – a similar concept to CIPS (De Muynck et al. 2013).

A different approach to expanding this project could be to look at how conservators decide between the various consolidation treatments available. This could look at the emphasis placed upon factors such as compatibility versus strength imparted and also at the weighing up of the different parameters analysed in testing pre-selection of a consolidant. One idea could be to integrate this decision making process with modern technology with the creation of an app. This at its heart could have a framework such as the overly simplified one suggested in figure 46. Such an app could help conservators decide if a new treatment they are unfamiliar with might be suitable for their collection. There could be links to published articles on any investigations into the treatment, collections it has been used on previously, distributors of any treatment components, and so on.

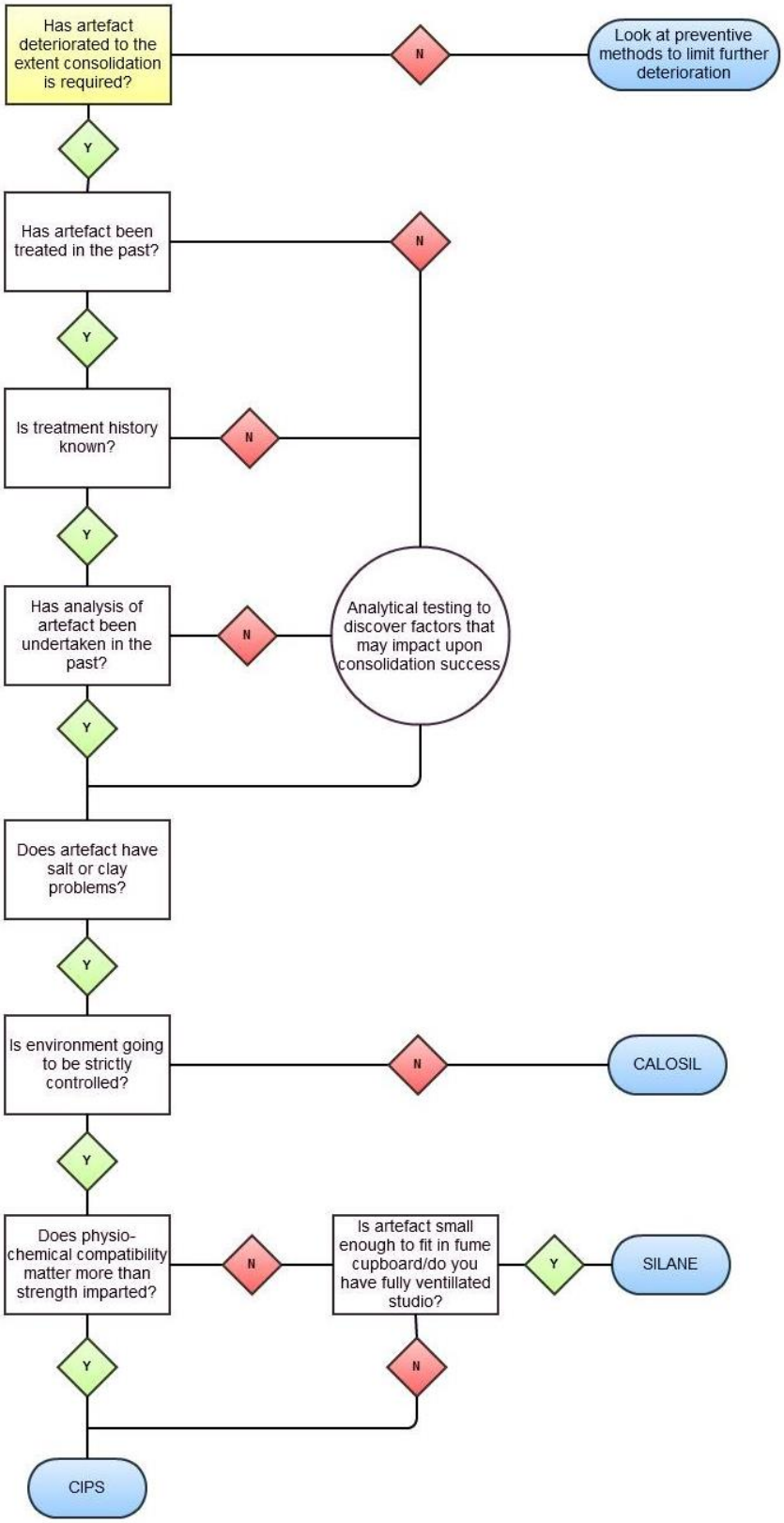



**Figure 46: Simplified example of a framework for an app to aid in consolidation treatment decision making**

# Chapter 10

*Conclusions*

The Back to Nature project was designed to assess three inorganic consolidants and the potential for their use on deteriorated limestone sculpture. There were four key objectives each with their own corresponding experimental phase:

| Objective | Experimental Phase |
|---|---|
| • Select analytical methods to investigate stone consolidants; size, shape and quantity of test replicates needed | 1) To develop a robust experimental methodology for the evaluation of the comparative performance of stone consolidants |
| • See if CIPS could be reproduced on the small scale; analyse CIPS components; test CIPS consolidation | 2) Evaluate the consolidating properties of CIPS |
| • Compare the consolidation potential of three inorganic consolidants with previously used organic consolidant | 3) To compare the performance of three inorganic and one organic consolidants on experimentally weathered limestone |
| • Assess the impact of the weathering state of test replicates upon interpretation of consolidation potential. | 4) To compare the performance of three inorganic and one organic consolidants on naturally weathered limestone |

**Table 22: Objectives vs. Experimental Phase**

Whilst there were specific experiments designed to investigate each objective, as described in chapters 5 – 8, information from all the experiments conducted is now used to collectively address the four objectives summarised above (described fully in Chapter 3).

## 1) Developing a robust experimental methodology for the evaluation of the comparative performance of stone consolidants

This thesis has generated a range of results illustrating the potential of the new inorganic consolidants (e.g. Chapter 7) however; the situation has been shown to be complex, illustrating the problems of providing clear-cut scientific answers to conservation problems. There have been differences in the extent of consolidation effectiveness shown, and also variable levels of data retrieved across all experiments. These differences can relate to a several factors:

- Different stone types were used in different experimental phases (Elm Park, Hartham Park, Australian stones, Basildon park, British Museum stones)
- Due to equipment requirements, and the premise behind the different experiments different specimen shapes and sizes have been used throughout the project – cubes, prisms, and miscellaneous shapes.
- The stones involved had weathering histories – some had been exposed to the Oxford environment for over 100, others had been stored inside after being cut from the quarry and were then subjected to a pre-weathering treatment in the lab.
- A variety of ways of measuring the effects of consolidants were employed – for example Equotip, DRMS, Karsten Tube, GrindoSonic etc – and there were also differences in the timing of measurements (immediately after application, a few weeks after, several months after)
- The application procedure (pipette, spray, poultice etc.) varied between consolidants and sometimes with the same consolidant between experiments – as did the number of applications for each treatment.

When attempting to assess the effectiveness of individual consolidants within this project, or comparing between different treatments, it is not possible to rule out some effects from the factors mentioned above. However, this is also the real situation that conservators will face. Over the last few decades there has been a move towards maximizing the number of, and the standardization of, methods to test the performance of stone consolidants (Doehne & Price 2010, Fassina 2008, Laurenzi Tabasso & Simon 2006, Sasse & Snethlage 1996). Stone materials requiring conservation and consolidation are unique and complex, often with large variations in surface and internal properties across small artefacts. Whilst it is possible to try and control the variables within laboratory experiments to assess consolidation effectiveness, artefacts requiring conservation will possess large, and usually unknown, variability. As this project was a collaborative endeavour between the British Museum and the University of Oxford, it was designed to maximise applicability of research to real life conservation decisions. As such, many design aspects of the experiments were directly developed from discussions with the stone conservators in the British Museum. For example, this includes the application methods used, and the use of miscellaneous shaped replicates with an unknown weathering history in the fourth phase of experiments.

In order to try and compare effectiveness of different consolidants, and also to gain an accurate interpretation of how a consolidant may behave on a deteriorated artefact, a two-step process for experimental investigation is recommended. The first step would be to compare different consolidants upon a large number of standard replicates, of the same shape, size, and origin, whilst controlling as many variables as possible. The second step would be to test the same consolidants again upon very deteriorated stone samples of different sizes and shapes. Where possible analytical methods used within the two stages should be kept the same. This means careful consideration of the deteriorated stone samples to be used within the second step and the type of methods that will or will not be possible to use on such samples, prior to beginning the first stage.

## 2) Evaluation of the consolidating properties of CIPS

Whilst Chapter 6 investigated the Calcite In-situ Precipitation System (CIPS) to determine it could be reproduced on the small scale and to give an initial impression of its consolidation abilities, CIPS was also used in the experiments detailed in Chapters 7 and 8 comparing inorganic consolidants with organic. CIPS had been used to consolidate stone materials in the past in a variety of situations, however had not been used on heritage stone in a museum environment (Geotechnical Consulting Group 2002, Soudain 2001). Several of the experimental results from this project show that CIPS has the potential to provide similar strength increases and depth of penetration as an organic silane Wacker SILRES BS OH 100, whilst being a much safer and environmentally friendly option and with greater compatibility than the organic treatment. Out of the three inorganic consolidants investigated within this project CIPS appeared to be the most effective and produce the closest consolidation to the silane treatment. However there would potentially need to be some refinements made to the production process and there are some aspects such as the salts introduced by the treatment to the stone that need to be investigated further. A logical next step in the assessment of this treatment would be to apply it to a very deteriorated museum artefact and monitor the effects.

## 3) Comparison of the performance of three inorganic consolidants and one organic consolidant

As the trend in stone conservation has moved towards compatibility of treatments with the original artefact material, research has turned to scientific developments in material science to overcome past problems with inorganic stone consolidants (Daniele & Taglieri 2010, Dei & Salvadori 2006, Chelazzi et al 2013). This project has shown that inorganic treatments arising out of these new scientific developments could overcome previous difficulties and do hold promise for future use within stone conservation. This is particularly apparent with the Calcite In-situ Precipitation System (CIPS). Other inorganic treatments, including CaLoSil, could become effective consolidants that have greater compatibility with a limestone

substrate than previously used organic treatments. However, more investigation into ways to maximise effectiveness and minimise negative aspects such as colour change, is needed.

## Investigation of the impact of the degree of weathering of test replicates

When dealing with valuable heritage stone, the testing of any treatments to be applied is usually conducted on stone replicates in a laboratory. However, many researchers in the past have criticised the testing of stone consolidants on solely fresh material (Wheeler 2008, Theoulakis, Karatasios & Stefanis 2008). The research undertaken within the Back to Nature project clearly indicates the impact the weathering state of test stone can have upon the results gathered. This is both in terms of the type of analytical methods it is possible to use on highly deteriorated samples, and with the different results and subsequent interpretation of consolidant effectiveness. The fact that some differences between results could be attributed to differences in stone type reinforces the fact that there is no one consolidant for all deteriorated stone.

## Overall Conclusion

The overall aim of this project was to assess the potential of inorganic consolidants for use with heritage limestone. The experiments conducted have shown that the CIPS treatment showed the most potential to rival consolidation seen with organic consolidants such as Wacker OH. CaLoSil could hold potential however refinement of the treatment would be needed. Ammonium oxalate would only be suitable if superficial/surface consolidation was required. Future investigations into stone consolidants should consider a two-step process, with initial testing on a large number of artificially weathered replicates, followed by testing on deteriorated samples of a variety of shapes and sizes. Analytical methods used to assess effectiveness should be kept the same between experiments where possible, so careful consideration needs to be given to which methods will work with the deteriorated stone before testing begins.

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# Appendices

# Appendix A: Deteriorated Egyptian Limestones Database

| Big Number | Reg. Number | PRN | Description | Dimensions | Find spot | Dates | Acquisition | Location | Photos | Notes |
|---|---|---|---|---|---|---|---|---|---|---|
| **69054** | 1979.1017.41 | YCA60372 | Statue; Head from a limestone sphinx; Published: Johnson, in Bierbrier (ed.) Portraits and Masks (1997). P.103 [pls.41.1, 3]. | Height 34.00 cm (max) Width 38.00 cm (max) | Africa, Egypt, Upper Egypt, Temple of Amenhotep III (Thebes) | 18th Dynasty | Transferred from Victoria and Albert Museum, Previous owner/ex-collection Henry Martyn Kennard, Acquired by the British Museum in 1979. | BKE/F7 5/2 | PS133627 Negative (RIGHT ¾ VIEW) | Silanes used previously: Dow Corning T40149 & Raccanello 55050. See p26 & 93 Bk1 |
| **1314** | 1900.0609.146 | YCA60346 | Stela; Round-topped limestone stela of Iahmose with relief detail including three rows of Hieroglyphic text above a scene of the deceased seated with his father, mother and wife; now fragmentary and unstable; Published: HTBM Part 5: Plate 17 PM III (2): 742 Hall, H R 'Hieroglyphic texts from Egyptian stelae, etc., in the British Museum, Part 5.' 1914 (pl.17) | Height 29.00 cm (originally) Width 23.50 cm (originally) | Africa, Egypt, Lower Egypt, Memphis | 2nd Intermediate | Purchased through Rev Chauncey Murch; Purchased from Mohammed Mohassib; Acquired by the British Museum in :1900 | BKE/5; BKE/F7 3/3; BKE/F7 4/3 | | Silanes used: T40149. See p5 Bk1. Lots of work to be done; many very small fragments. |
| **V&A 38-191-v** | | | BMRL 5182-30217-T | | | | | | | Very bad condition. Efflorescence visible. Silanes used: Wacker OH. See p13 Bk2 |
| **1755** | 1931.0613.12 | YCA60284 | Stela; Upper part of a round-topped limestone stela bearing a representation of the deceased offering to Bastet, Horus, Amun-Ra and another deity; Hieroglyphic text including cartouches of Takeloth II; surface worn and powdery. Inscription in: hieroglyphic script. | Length 56.50 cm Width 41.00 cm Thickness 5.20 cm | Africa, Egypt | 22nd Dynasty | Purchased from Mohammed Mohassib Acquired by the British Museum in 1931 | BKE/F7 4/3 | | Not in specified location – whereabouts unknown. |

| Big Number | Reg. Number | PRN | Description | Dimensions | Find spot | Dates | Acquisition | Location | Photos | Notes |
|---|---|---|---|---|---|---|---|---|---|---|
| **1192** | 1987.0112.18 | YCA57643 | Tomb-relief; Limestone panel from a tomb-relief: this panel bears two representations of Shery: in the upper, he is shown stepping forward; in the lower, he is seated and holds a staff of office. The text includes a cartouche. It is carved in good low relief. The surface is much weathered and is flaking through the action of salt. No colour remains. The panel, complete apart from the top, originally formed, probably, the reveal of a doorway. The tomb of Shery is interesting because its inscriptions mention the shadowy Second Dynasty King Sened whose mortuary service, from the evidence of this tomb, seems to have continued into the Fourth Dynasty. Bibliography: B. Porter & R. Moss, "Topographical Bibliography of Ancient Egyptian Hieroglyphic Texts, Reliefs and Paintings' III (2) (Oxford: Clarendon Press), 490. | Height 156.00 cm (case) Width 62.00 cm (case) Height 143.00 cm Width 51.00 cm | Africa, Egypt, Lower Egypt, Saqqara (Memphis) | 4th Dynasty | Purchased through Sir Ernest A T Wallis Budge; Purchased from Giza Museum; Acquired by the British Museum in 1897 | BKE/7 | | Water glass treatment; Silanes also used: Wacker OH. See p89 Bk1. Cover of case appears to have been removed recently. Interesting surface appearance. |

| Big Number | Reg. Number | PRN | Description | Dimensions | Find spot | Dates | Acquisition | Location | Photos | Notes |
|---|---|---|---|---|---|---|---|---|---|---|
| **783** | 783 | YCA60402 | Statue; Lower part of a limestone-seated dyad; columns of hieroglyphic text on the back and right side of the seat (left side lost). The texts on the back are arranged to the right of a standing figure in sunken relief, the upper part of which is missing. Inscription in: hieroglyphic script: on: seat Translation: The Osiris, Chantress of Amun, Hemetnetjer, justified; her daughter...?entjay ? Note: The text on the side is arranged in three vertical columns. Parts of three more on the back. | Height 41.00 cm (max) Width 40.00 cm Depth 30.00 cm | | 18th Dynasty (late) | Anastasi Collection Previous owner/ex-collection Giovanni Anastasi Acquired by the British Museum in: 1849 | BKE/F7 4/2 | | Remnants of previous treatment visible. |

| Big Number | Reg. Number | PRN | Description | Dimensions | Find spot | Dates | Acquisition | Location | Photos | Notes |
|---|---|---|---|---|---|---|---|---|---|---|
| **1726** | 1930.0308.12 | YCA629 | Limestone figure of Hati: a block figure squatting on a cushion with figures of Onuris-Shu and Mehit in front of it. There are several lines of incised text.<br>The titles of Hati would appear to indicate that he held office in the temple of Onuris at Thinis, probably the site of Nag el-Mashayikh (B. Porter & R. Moss, 'Topographical Bibliography of Ancient Egyptian Hieroglyphic Texts, Reliefs and Paintings' V (Oxford: Clarendon Press), 28-9). A temple of Ramesses III is attested there, and one of Hati's titles indicates that there was a construction of Ramesses II at Thinis as well. This statue may have come from Thinis or possibly Abydos where objects bearing references to Thinis have been found (B. Porter & R. Moss, 'Topographical Bibliography of Ancient Egyptian Hieroglyphic Texts, Reliefs and Paintings' V (Oxford: Clarendon Press), 67-8, 74). Bibliography: 'British Museum Quarterly' 5, 19; K.A. Kitchen, 'Ramesside Inscriptions' 7 (Oxford: Blackwell Press), p169; B. Porter & R. Moss, 'Topographical Bibliography of Ancient Egyptian Hieroglyphic Texts, Reliefs and | Height 41.00 cm<br>Width 25.50 cm<br>Diameter 29.50 cm | Africa, Egypt | Ramesside | Purchased from Mohammed Mohassib Acquired by the British Museum in 1930 | BKE/F6 1/1 | E/D2264 Negative; E/D2265 Negative; E/D2266 Negative; E/D2267 Negative; E/D2268 Negative ; E/D2269 Negative ; H26 Negative; PS088707 Negative; K63874 Kodachrome ( Detail of crossed arms.) ; K63875 Kodachrome ( Front of object - depicting the two (damaged) figures.) ; K60088 Kodachrome ( Entire object - front.) | Nylon treatment. Silane treatment: Wacker OH. See p79 Bk1. Appears to have deteriorated further since 1983 photograph, however part of the head has been reattached. |

| Big Number | Reg. Number | PRN | Description | Dimensions | Find spot | Dates | Acquisition | Location | Photos | Notes |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | Paintings' VIII (Oxford: Clarendon Press), 613; Johnson, in M. L. Bierbrier (ed.), 'Portraits and masks burial customs in Roman Egypt' (London, 1997), p.103 [pl. 41.2]; R. Schulz, 'Die Entwicklung und Bedeutung des Kuboiden Statuentypus', 34 (1992). [pl.99,c] and Volume 33 p.387. Titles/epithets include: Temple Scribe of Inheret Titles/epithets include: Lord of Thinis<br><br>Note: Incised. The name of the owner, the temple-scribe of Onuris Hati, is incised twice on the top of the statue. The names of Onuris-Shu and Mehit and a brief prayer appear on the front of the statue. Four horizontal lines of text containing a prayer to Onuris, Horus lord of Thinis and Meh[it] on behalf of Hati are incised on the right side of the statue. A similar inscription, much broken, appears on the left side of the statue. The name and titles of Hati are also incised on the back pillar. | | | | | | | |

| Big Number | Reg. Number | PRN | Description | Dimensions | Find spot | Dates | Acquisition | Location | Photos | Notes |
|---|---|---|---|---|---|---|---|---|---|---|
| **1074** | 1928.0413.7 | YCA56129 | Fragmentary limestone relief: a cross within a scalloped recess. | | Africa, Egypt | Coptic | Purchased from Maurice Nahman Acquired by the British Museum in 1928 | BKE/F3 9/1 | PS209608 Negative | Not in specified location. |
| **69016** | 1979.1017.3 | YCA55925 | Worn rectangular limestone relief depicting five saints among vine stems. | Length 71.00 cm Width 31.00 cm | Africa, Egypt, Upper Egypt, Akhmim (?) Written on storage box | Coptic 5th Century | Transferred from Victoria and Albert Museum V&A.401-1888 | BKE/F3 3/3 | | Needs deep consolidation |
| **469** | 469 | YCA60457 | Limestone seated naophorous statue of Mentuhotep; incised Hieroglyphic text on the back-pillar and sides of the shrine; unfinished; inscription in: hieroglyphic script on: back-pillar | Height 54.00 cm Depth 43.00 cm Width 23.00 cm | Africa, Egypt | Ramesside | Anastasi Collection Purchased from Giovanni Anastasi. Acquired by the British Museum in 1839. | BKE/15 | | Problems from damp wall; actively deteriorating. |
| **1048** | 1885.1101.2 | YCA60392 | Worn white limestone sphinx. See Brissaud and Zivie-Coche - Tanis 1987-1997, (1998). p.110, 171, 177 [25,b 31b]. | Height 45.00 cm Length 73.00 cm Width 21.00 cm | Africa, Egypt, Lower Egypt, Nile Delta, San el-Hagar, Chapel of Ptolemy II | Ptolemaic | Donated by Egypt Exploration Fund. Acquired by the British Museum in 1885. | BKE/15 | | Silanes: Wacker. See p 7 Bk1 |
| **1049** | 1885.1101.3 | YCA60393 | White limestone sphinx; some surface wear. Petrie, Tanis II, 31, Pl. xv (No.4) See C.Favard-Meeks in Brissaud and Zivie-Coche - Tanis 1987-1997, (1998). p.110, 177 [pl.31b]. | Height 44.00 cm Length 71.00 cm Width 20.50 cm | Africa, Egypt, Lower Egypt, Nile Delta, San el-Hagar, Chapel of Ptolemy II | Ptolemaic | Donated by Egypt Exploration Fund Acquired by the British Museum in 1885. | BKE/15 | | Silanes: Wacker OH. See p50 & 56 Bk1. |
| **90667** | W 444 * | | Extremely worn limestone sphinx | Length 74 cm Height 50 cm Width 22 cm | | | | | | First object in museum to be treated with silanes: Dow Corning T-4-01449 & Raccanello 55050 p1 Bk1 |

| Big Number | Reg. Number | PRN | Description | Dimensions | Find spot | Dates | Acquisition | Location | Photos | Notes |
|---|---|---|---|---|---|---|---|---|---|---|
| **1341** | 1901.0608.1 | YCA60391 | Stela: White limestone false-door of Qar: at the top there is a plain cavetto-cornice and the inscribed area is surrounded by a plain forus-moulding. There are three vertical panels on each side of the doorway. The lintel bears a simple ḥtp-dỉ-nsw formula, and the six vertical panels carry Qar's titles and dignities; his titles also occur on the small, subsidiary lintel. These texts are carved in sunk relief of moderate quality. At the bottom of each vertical panel there is a standing figure of Qar who is shown in various attitudes of authority; these figures are carved in sunk relief of a peculiarly gauche nature. The rectangular panel above the doorway has a representation of Qar seated behind an offering-table, carved in fair, low relief. Above the table is incised a short ḥtp-dỉ-nsw text. The surface in general is sound apart from that of the rectangular panel carved in low relief; some flaking can be detected here. No colour remains. Bibliography: B. Porter & R. Moss, "Topographical Bibliography of Ancient Egyptian Hieroglyphic Texts, Reliefs and Paintings' III (Oxford: Clarendon Press), 67; Part | Height 213.00 cm Width 132.00 cm Thickness 12.00 cm | Africa, Egypt, Lower Egypt, Tomb of Qar | 6th Dynasty | Purchased from R J Moss & Co Acquired by the British Museum in 1901 | BKE/19 | | Treated with PEG. Previously displayed on facade of stately home?? Height and aspect may be important |

| Big Number | Reg. Number | PRN | Description | Dimensions | Find spot | Dates | Acquisition | Location | Photos | Notes |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | 2, 302 | | | | | | | |
| **131** | 131 | YCA57370 | Rectangular limestone stela; striped cornice at the top, below which are five registers: 1 - Two scenes of seated figures before offerings and offering-bearers; two small figures below the offerings in the left scene; Hieroglyphic text above both scenes. 2 - Two scenes of kneeling female figures sniffing lotuses with standing figures before; columns of Hieroglyphic text. 3 - Five standing male figures separated by columns of | Height 87.00 cm (case) Width 56.00 cm (case) | Africa, Egypt | 12th Dynasty | | BKE/M1 3/1 | PS071427 Negative ( Whole object-front view.) 7F45 Glass Negative ( Whole object-front view.) | NB: Condition does not appear to be too bad?? |

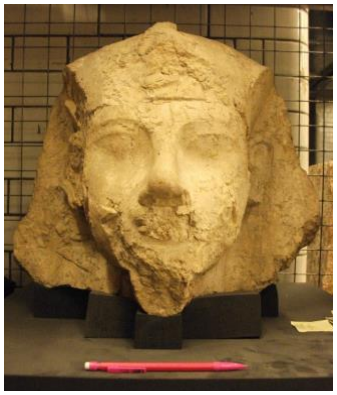
| Big Number | Reg. Number | PRN | Description | Dimensions | Find spot | Dates | Acquisition | Location | Photos | Notes |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | Hieroglyphic text; kneeling female figure sniffing a lotus to the left. 4 - Two male and four female standing figures separated by columns of Hieroglyphic text. 5 - Similar scene; seven figures. Published: PM V: p. 95 | | | | | | | |
| **1476** | 1909.0616.2 | YCA60394 | Limestone statue of a man wearing a lappet-wig and kilt; inlaid eyes of calcite and copper; wide plain back-plinth. BMRL 5183 - 23990 - w | Height 122.00 cm Width 34.50 cm Depth 49.50 cm | Africa, Egypt | Roman Period | Purchased from Panayotis Kyticas Acquired by the British Museum in :1909 | BKE/C/ B17 | K60089 Kodachrom e (Entire statue - front.) PS088704 Negative (FRONT VIEW OF ENTIRE MALE FIGURE) A50 Negative (FRONT VIEW OF ENTIRE MALE FIGURE WITH CANINE HEADED FIGURE SLIGHTLY IN SHOT) | Condition better than 1477 and 1478 |

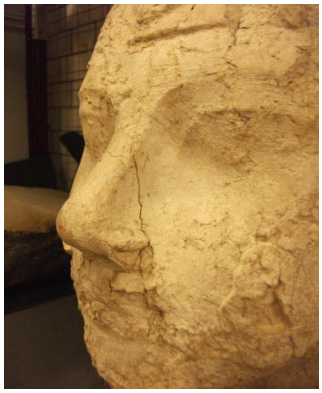
| Big Number | Reg. Number | PRN | Description | Dimensions | Find spot | Dates | Acquisition | Location | Photos | Notes |
|---|---|---|---|---|---|---|---|---|---|---|
| **1477** | 1909.0616.3 | YCA60370 | Limestone statue of a man wearing a toga-like garment; inlaid eyes of copper and calcite; wide back-plinth (chipped). | Height 128.00 cm Width 38.50 cm Depth 50.00 cm | Africa, Egypt | Roman Period | Purchased from Panayotis Kyticas. Acquired by the British Museum in 1910 | BKE/C/B17 | K60090 Kodachrome ( Entire statue - front.) K60094 Kodachrome (Head only - viewed from front/half right.) K60095 Kodachrome (Head and chest only - viewed from front.) K60096 Kodachrome (Close up of head viewed from front/half right.) PS088705 Negative (FRONT VIEW OF ENTIRE OBJECT) | Previous treatment visible |
| **1478** | 1909.0616.4 | YCA60395 | Limestone statue of a Maihesa; inlaid eyes of calcite and copper; head of a woman and a hawk behind either ear; wide plain back-plinth. | Height 127.00 cm Width 35.50 cm Depth 51.50 cm | Africa, Egypt | Roman Period | Purchased from Panayotis Kyticas. Acquired by the British Museum in 1911 | BKE/C/B17 | K60091 Kodachrome ( Front view of detail showing some sort of damage on the sculpture's right side.) K60092 Kodachrome (Entire figure - | Previous treatment visible |

| Big Number | Reg. Number | PRN | Description | Dimensions | Find spot | Dates | Acquisition | Location | Photos | Notes |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | | front.) K60093 Kodachrome (Detail (front) of right hand on abdomen.) | |
| **1262** | 1898.0817.6 | YCA57524 | Limestone tomb relief depicting Menankhpepy: Menankhpepy is shown on the left, standing and holding the staff and sceptre and dressed in full official uniform, including the leopard skin. He has also the 'good name' Mnỉ. On the right, in one horizontal and three vertical lines, is a simple ḥtp-dỉ-nsw text containing Mnỉ's titles. The whole is carved in a high relief of powerful but rather ungainly style. Some of the signs have been damaged. No colour is preserved. Bibliography: B. Porter & R. Moss, "Topographical Bibliography of Ancient Egyptian Hieroglyphic Texts, Reliefs and Paintings' V (Oxford: Clarendon Press), p. 110. inscription in: hieroglyphic script : Transliteration: Name of deceased : Mn-ʿnḫ-Ppy 'Good name' : Mnỉ | Height 49.00 cm Width 66.00 cm | Africa, Egypt, Upper Egypt, Dendara, Tomb of Menankhpepy | 6th Dynasty | Donated by Egypt Exploration Fund. Acquired by the British Museum in 1898. | BKE/F47/a/2 (AWAITING CONSERVATION) | K34262 Kodachrome ( Whole relief.) | |

| Big Number | Reg. Number | PRN | Description | Dimensions | Find spot | Dates | Acquisition | Location | Photos | Notes |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | Translation: Name of deceased : Menankhpepy 'Good name' : Meni Note: Hotep-di-nesu text conatining Meni's titles in high relief. | | | | | | | |
| **1775** | 1932.0611.6 | YCA71273 | Fragment of sandstone relief: stars and decorative border. | Length 35.50 cm (max) Width 21.50 cm (max) | Africa, Sudan, Kawa (Nubia) Africa, Sudan, Northern Nile, Northern Dongola Reach (Nubia) | | Excavated by Prof Francis Llewellyn Griffith Acquired by the British Museum in 1932 | BKE/F3 3/4 | | |

**69054**





**1314**






**V&A 38-191-v**






**1192**



**783**





**1726**



**469**





**90667;
1049;
1048**









1341



1476





1478





**Figure 47: Photographs of artefacts included in the database, labelled by BM 'big number'. All photographs author's own.**

# Appendix B: Contribution to conference proceedings for 12th International Congress on the Deterioration and Conservation of Stone

## AN EXPERIMENTAL ASSESSMENT OF 3 INORGANIC CONSOLIDANTS FOR USE ON MUSEUM ARTEFACTS IN COMPARISON TO ORGANO SILANES

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**Abstract**

Organo silanes 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.

Here are presented the findings from an experimental investigation into three inorganic consolidants being considered for use within 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), have been taken and assessed on 40, artificially pre-weathered, limestone replicates.

**Keywords**

Carbonate Stones, Consolidation treatment, Effectiveness, Inorganic

### 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 conservation treatment with the stone substrate (Sasse and Snethladge 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).

Organo silanes are consolidants that have been fairly popular in the past, and indeed are still used by many stone conservators. Used in the British Museum in the 1980's, there are a number of treated artefacts in their collections that demonstrate the success of silanes as stone consolidants. However, there are some stone artefacts, mainly limestone objects, where deterioration has worsened since being treated with organo silanes. This phenomenon has been seen elsewhere and effectiveness of silanes on carbonate stones is a debated topic (Wheeler 2008). One suggested reason for the issues sometimes experienced with silanes and carbonate stones, 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 the possibility of inorganic consolidants.

The British Museum has instigated an investigation into potential new inorganic consolidants to be used on their stone collections, in particular on limestone. Presented here are results from an experimental assessment of three potential new 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, 50x50mm cubic limestone replicates 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. Replicates were tested before and after weathering and before and after treatment, 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, destructive testing is ongoing.

## 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 50x50mm 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 (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 fluid 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 who can be contacted for more details.

Multiple applications of 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 for CIPS analysis, eight were treated by spraying with the mixed solutions; two of the 10 replicates were kept as controls. The replicates were treated every 24hrs for 6 applications.

### 2.2.2Ammonium 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 8 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 24hrs 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, Hamilton et al. 2011). Nano-particles of $Ca(OH)_2$ are suspended in different alcohols. After application, the alcohol evaporates to leave solid calcium hydroxide behind. This then reacts with atmospheric carbon dioxide to form calcium carbonate. Due to the small size of the particles, CaloSil can penetrate deep into the stone. CaLoSil E25 (calcium hydroxide particles dispersed in ethanol at 25g/L) was applied by spraying to 8 of the 10 replicates (with two remaining as untreated controls). After 3 weeks a second application was undertaken.

### 2.2.4 Wacker OH 100

Organo-Silanes have been commonly used since the 1960's (Wheeler 2008), and have been a very 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.

Silanes can be alkoxy silanes or silicone esters (Bradley 1986), the main difference for conservation purposes being that alkoxy silanes possess hydrophobic properties so strengthen and prevent entry of water (De Muynck et al. 2010), whereas silicone esters are solely used to improve internal cohesion (Bradley 1986).

The silane selected to use in this experiment is SILRES® BS OH 100, also known as Wacker OH 100. Produced by Wacker Chemie AG, SILRES® BS OH 100 is a solventless ethyl-silicate that penetrates into the stone forming a glass-like silica gel binder ($SiO_2$·aq.)(Wacker Chemie AG MTDS). The SILRES® BS OH 100 was applied by pipette (again to 8 of the 10 replicates with 2 left as untreated controls) 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, a variety of 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. | Destructive |

| | | |
|---|---|---|
| | Elemental mapping of consolidant distribution | |
| 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 help 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; the Wacker OH replicate group. This in turn was more than double the next highest increase, which was the replicate group treated with ammonium oxalate. The lowest weight and density increase was seen with the CaLoSil replicates.

### 3.2 Surface Hardness - Equotip

Surface hardness was determined using a Proceq Equotip (Equotip 3); a dynamic hardness test using rebound technique that calculates *Leeb hardness* using change in velocity (Viles, Goudie et al. 2010). 10 measurements were taken per 50x50mm area on the topmost surface of each replicate. Measurements were taken before artificial weathering, after artificial weathering/before treatment, and after treatment.

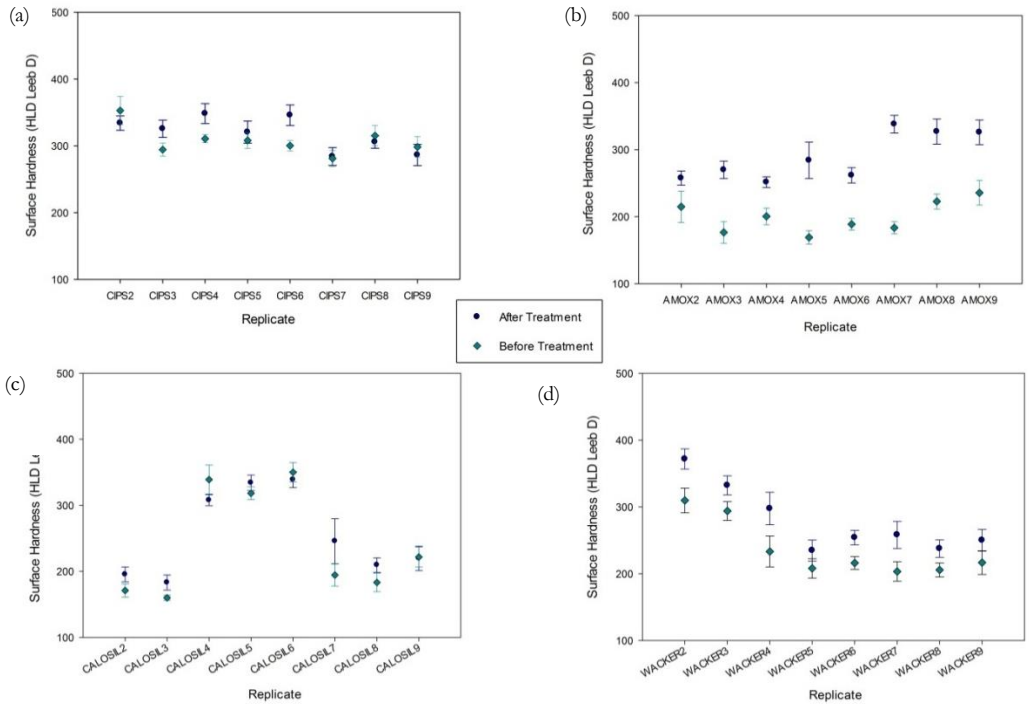



Figure 1: Graphs (a) – (d) to show change in surface hardness as measured by Equotip . (a) CIPS replicates; (b) AmOx replicates; (c) CaLoSil replicates; (d) Wacker replicates.

Figure 1 shows before treatment (u) and after (l) treatment Equotip values for each replicate, 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). Similarily, 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 was 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 consolidant 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 - Pundit

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 Elasticity 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 E 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 - Spectrophotometer

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*) were 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 50x50mm area on the top treated surface to give a mean colour difference. Overall change in colour (ΔE00) was examined, along with a more detailed look at change in colour, 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 blocks and the untreated blocks 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 Water Penetration - Karsten Tubes

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.

(a) (b)

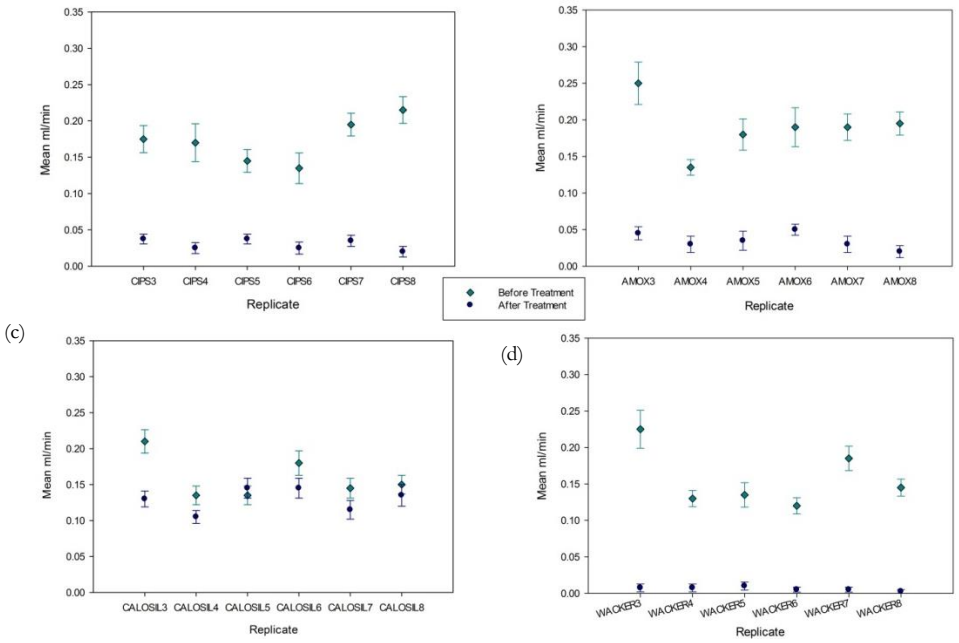



Figure 2(a-d): Graphs to show change in mean ml/min water penetration of replicates before (u) and after (l) treatment**.** (a) CIPS replicates; (b) AmOx replicates; (c) CaLoSil replicates; (d) Wacker replicates.

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).

None of the treatments used were designed with hydrophobic properties in mind, however some decrease in water penetration capacity is to be expected as the consolidant forms new bonds in the spaces between the individual grains of the stone. Completely reducing the water penetration can be undesirable however as this can prevent the stone from dealing with changes in relative humidity, and can cause stress between the untreated substrate and the treated zone near the surface of the stone.

### 3.6 Destructive analysis

The next stage in this investigation will be to undertake the destructive testing of the replicates. This will include observing thin sections on a petrological 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**

There are many consolidants available to treat deteriorated stone artefacts and the best one to use will depend upon a variety of factors including the stone itself, its location, deterioration problems and history. Preliminary testing looking at treatment effectiveness, compatibility with the stone and how it changes the stone appearance (along with other parameters), can help identify which consolidant would be best suited to the artefact.

Presented within this paper are the results from the non-destructive analysis of 3 inorganic consolidants being considered for use on British Museum limestone artefacts, in comparison with a previously used organic treatment, Wacker OH (SILRES® BS OH 100).

Surface hardness testing using an Equotip 3 showed the ammonium oxalate treatment provided the greatest increase in surface strength, far larger than that demonstrated by the organic consolidant Wacker OH, although the increase shown with the Wacker was statistically significant. Both the CIPS and the CaLoSil had some individual replicates which demonstrated an increase in surface hardness, but overall neither of these treatments provided a statistically significant increase in surface hardness. The most effective consolidant in this instance is the ammonium oxalate treatment, however these results should be used in conjunction with analysis of depth of penetration and the interface between consolidated areas and inner stone substrate; a very solid surface crust could pose many problems for an artefact.

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. Whist 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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