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Evaluating the effectiveness of calcium hydroxide
nanoparticle dispersions for the consolidation of painted
earthen architectural surfaces

A thesis submitted in partial satisfaction
of the requirements for the degree Master of Arts
in Conservation of Archaeological and Ethnographic
Materials

by

Dawn Elise Lohnas

2012

ABSTRACT OF THE THESIS

Evaluating the effectiveness of calcium hydroxide nanoparticle dispersions
for the consolidation of painted earthen architectural surfaces

by

Dawn Elise Lohnas

Master of Arts in Conservation of Archaeological and Ethnographic Materials

University of California, Los Angeles, 2012

Professor Ioanna Kakoulli, Chair

This paper describes a laboratory evaluation of the effectiveness of a calcium hydroxide nanoparticle dispersion (CaLoSiL) in consolidating manufactured adobe blocks with painted clay surfaces. The particular challenges faced in the conservation of painted earthen surfaces are discussed. Additionally, a review of past consolidation efforts and the properties of consolidants typically used in the treatment of wall paintings is given, with a particular emphasis on inorganic mineral treatments. For this study, test blocks were created based upon the description of Moche painted adobe surfaces in the literature. Blocks were plastered with a clay plaster layer, which included a cactus-mucilage extract as a binder. After the plaster layer had been artificially aged using cycles of fluctuating heat and relative humidity, a painted clay layer was added which consisted of a mixture of kaolin and charcoal. The consolidant (CaLoSiL) was applied to the block surfaces via spraying, and allowed to set for three weeks. Surface absorption tests, pH

tests, the Scotch Tape test (ASTM D4214-07), X-Ray Diffraction (XRD) and Scanning Electron Microscopy with Energy Dispersive X-ray Spectroscopy (SEM-EDS) were used to examine any physical or chemical changes in the blocks. Microscopy, photography, and Munsell Color Charts were used to evaluate visual differences before and after consolidation. Cross-sections taken before and after consolidation were examined using digital microscopy and Scanning Electron Microscopy (SEM). Overall, the samples showed some whitening following consolidation, but also an improvement in cohesion of the paint layers. While the microscopy results were somewhat inconclusive, XRD revealed the presence of a calcium silicate hydrate (plombierite) on paint layers from the treated samples. Suggestions for future studies which might incorporate additional variables and testing techniques are given.

The thesis of Dawn Elise Lohnas is approved.

David A. Scott

Ellen Pearlstein

Ioanna Kakoulli, Committee Chair

University of California, Los Angeles

2012

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Chapter 1. Introduction

When considering conservation products for the consolidation of painted porous architectural surfaces, the use of inorganic mineral treatments that are behaviorally chemically and physically similar to the original components offers an alternative to the organic polymeric materials extensively used on museum artifacts. By their very nature, inorganic mineral treatments are more stable and they tend to be much more durable than organic-based treatments, which are somewhat perishable and subject to chemical alterations in uncontrolled environments (Matteini 2003).

1.1. Aim

The focus of this thesis is to evaluate the use of a relatively new method of treating porous, painted architectural surfaces, which involves the use of calcium hydroxide nanoparticle dispersions for the consolidation of wall paintings. Inorganic nanoparticle-based consolidants offer many advantages over traditional inorganic treatments with larger-size particles, due to the specific properties obtained by the use of submicron size particles (Baglioni and Giorgi 2006; Baglioni, Giorgi, and Dei 2009). While inorganic nanoparticle consolidants have principally been tested and used successfully to impart cohesion and stability to historic European lime-based as well as archaeological Central American lime-based wall paintings (Baglioni, Giorgi, and Dei 2009), their effectiveness on the consolidation of powdery paint layers on clay supports has not yet been fully investigated. This study aims to fill this gap in the technical literature with the design of a pilot project focusing on calcium carbonate nanoparticle dispersions in alcohol for the consolidation of powdery painted surfaces on clay-based plasters and earthen supports. It

further aims to provide a laboratory methodology for vetting the performance of this type of consolidant on earthen architecture.

1.2. Principles/Terminology for this Study

For the purposes of this project, Warren's (1999) definition of a consolidant will be used as a reference:

...a consolidant acts at the near-molecular level by fixing or inhibiting the capacity for movement between very small particles, thereby altering the characteristics of the material in terms of its behavior, particularly in the presence of water. It tends to make the material stronger in compression and tension, and may affect inherent characteristics, such as heat and sound transmission and rigidity. (121)

This study aims to test a consolidant that will re-establish cohesion of loose particles, thus increasing the strength and durability of the material being treated. The performance of the consolidant and the way in which it affects the overall physical and chemical characteristics of the surface being treated will be assessed.

1.3. Experimental Methodology

Blocks made of sun-dried clay-rich soil with clay-based painted surfaces were created based upon technical descriptions in the literature of painted earthen architectural blocks created by the Moche culture of Peru (see *Chapter 2* for specific compositional description of blocks and their painted surface). Blocks were consolidated with CaLoSiL, a commercially available nanoparticle dispersion of calcium hydroxide (see *Appendix 8* for technical data). The effectiveness of the treatment, and any changes incurred as a result of treatment, were evaluated using photography, absorption tests, scotch tape tests, X-ray diffractometry, digital microscopy, and scanning

electron microscopy (see *Section 5.5* for a more thorough discussion of these techniques and the rationale for choosing each).

Chapter 2. Earthen Architectural Painted Surfaces

To examine the effectiveness of a mineral nanoparticle consolidant on a clay plaster wall painting facsimile that is representative of currently existing archaeological surfaces, the blocks created in this study were based upon the materials and techniques used to create the ancient Moche wall paintings of coastal Peru.

2.1. Moche Wall Paintings: History of Techniques

Moche is the name used to refer to the culture, site style and state that dominated the Peruvian North Coast around 100-750CE (Stone-Miller 2002). The Moche civilization was incredibly powerful, with large adobe mounds which, in addition to their material culture, demonstrated the wealth and power of the Moche state. Adobe refers to sun-dried brick made of mud that may or may not contain organic additives and can be shaped by hand or in a mold. This method of brick-making uses the shrinkage characteristics of clay and earthen materials to impart stability, allowing the solid grains to be attracted to one another by mutual attraction forces (Velde 2008: 15). Monumental structures were pyramidal, stepped, or truncated, and could be composed of millions of adobes (Mujica Berreda et al. 2007, 91). Such large-scale architecture often contained wall paintings painted in bright colors.

It is important to note that during the Moche state occupation, a relatively singular painting technique was used on monuments throughout the Moche valley (Bonavia and Lyon 1985). Surfaces were decorated on adobe structures throughout the Moche state. Past studies of

Moche earthen architectural painted surfaces have found that a single white preparatory ground layer was used prior to painting the polychrome layers (Bonavia and Lyon 1985). A study by Kakoulli (1997) identified a single plaster layer, which was a mixture of kaolinite, illite, smectite, calcite and quartz. It is possible that a similar layer was used on many Moche mural paintings, such as those described in the literature (Argumendo 1986).

Scientific investigations of Moche mural paintings have found that the colors utilized were primarily mineral in origin (see *Table A1.1* for specific pigments and studies). Red pigments have most commonly been identified as hematite (Fe_2O_3) (Bonavia and Lyon 1985; Argumendo 1986; Casoli et al. 2000), and yellow has often been identified as a yellow ochre ($\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$) (Argumendo 1986; Kakoulli 1997; Uceda et al. 1993). Black seems to most commonly be acquired from charcoal (Argumendo 1986; Kakoulli 1997; Scott et al. 1998), while a blue/gray color is typically identified as a mixture of black and white pigments. The white pigments are most commonly found to be calcite (CaCO_3) (Casoli et al. 2000; Scott et al. 1998) although the use of a white clay such as kaolin ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$) has also been identified (Kakoulli 1997).

The identification of organic binders in archaeological wall paintings can prove quite challenging, and Moche wall paintings are no exception. Binders examined by gas-chromatography mass-spectrometry by Casoli et al. (2000) proved to be of vegetal origin. Argumendo (1986, 77) postulates that juice of *Trichocereus pachanoi* (San Pedro cactus) was used as a medium. Hoyle (1990), on the other hand, cites the use of gum from *Opuntia ficus indica*, the prickly-pear cactus. According to Muelle (1939) indigenous peoples in the highlands cut slices from cactus (Muelle mentions the use of *Cereus cacti*), leaving them in water overnight to

release their viscous sap. A sort of gum solution is thus prepared, in which the earth pigments are dissolved. Other techniques for extracting the gum, such as soaking the cactus for 14-25 days (Beas 1991), are also described in the literature.

It is possible that another vegetal material was used as a binder, alone or in combination with the cactus. The gum of the zapote tree (*Quararibea cordata*), which grows on the North Coast of Peru (Hodge 1960), may have been utilized, as it is locally available and is still used as a fixative in the preparation of wall paintings in some regions. In addition, the binder may have come from the gum of the *Acacia macracantha* tree (Bonavia and Lyon 1985), as this too is commonly found in Peru (Towle 1961).

2.2. Challenges in the Conservation of Painted Earthen Surfaces

2.2.1. *Materials and Construction*

The range of earthen materials such as clays, soils, and organic fillers used to create architectural structures and their decorated surfaces poses a number of conservation challenges, as they are susceptible to damage from a number of different phenomena. The more general deterioration problems of painted earthen architectural surfaces will be discussed below, in order to illustrate some of the challenges to be expected when conserving painted earthen surfaces, such as those created by the Moche.

2.2.2. *Weathering*

As with any building, earthen architecture is often exposed to a variety of harsh conditions that can lead to the deterioration of the constituent components. Deterioration of underground and

buried structures is accelerated by excavation, as they become subject to new environmental conditions aggravated by mechanical and chemical damages caused by natural means such as wind, temperature, and moisture (Oliver 2008). Built structures that have been buried begin to dry out immediately following excavation. Rapid drying can accelerate deterioration problems, weakening bonds between earthen materials and causing salt crystallization leading to the powdering of dry surfaces (Torraca 1970).

The high porosity of earthen structures (and their decorated surfaces) also makes them susceptible to permeation by liquids and gases, which may carry salt solutions, atmospheric pollutants and other aqueous vapors harmful to their structural integrity. Water in the form of rain, snow, dew, condensation and groundwater can all penetrate the structure. Moisture cycles cause expansion and contraction of the hygroscopic constituent materials, and are considered the primary cause of damage in earthen structures. As water infiltrates the structures, it can cause severe expansion of the clay minerals and dissociation of the clay plates, which may lead to the loss of material. On drying, the clay tends to contract, which can lead to cracking, further threatening the overall stability of the system (substrate and surface).

Nearly all soils and walls contain soluble salts, which may be concentrated in particular areas or dispersed throughout the porous matrix (Arnold and Zehnder 1991). Solutions of salts can reach the surface of a wall because of rising damp (via capillary forces) or from rainwater penetrating the structure from the exterior. Salts may form efflorescences (creating crystals on the surface), or subflorescences (salts evaporating within the interfaces e.g. between the paint layer and plaster, the plaster and wall/structure), which further weakens the cohesion of the materials (Arnold and Zehnder 1991). As the temperature (T) and relative humidity (RH)

fluctuate, salts crystallize and solubilize, putting stress on the wall painting materials as the salts expand. Variations in RH can lead to cycles of wetting and drying caused by solution and crystallization of soluble salts (Hammer 1987). This cycle can lead to flaking and disintegration of the paint layer.

Unprotected structures may suffer the direct action of winds, sunlight, and rain, which can be extremely damaging. The mechanical action of winds can accelerate evaporation processes, which may worsen damage caused by salt crystallization (Torraca 1970). Wind also causes mechanical damage as particulates transported by the wind often hit the painted surface, causing micro pitting and erosion. Sunlight may contribute to evaporation, and can cause fading of light sensitive pigments and breakdown of organic media through oxidation and cross-linking. Moreover, natural disasters, such as earthquakes, hurricanes, and other extreme weather events pose imminent threats to earthen decorated surfaces as well as their substrates.

Wall paintings are also susceptible to microbiological and higher plant growth. Their porous nature makes their surface receptive to microbial spores and vegetative cells transported by airborne particles. Seepage and capillary rise from the dampness of the rains and high humidity can result in flora and microflora development. Biodeterioration due to fungi, algae, and lichens are all common causes of mural deterioration (Torraca 1970). Decohesion and flaking of surface layers, powdering, and formation of small blisters may all lead to eventual loss of part of the painting itself (Dei and Salvadori 2006). Finally, damage incurred due to human or animal activity is a potential problem for in-situ sites, with vandalism or damage due to animal nesting and burrowing posing potential concerns.

2.2.3. Preventive and Passive Protection Measures

The consolidation of decorated surfaces is only one of a great number of measures that must be considered when preserving earthen architecture. Preventive and passive measures should always be considered prior to undertaking remedial conservation measures. These may include drainage modification or capping of walls to protect them from water damage (Oliver 2008). Wall capping, however, can be problematic, particularly if not well maintained (Caperton 1988; Caperton 1990). Reburial or building shelters over at-risk structures should also be considered.

Chapter 3. Consolidation and the Properties of Consolidants

3.1. Consolidation

A great deal of experimentation has been carried out using a wide range of consolidation treatments to impart increased stability upon earthen architectural structures and their surfaces (Chiari 1987; Warren 1999). Generally speaking, consolidants are used on friable and fragile surfaces, in order to increase stability, cohesion, or strength.

3.2. Properties of Consolidants

Choosing appropriate consolidants for porous building materials is a challenging task. The ideal consolidant should not alter the structure of the original material too greatly, as this could potentially lead to further damage. The material should leave pores and capillaries open (Chiari 1990) and not be extremely hydrophobic, as this could alter the transmission of water vapor. Surface consolidants on painted surfaces in fluctuating climatic conditions that cause differential dimensional change of the layers and differences in water vapor permeability can ultimately cause additional problems, such as accelerated deterioration of unconsolidated regions.

Consolidants should therefore create a surface that will respond in a manner similar to the original materials (Agnew et al. 1987).

Preferably, the consolidant should not cause any change to the surface of the paint either in the saturation of color, or in the gloss or texture, and should also be photochemically stable (Laurenzi Tabasso 1995). Additionally, it should have sufficiently low viscosity to ensure thorough penetration, while also providing mechanical strength and abrasion resistance (Laurenzi Tabasso 1995). Hardness is also a factor to consider, as certain consolidants cause problems of brittleness, which may lead to further damage (Battle 1983).

Finding a consolidation product that meets all requirements is very difficult; however, understanding the needs is important in informing decisions for choosing an appropriate material. Additionally, it should be recognized that particularly in porous structures such as wall paintings, consolidation is not a reversible process, so the choice of the consolidant should allow for retreatability (Agnew et al. 1987). Due to the large scale of painted decorative surfaces, consolidants should also be inexpensive, eco-friendly and non-hazardous with good working properties for application in the field and good performance, including in uncontrolled environments.

Chapter 4. Literature Review

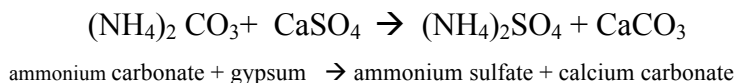
4.1. Inorganic Mineral Treatments

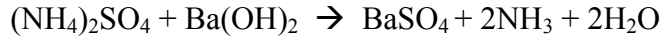
The use of inorganic mineral treatments has a rich history in conservation. An overview of the historic use of these treatments will be given, with a specific emphasis on the use of calcium hydroxide-based consolidants.

4.1.1. Historic Overview of Inorganic Mineral Treatments

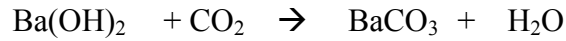
Inorganic mineral treatments have been tested extensively for their application as consolidants (Elert et al. 2008; Giorgi, Dei and Baglioni 2000; Matteini, Lanterna and Nepoti 1996; Hansen et al. 2003; Matteini, Moles and Giovannoni 1994). The first mineral treatments were carried out in 1862 by A. H. Church (1862) who developed baryta water (a dispersion of barium hydroxide in water) for the treatment of the wall paintings at the Westminster Chapter House in London. A century later, during the floods in Florence in the 1960s, the Ferroni-Dini method, was published which involved the application of a solution of ammonium carbonate ((NH₄)₂CO₃) followed by barium hydroxide (Ba(OH)₂), for the desulfation of gypsum (CaSO₄), a low solubility salt. This was possible through the transformation of gypsum into insoluble compounds with the formation of barium carbonates and barium sulfates. This method was able to arrest and mitigate the severe deterioration of important wall paintings in the city of Florence through a series of chemical reactions with consolidative properties.

The chemical formula for the transformation is as follows:





ammonium sulfate + barium hydroxide → barium sulfate + ammonia + water



barium hydroxide + carbon dioxide → barium carbonate + water

The transformation of the gypsum into the much less soluble barium sulfate, poses less risk to the painting's surface, pacifying the action of gypsum salts. The treatment is thus highly durable, and by transforming the potentially harmful gypsum (which could potentially form soluble salts), protects the painting indirectly.

While many consolidation studies utilizing inorganic mineral treatments have been carried out in the field (Matteini 1987; Matteini 2003; Hansen et al. 2003; Lanterna et al. 2000; Matteini, Moles, and Giovannoni 1994) as early as the late nineteenth century (Church 1862), these have often focused on paintings on stone and on lime-based plasters (Crosby 1981; Matero 1995). In comparison to lime-based plasters and stone surfaces, relatively little research has been conducted on the application of inorganic mineral treatments on earthen plasters and earthen supports (Matero 1999). Matero (1999:61) speaks directly on the challenges posed by such studies:

developing an effective preservation strategy that is conservative yet responsive to the existing and varied contexts of any ruin site and takes into account the ephemeral nature of surviving building materials (such as adobe and plaster), the vulnerability of the ruin's condition and the increasing demands for public interpretation is a difficult task.

Reaction products of clay-based structures treated with highly alkaline mineral solutions create partial crystallization, which imparts a strength and stability to the clay with cementing properties (Elert et al. 2008). The reaction between lime additives and clays to produce these microcrystalline alterations are called pozzolanic reactions, which have been widely utilized in industry to produce stronger cements (Baronio and Binda 1997; He, Osbaeck, and Makovicky 1995). While there has been considerable research carried out on the transformation of clay minerals to form slightly crystalline phases at high temperatures (He, Osbaeck, and Makovicky 1995; Baronio and Binda 1997), relatively few studies have investigated the products formed at lower temperatures, which could be applicable to the consolidation of earthen architecture. One such study includes the research by Elert et al. (2008) who have studied the alkaline reactions of $\text{Ca}(\text{OH})_2$, NaOH and KOH with clay-rich soils under ambient conditions. The authors detected mineralogical changes in samples, finding calcium silica hydrates similar to tobermorite and calcium aluminosilicates, which are the typical products produced by pozzolans (Elert et al. 2008). Calcium silicate hydrate gels typically form upon $\text{Ca}(\text{OH})_2$ treatment of clays. Elert et al. (2008) found $\text{Ca}(\text{OH})_2$ had limited effect on in situ consolidation of earthen structures or clay-rich soils, likely due to its low solubility in water. The recent introduction of nanoparticle dispersions in alcohol, however, overcomes the issue of the poor solubility of calcium hydroxide in water, improving the overall performance of the consolidant (see Section 4.1.4, below).

4.1.2. Past Consolidation of Painted Plaster Surfaces

Preliminary consolidant tests on decohesive unpainted earthen architectural surfaces have only recently been introduced, with promising results (Elert et al. 2008). Other inorganic

treatments on earthen architecture include ‘traditional’ products such as ethyl silicates (Ferron 2007; Beas Guerrero de Luna 1993). Organic polymeric products (synthetic and natural) have been the most common media for consolidation for earthen materials. Beas (1993) tested the consolidative effectiveness of the acrylic resin B-67, the ethyl silicate Conservare OH, as well as extract from the tuna cactus, on clay-based plasters. The latter has been the subject of several studies (Hoyle 1990), as it has been used in Peru for hundreds of years. Beas found that Conservare OH imparted the best stability to the clay-based plaster. While these studies are quite informative in regards to the treatment of earthen plasters, they rarely focus on the consolidation of the paint layer on such surfaces. There is, however, a degree of cross-compatibility with some of the techniques mentioned.

The unfortunate destruction of many paintings due to past conservation or preservation efforts demonstrates the importance of using a material that is compatible with the existing paintings and the traditional techniques. The painting technique used on adobe structures in Peruvian wall paintings is inherently unstable, as the relatively fragile binders are quite susceptible to climatic changes, and the mud plaster support can be quite sensitive as well (Argumendo 1986). In a study by Gammarra (1983) the author evaluated the use of Primal AC-33 (an acrylic dispersion), Curasol (a polyvinyl acetate dispersion), Calaton CB (N-methoxymethyl nylon, commonly referred to as soluble nylon), Paraloid B-72 (an ethyl methacrylate copolymer), Mowilith DM-1 H (a polyvinyl acetate), and Bedacryl 122X (a butyl methacrylate). Of these, the products most used in Peru include Paraloid B-72, Bedacryl, Mowilith DM-1 H and Calaton (Argumendo 1986). Morales Gammara, however, reported that none of these materials had the desired effects in consolidating the plaster and decoration.

Ultimately, an ethyl silicate was chosen, although its irreversibility and structural alteration to the adobe was acknowledged. Chiari, Burger & Salazar-Burger (2000) describe the successful use of tetraethyl orthosilicates in the conservation of a clay plaster frieze on a stone wall. It should be noted, however, that this piece was reburied after treatment, which may have aided in its overall preservation. While overall preservation of the frieze was excellent, reexamination of the piece 12 years later did indicate that adherence of the treated layer to the original layer was slightly lacking, and the authors advised repeating the treatment.

The successful use of Acryloid B-72 in toluene and xylene (1:1) on plastered earthen supports (without causing any change in surface appearance) has been reported by Matero and Bass (1994). The use of these treatments, however, can pose many problems. Firstly, the use of xylene and toluene as solvents is undesirable for large surfaces, as these materials pose a number of health risks, and their slow evaporation can result in undesirable solvent retention in the wall painting. Additionally, synthetic polymers can create an impermeable surface, which has been shown to cause damaging salt crystallization beneath the applied polymer layer (Giorgi et al. 2006).

Organic polymeric materials used for the consolidation of archaeological wall paintings in Mexico have, in combination with drastic changes in T and RH and the mechanical action of dust, wind and rain, caused detachment and flaking of the paintings, and a general acceleration of the reactions involved in the painting's degradation. The use of Paraloid B-72 on a Mayan mural painting in Bonampak Chiapas, has caused an alteration of the design and color of the surface, while also causing a whitish bloom, which may have been due to the high humidity of the

environment (Espinosa 1986). Exposure to the elements promotes degradation, as oxidation, breakdown and cross-linking of the polymer chain occurs, which can all lead to a loss of pigment adhesion, yellowing of the polymers, and a decrease in polymer solubility and reversibility (Giorgi et al. 2006).

4.1.3. Calcium Hydroxide

The use of lime (calcium hydroxide) as an alkaline consolidant has been employed since ancient times, with the application of lime to consolidate gypsum-bearing earthen materials (Warren 1999:112). Traditionally, the use of calcium hydroxide as a consolidant for wall paintings has been employed on lime-based paintings, and more precisely paintings executed in fresco, as the calcium hydroxide reacts with the carbon dioxide in the air, following the same reaction as the original lime-based plasters, forming calcium carbonate. Certain risks may accompany the treatment, however. A surface aggregate that is poorly formed may create a new calcite layer that leads to powdering and lack of consolidative efficacy (Hansen et al. 2003), while the formation of a white veil (from the formation of calcium carbonate on the surface) may disfigure the paintings. Moreover, if there is a significant difference between the newly formed calcium carbonate and the substrate (such as the grain size, texture, or crystal habit), this may result in differential dissolution, which will ultimately affect the longevity and effectiveness of the treatment (Hansen et al. 2003). In addition, the carbonation of the calcium hydroxide may alter the pore properties of the material, creating a consolidated surface layer with different properties than the untreated substrate (Hansen et al. 2003).

Because of the limited solubility of calcium hydroxide, the limewater must be applied in successive coatings to avoid aggregation and separation of the phases. This introduces more water to the structure, which can pose a risk to the materials through the mobilization of soluble salts, and may also lead to dissolution and re-crystallization of carbonates. The addition of sugars, carbohydrates, and other organic materials to the aqueous solutions of calcium hydroxide to modify their setting times and properties can also help to increase the concentration of the solution, thereby decreasing the number of applications necessary (Hansen et al. 2003). However, these additives may cause additional unforeseen complications through their own interactions with the environment, and they could be susceptible to biological damage. The use of ethanol instead of water reduces the tendency for aggregation and the formation of a white film on the consolidated surface (Hansen et al. 2003). Moreover, the introduction of nanoparticles of calcium hydroxide (diminishing the size of the particles in the dispersion, discussed below) further decreases the risk for particle aggregation and the formation of a white film altogether.

4.1.4. Mineral Nanoparticles

Recent developments in technology have allowed for an improved form of inorganic mineral treatment, involving the application of nanoparticle dispersions of inorganic materials. The application of nanoparticle dispersions of calcium hydroxide in alcohol is comparable to the application of very concentrated limewater solutions, while overcoming the issue of the poor solubility of calcium hydroxide in water (Baglioni, Giorgi, and Dei 2009). The smaller size of the particles creates greater stability in the dispersions (Blee and Matisons 2008). Other

advantages include higher penetration into the painted layers (Blee and Matisons 2008). Nanoparticles with dimensions between 150-280nm are especially well suited for wall paintings consolidation, as their small dimensions allow for high stability in the small pores of the lime plaster (Baglioni, Giorgi, and Dei 2009). The problem of creating a white haze on the surface of the wall paintings (commonly encountered with applications of limewater) is virtually eliminated (Blee and Matisons 2008).

These treatments were first used successfully on wall paintings applied in fresco, and stone surfaces in Europe (Ambrosi et al. 2001), with stable nano dispersions of calcium hydroxide successfully applied as a consolidant and fixative to re-adhere lifted paint layers during restoration treatments (Giorgi et al. 2006). Treatment with nanoparticle dispersions of calcium hydroxide has also been successfully and extensively implemented at Calakmul, Campeche, Mexico (Giorgi et al. 2006; Giorgi et al. 2010). The application of this technique in the humid jungle environment of Calakmul demonstrates that the treatment is capable of withstanding extreme climates, which is not necessarily the case for more fragile organic polymer treatments (as previously discussed).

Chapter 5. Experimental Methodology: Materials and Methods

5.1. Creation of the Test Blocks

Test blocks were produced using molds to create standard-size cubes (5x5x5cm) for laboratory testing. The composition of the test blocks used in this study was based on descriptions in the literature of earthen painted plasters (see *Table A5.1* for overview of common pigments found in

analysis of Moche painted earthen architecture) and laboratory trials. Compositional analysis of earthen architectural samples has been conducted in the past to better evaluate the condition of structures in order to inform laboratory tests as well as conservation treatments (Beas Guerrero de Luna 1993; Beas 1991; Fodde 2000; Ferron 2007; Kanan 200; Matero et al. 2000; Shekede 2000). Blocks were numbered 1-15 (see Image A3.3) to allow the blocks to be specifically monitored and tested throughout the experimental process. Note that block 12 was ultimately omitted from the project, as it was used as a source of initial testing that rendered the block unusable for comparative purposes.

5.2. Earthen Constituents

Carrying out laboratory tests using original materials or samples from earthen wall paintings has many advantages, but access to samples can pose a challenge. For the purposes of this study, it was therefore decided to replicate original materials using dry components of known composition that would be representative of the region under investigation. Similar methods of producing test blocks for laboratory testing has been used in previous conservation studies (Walker 2000; Ferron 2007).

Based on studies of the original materials of Moche paintings (Kakoulli 1997) as described earlier, the blocks produced for this study contained montmorillonite and kaolinite, as well as sand and straw. The inclusion of expansive and non-expansive clays (montmorillonite and kaolinite, respectively) was necessary to determine the effectiveness of the pozzolanic reactions expected from the use of an alkaline consolidant.

Blocks were made in batches of three, with a ratio of approximately 3: 5: 4: 3 kaolin: montmorillonite: sand: straw, by volume. Ingredients were measured by weight to ensure uniformity in block composition. 64.1g of kaolin (yellowish white kaolinite supplied by Kremer Pigments $\text{Al}_2(\text{Si}_2\text{O}_7)\cdot x\text{H}_2\text{O}$), 271.8 g montmorillonite, 366.6g sand, and 13.2g straw was used per “batch” (see *Appendix 8* for suppliers) The clay and sand were thoroughly mixed before adding the straw. Straw was cut into pieces approximately 2.5-5cm in length. The straw was then incorporated with the dry components adding deionized water (approximately 150-200mL water) until a desirable consistency was reached. The mixture was poured into pre-fabricated wooden molds, which were open on the top and bottom to allow for easy removal and drying. Once the blocks were sufficiently hardened (after two or three days), they were removed from the molds and allowed to dry for an additional two weeks exposed to direct sunlight in a sunlit room.



Figure 1: Earthen architectural test blocks before plastering

5.2.1. Surface Plastering

Once the adobe blocks had been allowed to dry, their surfaces were covered with a clay plaster layer, consisting of montmorillonite and kaolinite clays. In addition, sand, water and a gum-like extraction from soaked cactus mucilage were added to this mixture. This has traditionally been used as an additive in earthen constructions in many regions of South America (Beas 1991). The sulfuric acid esters in the vesicular cells of the parenchymatous structure of the cactus have conglomerating properties, which also prevent against bacterial growth (Hoyle 1990). After consulting the literature and attempting several different techniques, the chopped prickly pear cactus (from the *Opuntia* genus, likely *ficus-indica*) was soaked in deionized water for 24 hours, as described by Hoyle (1990). It was then used within 48 hours, as Hoyle warns that after this time the cells begin to decompose resulting in loss of viscosity. The overall composition of the plaster consisted of 2 parts (by volume) sand to 2 parts clay (1.5 parts montmorillonite and .5 parts kaolin), .25 parts cactus and .5 parts water, which was applied to the surfaces of the blocks in a layer approximately .5cm thick.



Figure 2: Plastered test blocks before painting, after accelerated aging

5.2.2. *Painting Technique*

Following a series of tests applying various ratios of pigments and binders on block facsimiles, blocks were painted with a mixture of kaolin and charcoal (in a 1:1 ratio, by volume) in deionized water, with half of the blocks painted with a cactus binder as well. Blocks 1-6 were painted with a ratio of 4:1:1 pigment: water: cactus mucilage binder. Blocks 7-13 (excluding Block 12, which was eliminated during initial accelerated aging of the plaster layers) were painted with a 3:1 ratio of pigment: water. Paint was applied using a microspatula, and leveled to create an even surface. Scotch tape was applied in layers along each of the edges, in several layers, in order to provide a uniform height (of approximately 1mm) to which the paint layers were leveled on each block.

5.3. Artificial Accelerated Aging

5.3.1. *Relative Humidity (RH) and Heat Cycles*

Accelerated aging using cycles of heat and RH was used on the block facsimiles in order to create relatively decohesive surfaces, in an attempt to approximate the state of preservation of original Moche painted surfaces. Blocks were run through several cycles of heat and RH in order to provide a sufficiently decohesive surface for consolidation testing. Due to time constraints, only the plaster layers could be continually cycled through fluctuations in T and RH, as described below.

5.3.2. *Past Studies Utilizing Artificial Accelerated Deterioration*

The methods used for accelerated deterioration were based on erosion tests similar to

those conducted by Walker (2000), Ferron (2007) and Sassoni et al. (2011). Walker evaluated three methods: spray tests, wet-dry cycles and drip tests. In the spray test, each face of the block was sprayed at a set distance with a known pressure, while in wet-dry cycles the test block went through cycles of immersion in water and heat (70°C). After each heat cycle the block was scrubbed with a wire scratch brush. Ferron (2007) used a system similar to the wet and dry cycles described by Walker to evaluate the effectiveness of consolidants. She cycled her samples through periods of partial immersion in water and heat exposure (60°C). Sassoni et al. (2011) used heating (at temperatures of 100°C, 200°C, 300°C, 400°C and 500°C, for one hour) to artificially damage test blocks. Additionally, wet-dry cycles were used by Sassoni et al. (2011) by water-saturating the samples and then drying them under a fan until they reached a constant weight. The tensile strength of the samples was measured and compared to that of untreated samples and treated samples not subjected to wet-dry cycles. While some of the techniques used by Walker (2000), Ferron (2007) and Sassoni et al. (2011) were judged to be too aggressive for this project, the methods used here aimed to degrade the materials significantly enough to allow for a perceptible change following consolidation.

For this study, water was poured on the blocks three times throughout the aging process, along with exposure to cycles of heat (60°C) and elevated humidity. Blocks were aged before painting because the paint was water-soluble and the unpainted blocks could therefore withstand more severe aging. It was hoped this aging would weaken the earthen substrate, so that it would more accurately represent the ancient Moche earthen architecture that survives today. Wet-dry cycling was used due to the fact that water damage (particularly rainfall) has been shown to be the most prominent cause of damage to earthen materials (Chiari et. al 1999). 50mL of water

was poured on each of the block surfaces a total of 3-4 times (4 times during the first cycle, 3 during each of the succeeding cycles) from a distance of 5cm.

5.3.3 Temperature (T) and Relative Humidity (RH) cycles

Unfortunately, the laboratory used during testing was not temperature controlled. Therefore, although certain RH values were attained in a sealed chamber (see *Table 5*), the RH fluctuated with changes in ambient temperature (AT). The sealed chamber was used in combination with saturated salt solutions to expose the plaster layers to elevated RH, in order to create a slightly decohesive surface, to which the paint layer would subsequently be applied.

The cycling described in the table below was used on the unpainted, plastered blocks, until the blocks were painted. Temperature (T) ranges are given for the range of temperatures measured on a given date (incident AT readings were taken with a psychrometer or thermometer, while the RH was recorded with a hygrometer). The blocks were then subjected to one final cycle of increased RH, before being allowed to set in the uncontrolled laboratory environment.

Table 1: Artificial Accelerated Deterioration of the Plastered Blocks

Date	RH (%)	AT (°C)*	Description
11/23/10	70	20-22	Exposed to 70% RH for 24 hrs
11/24/10	unk	60	Exposed to 60°C for 24 hrs
12/4/10-12/10/10	50**	17-26	Placed in desiccator
12/10/10-12/13/10	60-80	17-21	Removed from desiccator to photograph; poured 4 pours of 50mL deI water from 5cm away (poured into center); then returned to desiccator
12/13/10	37	22	Removed from chamber, 3 pours 50mL deI water 5cm from surface

Date	RH (%)	AT (°C)*	Description
12/13/10-12/14/10 (24hrs)	40	20-22	Exposed to ambient laboratory conditions for 24 hours before being returned to dessicator
12/14/10-12/15/10 (24hrs)	70-87	19-21	Returned to dessication chamber for 24 hours
12/15/10	50	23	Removed from chamber and exposed to 50% RH for several hours
12/15/10-12/16/10	85	20-23	Returned to dessicator for 24 hrs
12/16/10-12/18/10 (24hrs)	45	22-23	Removed from dessicator, placed in front of window to dry
12/18/10	60	20-22	Another aging cycle, 3 pours 50 mL deI water, 5cm from surface
12/18/10-1/23/11 (44 days)	35-70	20-23	

*AT and RH readings based on incident readings as well as readouts from an Onset HOBO U12 datalogger in the laboratory space, see Appendix 2 for graph of detailed readings from the datalogger.

**Readings in bold are incident readings taken while blocks were inside a desiccator.

5.4. Application of the consolidant

5.4.1. *CaLoSiL*

The consolidant applied to the blocks is commercially known as CaLoSiL, an alcohol-based plaster strengthener (which can also be used on stone or masonry) based on colloidal calcium hydroxide chemistries (see Appendix 8 for detailed description of properties). While CaLoSiL may be produced using ethanol, propanol or 2-propanol, here the product used was ethanol-based, as short-chain alcohols have been used successfully in creating stable nanoparticle dispersions (Ambrosi et al. 2001). As with the traditional $\text{Ca}(\text{OH})_2$ treatments, the consolidation mechanism of CaLoSiL is based on the formation of calcium carbonate by reaction with atmospheric carbon dioxide. According to the manufacturer, penetration depth depends upon method of application, mineralogical composition and surface properties, the porosity and

absorbency of the material being consolidated, its moisture content, as well as the T and RH of the environment. The manufacturers recommend applying CaLoSiL via dipping, injection, applying as a coating, or spraying, as was done here.

5.4.2. *Application Method*

Trials were carried out on blocks in order to determine the best method of application for the consolidant. Different methods were tested: application through brushing, poulticing, and spraying. Application of the consolidant via brushing involved applying the material using a saturated brush, applied through Japanese tissue paper (as described by Baglioni 2006).

Application via poultice, involved applying the consolidant by saturating the surface with a paper pulp poultice (Arbocel 200), which was then covered with cling film in order to maintain a moist surface. 5mL of CaLoSiL were applied per gram of Arbocel, with an additional 2mL of CaLoSiL added after the first half hour. The poultice was applied for approximately an hour (and re-wet with an additional application of the consolidant after the first half hour). For a description of the spray application, see below.

In these preliminary trials, the use of poultices caused an unacceptable whitening of the surface that was very difficult to eliminate, brushing caused slight whitening and removal of loose particles (through the mechanical action of the brush), with spraying causing no discernible whitening nor other negative effects (*Figure 3*). To avoid over-saturation of the surface and to better control the application of the consolidant a diluted version of CaLoSiL was used with a ratio of 1:1 per volume ethanol to CaLoSiL. Based on this preliminary testing, it was therefore

decided to consolidate the remainder of the blocks using an atomizer, to create a fine mist using CaLoSiL at a lower concentration.



Figure 3 (from left to right) Block 2 following spray application of pure CaLoSiL on the right (see light area, to the right of the red dotted line), and application of CaLoSiL diluted in ethanol (1:1) on the left; block 3 following test application of poultice (white area); and block 8 following brush application of CaLoSiL (visible on bottom of block), followed by the application of ammonium bicarbonate poultice (visible in upper portion) in an attempt to remove the white veil formed. Tidelines are the result of the “Surface Absorption Test” (see Section 5.5.1)

The blocks were sprayed from a distance of 10cm with the painted surfaces in a vertical orientation (*Figure 4*). The challenge with this method of application was in spraying the entire surface evenly without over-saturating the block. Owing to the small surface area of the block, acquiring consistent results, even with the controlled mist of the atomizer, proved incredibly difficult. As the T and RH can affect the penetration of the consolidant, these measurements were recorded. The RH was 50%, and the T 22°C during application.



Figure 4: Spray application of the CaLoSiL, on a painted test block, using an atomizer

5.5. Examination and Analysis:

Since there are no standard procedures for evaluating the effectiveness of surface treatments on earthen plasters, many experimental tests in the literature (Beas Guerrero de Luna 1993) are based on those of the American Society for Testing Materials (ASTM, www.astm.org). Unfortunately, many of these tests require the use of standardized machines (such as the vapor transmission, adhesion, and capillarity test), which were not available for this study.

With the time constraints for this particular experiment (which took place over a 9 month period), the overall number of samples was limited to allow for a more manageable test group. Many tests to evaluate consolidative efficacy on wall paintings are quite destructive and require sample quantities not always easily obtainable from historic/archaeological sites. It was felt that a focus on techniques that were minimally invasive and relatively non-destructive would not only allow for multiple tests to be implemented on the prepared samples, but would allow for the evaluation of techniques that might eventually be used as tests in the field. Initially, the

analytical techniques chosen for this study were therefore those generally available in an objects conservation laboratory. It was later decided that X-Ray Diffraction analysis and Scanning Electron Microscopy with Energy Dispersive X-Ray Spectroscopy might be most useful in identifying chemical transformations that occurred following treatment, particularly in order to determine the depth of the consolidant's penetration. The techniques ultimately chosen had varying degrees of success in analyzing the effectiveness of the consolidation treatment.

5.5.1. Surface Absorption Test

An absorption test (based on Teutonico 1988) was used to detect changes in the hygroscopic properties of the blocks after consolidation. The test was slightly altered to accommodate the sensitivity of the surface; while Teutonico suggests applying 1.5mL of water, this would have destroyed the painted surface completely. Instead, three drops of deionized water (at a speed of 3 drops per 43 seconds for the first round of testing, and 3 drops per 51 seconds for the second round of testing), totaling 0.15mL were applied to the block's surface via buret (environmental conditions were 30% RH at T 22°C during the first round of testing, and 53.2% RH at T 22°C for the second round of testing). Total absorption of the water was determined as the point at which the water was completely absorbed into surface (when the surface appeared matte again).

5.5.2. Scotch Tape Test

The cohesion test used is based on the modified method of the ASTM D4214-07 "Standard Test Methods for Evaluating the Degree of Chalking of Exterior Paint Films" used also by Ferron (2007). Here, a piece of Scotch tape (Scotch®Magic™ tape, the original, matte finish, invisible tape) was pressed onto the surface using enough finger pressure to remove all visible air bubbles

and make good contact between the tape adhesive and the surface. The tape was then peeled off in a single smooth motion and placed onto a white board for better visualization and evaluation. This was done before and after consolidation to evaluate changes in the surface cohesiveness. It was hoped that following consolidation an improvement in the cohesion of the surface would occur, which would be seen as a reduction of the particles pulled up by the tape.

5.5.3. pH Tests

pH tests were somewhat problematic due to the sensitivity of the surface, which eliminated the possibility of using a pH meter, as the amount of water required for the meter caused significant damage to the painted surface. Even the use of pH strips tended to lift the pigment from the surface. For this reason, readings were only taken with small strips toward the bottom edge of the painted surface of each block. De-ionized water was used to wet a small part of the surface of each block. Non-bleeding pH indicator strips (colorpHast) were first wet with de-ionized water and then pressed against the dampened surfaces (these indicator strips contain indicator dyes that are covalently bound to the reagent paper, so as not to transfer onto the surface being tested).

5.5.4. Visual Changes: Microscopy, Photography, Munsell Color Charts

The blocks were photographed (using a Nikon D80 Digital Single Lens Reflex camera) and color corrected (as described by Pozeilov 2008) before, during and after treatment. Images were taken of the paint layers using stereomicroscopy and overall images of the block surfaces were taken using a visible, diffuse lighting setup. Additionally, Munsell color charts were used in order to record the color of the painted surfaces before and after consolidation. Munsell Color charts were used to compare the hue, chroma and value of each of the respective surfaces before and after

consolidation (*Figure A3.2*). According to the Munsell system, *hue* is defined as the difference between one color and another, while *chroma* may be defined as the relative saturation that distinguishes a pure hue (higher chroma) from a gray shade (lower chroma), and *value* defines the relative addition of white to create a light value and black to create a dark one (Adobe 2000).

5.5.5. Cross-sections

Cross-sections were taken from each of the blocks by cutting a sample containing the pigment and plaster layers from the edge of each of the blocks with a scalpel. Two groups of samples were prepared: one group was left unmounted for examination and analysis using digital optical microscopy and variable pressure scanning electron microscopy (VPSEM), while another group of samples were prepared as polished cross sections. For the preparation of polished cross sections, the samples were submerged in a two-part epoxy resin (Buehler epoxicure epoxy resin and hardener) and allowed to set. Samples were taken from the blocks before consolidation, with another set of samples taken from the same region, after the consolidant had been applied and allowed to set for three weeks.

Once cured, the samples were polished using sandpaper (3M), followed by Micro-Mesh™ cushioned abrasives and polishing compounds (Leco microid diamond compound, 3microns and 1micron, respectively) in mineral spirits to avoid the dissolution of the paints in an aqueous medium. Mineral spirits were found not to affect the paint or earthen substrate and were therefore used to polish the unconsolidated samples. Consolidated samples were dry polished only (using Micro-Mesh™), so as to avoid the possibility of disturbing the applied consolidant.

5.5.6. Digital Microscopy

Unmounted stratigraphic samples were photographed on a VHX-1000 Keyence Digital Microscope. Images of the overall cross-section were taken at 100x magnification, while details of the interface between the paint and plaster layers were taken at 100x, 150x, and 200x magnification.

5.5.7. Variable Pressure Scanning Electron Microscopy (VPSEM)

The unmounted stratigraphic samples were further analyzed using the FEI Nova NanoSEM 230 field emission gun variable pressure scanning electron microscope, in order to examine intergranular consolidation at the high magnifications achievable on this microscope using a field emission gun for the electron source. The samples were examined at variable pressure so that no conductive coating was required over the surface. Images were taken using the secondary detector at three different locations and three different standard magnifications along the paint layer of each of the samples to facilitate comparison. Images at three different magnifications were taken at one other location along the interface between the paint layer and the substrate, as well as in the substrate layer. Polished cross-sections were also analyzed using the SEM's backscattered electron detector combined with Energy Dispersive X-ray Spectroscopy (EDS), to develop elemental maps of the Ca (indicative of the distribution of the $\text{Ca}(\text{OH})_2$ consolidant in the samples).

5.5.8. X-Ray Diffraction (XRD)

Samples were taken from the left side of the blocks of the uppermost paint and plaster layers. XRD analysis was used to analyze significant mineralogical changes in the clay plaster and paint

layers. As previously stated, it is possible that the clays may form slightly crystalline phases following consolidation, as studied by Elert et al. (2008), who found calcium silica hydrates similar to tobermorite and calcium aluminosilicates (Elert et al. 2008). XRD patterns were collected using a Rigaku R-Axis Spider with Cu-K(alpha) radiation target. The instrument was set to 50kV and 40mA with a 900 second exposure. Results were compared to the International Center for Diffraction Data (ICDD) using the program JADE v. 8.2 from Materials Data Inc.

Chapter 6. Results

6.1. Surface Absorption Test

The results for the surface absorption tests were inconclusive, with evaporation times showing no trend of decreasing or increasing following consolidation (see *Table 6.1* and Chart 6.1, below). It seems that this was dependent upon the block and the location where the tests were carried out. Reasons for these unexpected results are given in the Discussion (Chapter 7).

Table 2: Surface Absorption Test Results

Block	Evaporation Time (BT)	Evaporation Time (AT)
1	15.7s	25.3s
2	17.1 s	21.7s
3	15.0s	15s
4	46.8s	34.3s
5	45.6s	46s
6	47.4s	29.2s
7	6.4s	10.2s
8	16.8s	11.2s
9	5.8s	7.6s
10	58.8s	58.7s
11	50.7s	35.1s
13	58.7s	52.8s
14	105s	171s
15	95s	111s

Figure 5: Surface Absorption Test Results

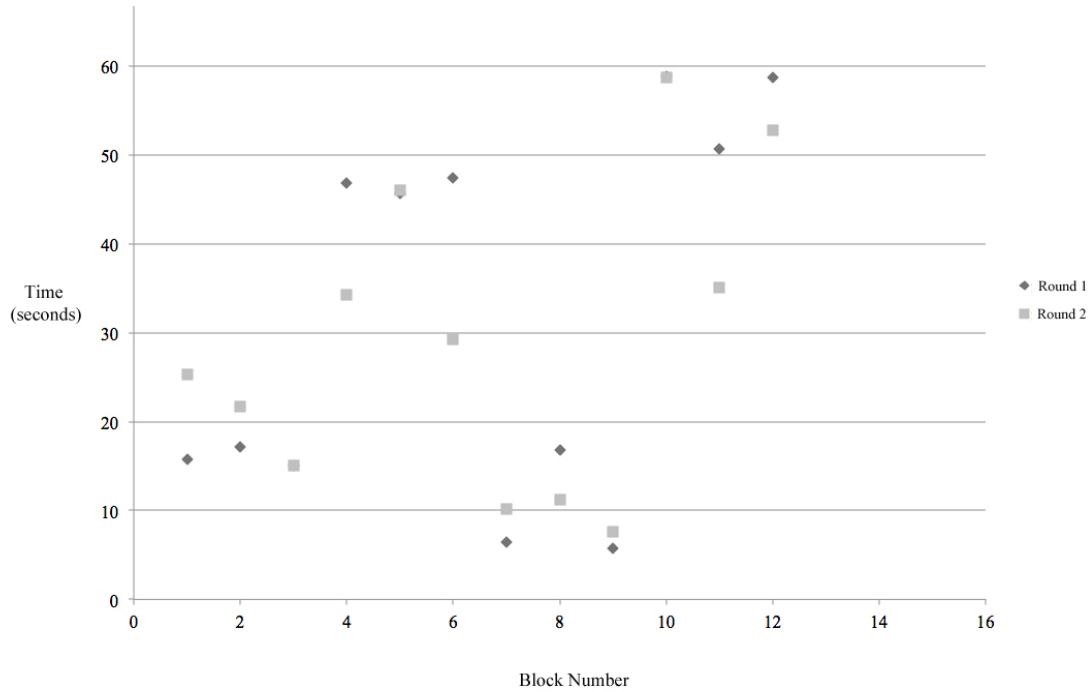


Figure 6 details of the results of the Scotch Tape Tests for two of the blocks, before and after treatment (note: block 4 contains paint without a cactus mucilage binder, while block 10 contains a cactus mucilage binder)

6.2. Scotch Tape Test

Scotch Tape Tests showed an improvement in the cohesion of the paint layer after consolidation, though the consolidation achieved seems to be superficial. While the Scotch Tape Test on the consolidated samples seems to have removed more material from the surface, there is a clear indication of pigment clustering suggesting strengthening of the bonds between the loose particles of the paint layer (*Figure 6 and Figure A3.1*).

6.3. pH Tests

The pH tests showed variable results, which may have been due to a number of factors (considered in Chapter 7). The blocks show a general increase in pH, with a slight increase in pH value seen for all of the blocks, including the untreated samples.

Table 3: Results of pH Tests

Block number	pH before consolidation	pH after consolidation
1	5.0	9.5
2	4.5	6.0
3	5.0	5.0
4	4.5	7.5
5	5.0	6.0
6	5.0	6.0
7	5.5	8.5
8	5.5	9.0
9	4.5	7.0
10	5.0	5.5
11	5.0	7.0
13	5.0	5.5
14	3.0	5.0
15	3.0	5.0

6.4. Visual Changes: Microscopy, Photography, Munsell Color Charts

There were no discernible visual changes between consolidated and unconsolidated surfaces when examined using stereomicroscopy. Diffuse light photography recorded the slight lightening of some of the blocks, with significant lightening occurring on blocks that were fully saturated with the consolidant solution (*Table A1.2; Figures A3.3 and A3.4*).

Using the Munsell Color charts to compare the blocks before and after treatment, samples had either lightened or showed no change in color. It should be noted that one of the control blocks (Block 6) although not consolidated, also showed a slight lightening, while some of the consolidated blocks showed no discernible shift in hue, value or chroma.

Table 4: Munsell Color Chart Readings

	Munsell Color BT	Munsell Color AT
Block 1	2.5YR 4.5/0	2.5YR 5.5/0
Block 2	2.5YR 4.5/0	2.5YR 5/0
Block 3	2.5YR 4.5/0	7.5YR 8/0
Block 4	2.5YR 3/0	2.5YR 3/0
Block 5	2.5YR 3/0	2.5YR 4/0
Block 6 (control)	2.5YR 3/0	2.5YR 3.5/0
Block 7	2.5YR 4.5/0	2.5YR 4.5/0
Block 8	2.5YR 4.5/0	7.5YR 5.5/0
Block 9	2.5YR 4.5/0	2.5YR 4.5/0
Block 10	2.5YR 3/0	2.5YR 3/0
Block 11	2.5YR 3/0	2.5YR 3.5/0
Block 13 (control)	2.5YR 3/0	2.5YR 3/0
Block 14	2.5Y 7.5/2	2.5Y 8/3
Block 15 (control)	2.5Y 7.5/2	2.5Y 7.5/2

6.5. Digital Microscopy

Results with digital microscopy, while quite subjective, indicated there may be some pore filling of the paint layer by the deposited calcium hydroxide, visible as increased whitening between the paint layer's granules, particularly at high magnification (200x) (*Figures A3.5 – A3.10*). It was difficult in many cases, however, to observe discernible differences between consolidated and unconsolidated samples.

6.6. VPSEM

Results from the VPSEM analysis were somewhat inconclusive. As with the digital microscope images, there seems to be some pore filling in the paint layer (*Figure 6 and Figures A3.11 and A3.12*).

EDS mapping did not show any elemental differences between the consolidated and unconsolidated samples. While an increase in calcium was expected in the consolidated samples, calcium was virtually absent in both (*Figures A3.13 and A3.14*).

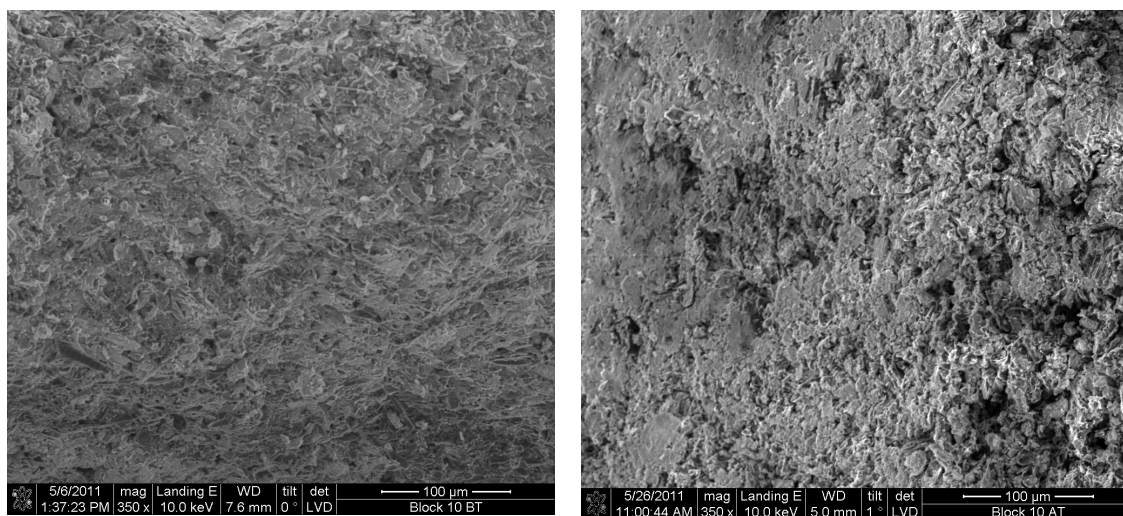


Figure 7: Scanning electron micrographs of the paint layer on Block 10, before (left) and after (right) treatment.

6.7. XRD

XRD analysis showed the possible presence of plombierite (a calcium silicate hydrate) on paint layers from the treated samples (*Figures A3.15–A3.20*). This is in line with previous studies that describe the formation of calcium silicate hydrates in the pozzolanic reaction which occurs between clay minerals and calcium silicate hydrates (Elert et al. 2008; Eades and Grim 1960). No discernible differences in mineralogical composition were detected in the samples taken from the plaster layers before and after consolidation.

Chapter 7. Discussion

7.1. Examining Effectiveness of the Consolidation Treatments

A discussion of the advantages and disadvantages of each method and technique chosen for this study (*Table A7.1*) is presented in this section.

7.1.1. Surface Absorption Test

The surface absorption tests were inconclusive. The blocks were originally painted in two different “batches” (with blocks 4-6 and 10-13 painted together, and 1-3 and 7-9 together). These “batches” responded differently to the absorption tests (with blocks 4-6 and 10-13 taking significantly longer to evaporate), indicating some sort of inconsistency between the two groups. This is inexplicable because the same amount (w% and v%) of pigment and binder was used on each group of blocks. This demonstrates the difficulties of creating standardized samples, even within such a small group. It was also, at times, difficult to discern at what exact point the water had completely evaporated, particularly because the surface had a slight sheen. Additionally, areas that were white due to consolidation and complete saturation of the paint layer (such as the

poultice region in block 8) seemed to respond differently to water. Although the water seemed to be absorbed more quickly, the drop did not disturb the surface as significantly and did not seem to penetrate the consolidated area. Finally, the somewhat uneven surfaces of the blocks were also problematic. In some areas the water drops pooled slightly, perhaps slowing the evaporation time, while in other cases the water rolled slightly toward the edge of the block, which seemed to lead to faster evaporation. In other words, this test did not provide a good qualitative analysis of the stability of the painted surface, and the quantitative results obtained were somewhat subjective, based upon when the block's surface "appeared dry."

7.1.2. Scotch Tape Test

The Scotch Tape Test seems to be one of the more straightforward, reliable tests for directly examining surface cohesion. It did, however, have its own limitations. The test relies upon the operator to apply even pressure across the surface of the block. It is possible that variation in pressure (and therefore in the tapes' adhesion to the surface) can vary across testers and experiments, even within the same trial.

All of the samples appeared to be slightly more decohesive at the end of the trial (including the control blocks). Of the two batches of blocks that were prepared at the same time, those prepared without the cactus binder (Blocks 10 and 11) showed an improvement in overall cohesiveness following consolidation, while those prepared with the cactus binder (Blocks 4 and 5) were ultimately less cohesive than the unconsolidated control (Block 6) (see *Figure 5* and *Figure A3.1, Appendix 3*). The overall tendency of the particles to adhere to one another following treatment (rather than lifting the fine, evenly distributed particles apparent before

consolidation (see *Figure 5* and *Figure 3.1, Appendix 3*) suggests that the consolidation was effective (providing a bond among the loose particles), however, overall consolidation would likely have been more effective if the solution had penetrated further, which would lessen the lifting of the surface paint layer.

7.1.3. pH Tests

As previously mentioned, pH tests were complicated by the sensitivity of the painted surfaces, which eliminated the possibility of using a pH meter. Unfortunately, pH paper strips are not as accurate as pH meter readings, and as colorimetric devices, are only able to offer semi-quantitative results (Tse 2007). Because the color change occurs within a range of pH, visual evaluation will at best provide an accuracy of 0.3-1pH unit (Lawn and Pritchard 2003). The variable results may have been due in part to this factor.

With the limitations of the paper pH strips in mind, the blocks showed a general increase in pH, although a slight increase in pH values was also seen in most of the unconsolidated control blocks (with time). This may be due to small inaccuracies from the pH paper strips, or reader error in interpretation. pH variations among the treated blocks could also be attributed to different levels of consolidant application. Additionally, in some cases, excess amounts of consolidant may have rendered the surface insoluble, making an accurate reading with the pH strips difficult to obtain. Block 3, for instance, was heavily consolidated, and a highly alkaline surface would thus be expected. The neutral pH reading, however, indicates that the strip may only have been measuring the pH of the deionized water used to wet the surface (as the surface layer may have become insoluble following carbonation).

7.1.4. Visual Changes: Microscopy, Photography, Munsell Color Charts

Despite the subjectivity inherent in the tests used to evaluate visual changes, they provided some useful findings, clearly demonstrating lightening in many cases. Regular, diffuse light photography captured the lightening of the blocks before and after treatment, making it clear that most of the blocks showed discernible whitening following consolidation. Digital microscopy seemed to capture an increase in whitening among the granular interstices of the layer, although this was difficult to discern in many cases. The Munsell color chart, which aimed to provide a system for accurately cataloging lightening and shifts in chroma on the painted surfaces, was also somewhat subject to user interpretation.

7.1.5. Scanning Electron Microscopy (SEM)

Scanning electron microscopy provided an excellent view of the intergranular structure of the pigment particles. Generally speaking, there did seem to be a slight “filling in” of the pigment layer before and after treatment. Unfortunately, it is impossible to say with certainty whether some of the changes visible on the blocks are due to differences within the paint layer itself, or the result of consolidation of the surface as different samples were used before consolidation and after for this examination. It does appear, however, that SEM can be used to image changes that occur on the surface (morphology and topography) and the interfaces of the paint layer(s). It would have been more effective, however, if the exact same region was imaged before and after treatment.

SEM-EDS showed great promise as a technique that would be able to image the extent of the consolidant penetration. It was hoped that the analysis of a cross-section would reveal the

calcium (resulting from the applied calcium hydroxide solution) present, but alas no noticeable difference between the treated and untreated samples was detected. This may suggest that the deposited calcium on the sample remains below 1 wt%, which is below the detection limit of the detector. In the future, micro x-ray fluorescence spectroscopy (μ XRF) with sensitivity at trace quantities could be used to supplement the investigations, while additional samples would need to be analyzed to confirm the reproducibility of the results.

7.1.6. X-Ray Diffraction (XRD)

X-ray diffraction provided the most reliable data for identifying transformations that occurred to the paint layer following consolidation. As previously mentioned, this technique has been successfully used in other studies to identify the transformations that occur in clay minerals following alkaline consolidation (Elert et al. 2000). Apparent transformations in samples from the painted surface suggest that the calcium hydroxide was able to change the structure of the clay minerals to form a calcium silicate hydrate network. The lack of any transformation in the plaster layer directly below the paint indicates that the consolidant did not penetrate deeply enough to reach the plaster layer below.

7.2. Assessment of Experimental Methodology

The development of experimental laboratory trials and painted earthen architectural facsimiles for testing posed a number of difficulties. Developing blocks that were sufficiently decohesive to allow the efficacy of the consolidant to be clearly demonstrated was the first major challenge encountered. Although a number of different ratios of constituent components were tested prior to the development of the blocks, it was (1) very difficult to create sufficiently decohesive blocks

for testing (even with artificial accelerated deterioration) without deviating too far from the traditional adobe blocks of the Moche culture that we were attempting to mimic; and (2) it was very difficult to obtain consistent and reproducible results for a number of blocks even when all parameters used were exactly the same. While the blocks were sensitive to extreme exposure to water, it was difficult to achieve adequate deterioration and decohesion, while maintaining relative uniformity among the samples. A great deal of time was devoted to artificial accelerated aging tests. In retrospect, due to the fact that the consolidant did not penetrate to the plaster or adobe layers, it may have been useful to devote more time to the aging of the paint layers as well, though the paint layer seemed quite decohesive prior to testing. The fluctuations in RH in the laboratory workspace may have caused an unintentional deterioration as they acted upon the already fragile paint layer. These same fluctuations, however, are problematic in terms of creating reproducible results, particularly as T and RH can affect not only the application of the consolidant but the results of tests such as the absorption test.

The challenges encountered in finding techniques to accurately identify and quantify changes following consolidation cannot be understated. The inherent nature of earthen architectural samples makes the application of many techniques for traditional wall painting and other cementitious materials analysis slightly problematic. Due to the aging of the plaster layer, the plaster separated from the block substrate during sampling, and the paint had a tendency to not only powder and crumble, but also separate from the plaster below. This made the acquisition of stratigraphic samples quite difficult. While the use of thin sections may have been helpful for the analysis of the porosity of the sample before and after treatment, it was not possible to acquire sufficiently large samples, given these issues. The fragility of the paint surface itself also made

traditional tests to evaluate porosity extremely difficult, as any water applied to the surface of the paint altered the structure, while water applied to the block or plaster tended to disintegrate the samples. Focusing on developing and adapting techniques to determine consolidative efficacy would therefore be an important area for further research (see *Section 8.2*). Indeed, it seems that identification of and access to suitable methods of evaluation would be critical for future work.

Chapter 8. Conclusions

8.1. Preliminary Results

The preliminary results of this study suggest that more tests should be conducted in order to have a better understanding of the application of calcium hydroxide nanoparticle dispersion in the consolidation mechanisms and performance of earthen polychrome surfaces. One of the primary concerns with this treatment is how to control the whitening that occurred on many of the consolidated blocks. The difficulty in achieving uniform applications using the spray application technique is another problem that cannot be ignored and more research on the spray deposition in such applications is required. The range of whitening among the samples (and even on the surfaces of single blocks) demonstrates that different amounts of the consolidant seem to have been applied to each, despite the care taken to apply the consolidant mist at the same distance and pressure. This variability is problematic in terms of analyzing the results using small samples, which may not be representative of the consolidant application on the entire surface. Additionally, if the blocks were particularly subject to whitening after a certain “saturation point” (as seems to be the case here) controlling this application would be especially important.

Due to the sensitivity of the paint surface testing the efficacy of the mineral nanoparticle consolidant proved difficult. The absorption tests were inconclusive, while the Scotch Tape Tests did show consistent results for the success of the treatment. More testing regarding methodology of application, concentration of the material and number of treatments would need to be carried out in order to achieve statistically viable results and to confirm the usefulness of the treatment. More work should be done to reach a more definitive conclusion regarding the appropriateness of this technique for the consolidation of clay-painted earthen surfaces.

8.2 Future Work

In conclusion, further work should be carried out with a variety of different parameters considered. With more time, more thorough accelerated deterioration of the painted samples, both before and after treatment could be carried out. Creating more decohesive painted surfaces might allow for better eventual analysis of the consolidative efficacy of the solution. Eventually, it might be ideal to test the effectiveness of the consolidant on blocks exposed to an outdoor environment, in order to mimic the actual exposure experienced by Moche wall paintings (perhaps under partial cover, due to the surfaces' extreme sensitivity to water). Simultaneous testing on selected areas on original wall paintings would also provide a 'reality check' and will help establish the validity of the laboratory testing.

While XRD was able to successfully identify the transformation that had occurred in the top layers of the blocks, the use of additional techniques that will analyze depth of the consolidant penetration will need to be investigated. Tests such as bulk indentation to measure mechanical strength and porosity measurements should also be implemented in addition to the

Scotch Tape test and the absorption test, in order to provide more information regarding the effectiveness of the consolidation treatment.

A larger group of test block samples would also be ideal in the next experimental campaign. This would allow for the creation of statistically viable results, while also providing a better understanding of some of the observed phenomena, such as in the Scotch Tape tests. The use of more tests would also be possible with a larger group of samples, since destruction of the blocks (partial or total) would not be problematic. Tests such as those for water resistance, vapor transmission, and capillarity could be especially useful in demonstrating the effects of the calcium hydroxide nanoparticles on the blocks and their painted surfaces. It is possible, however, that other less destructive tests might need to be pursued, due to the sensitivity of the painted surfaces.

Finally, with more time and a larger experimental design, different variables could be considered. While application using a spray technique is ideal for many reasons (most notably, its ability to be applied quickly on a large scale), different concentrations of the consolidant solution are worth considering. Varying the distance at which the consolidant is applied could also be considered. Mockups could be made of simple painted surfaces in order to experiment with some of these variables before applying them to the final earthen architectural blocks. The manufacturers also recommend the addition of acetone or pentane to increase penetration, which could also be more formally evaluated. The use of a solvent that evaporates more slowly (such as 2-propanol as opposed to ethanol) may help to decrease whitening and further penetration of the dispersion as well. The comparison of CaLoSiL to other commercially available mineral nanoparticle treatments, such as Nanorestore, could also be considered.

Appendix 1: Tables

Table A1.1: Pigments analyzed in the literature for Moche painted surfaces

Author	Reds	Yellows	Greens	Blue	Blacks	Whites	Technique used for ID
Argumendo (1986)	Hematite	Ochre	Blue and yellow ochre	Gray clay with bluish tone	charcoal	limestone	Unknown
Bonavia (1985)	Hematite	Iron oxide			Magnetite	Limestone	“analysis requested by author”
Casoli et al. (2000)	Hematite	Ochre, goethite		No certain identification	Carbon	Calcite	X-ray powder diffraction (XRD)
Kakoulli (1997)	Red ochre	Yellow ochre, goethite			Charcoal	Kaolinite and calcite	Binocular microscopy, Polarized light microscopy (PLM), FTIR
Kroeber (1930)	Earth	Earth		Dilution of black with white	Charcoal	Plaster	Postulation
Scott et al. (1998)	Hematite	yellow ochre (possible)	Chrysocolla (possible)	Charcoal and calcite (possible)	Charcoal	Calcite	PLM, powder XRD, XRF
Uceda et al. (1993)	Red ochre	Yellow ochre			Iron oxide heated to 600°C	Chalk	Unknown

Table A1.2: Descriptions of consolidation application on test blocks

Block	Binder	Consolidated?
1	Cactus mucilage binder	Heavy spray at 5cm
2	Cactus mucilage binder	Sprayed right side; slight whitening at 10cm; sprayed Left side with 7.5%
3	Cactus mucilage binder	Tested with poultice and 7.5%, 15%; no noticeable difference (cleaned 7.5% etOH, no noticeable difference)
4	Cactus mucilage binder	Surface completely saturated; whitening (slight) visible; swabbed with etOH (<i>not</i> effective)
5	Cactus mucilage binder	Surface completely saturated; whitening (slight) visible; swabbed with etOH (<i>not</i> effective)
6	Cactus mucilage binder	Control sample (left unconsolidated)
7	Pigment only	Not entirely uniform application; <i>slight</i> whitening visible, swabbed with etOH (<i>not</i> effective)

Block	Binder	Consolidated?
8	Pigment only	Tested brushing on surface and ammonium bicarbonate surface (extensive whitening, poultice ineffective in reducing whitening)
9	Pigment only	Not entirely uniform application; <i>slight</i> whitening visible, swabbed with etOH (not effective)
10	Pigment only	Surface completely saturated; whitening visible
11	Pigment only	Surface completely saturated; whitening visible (except lower left corner)
12	Pigment only	Control sample (left unconsolidated)
14	Plaster only	Surface seemed saturated; no apparent whitening
15	Plaster Only	Control sample (left unconsolidated)

Appendix 2: Experimental

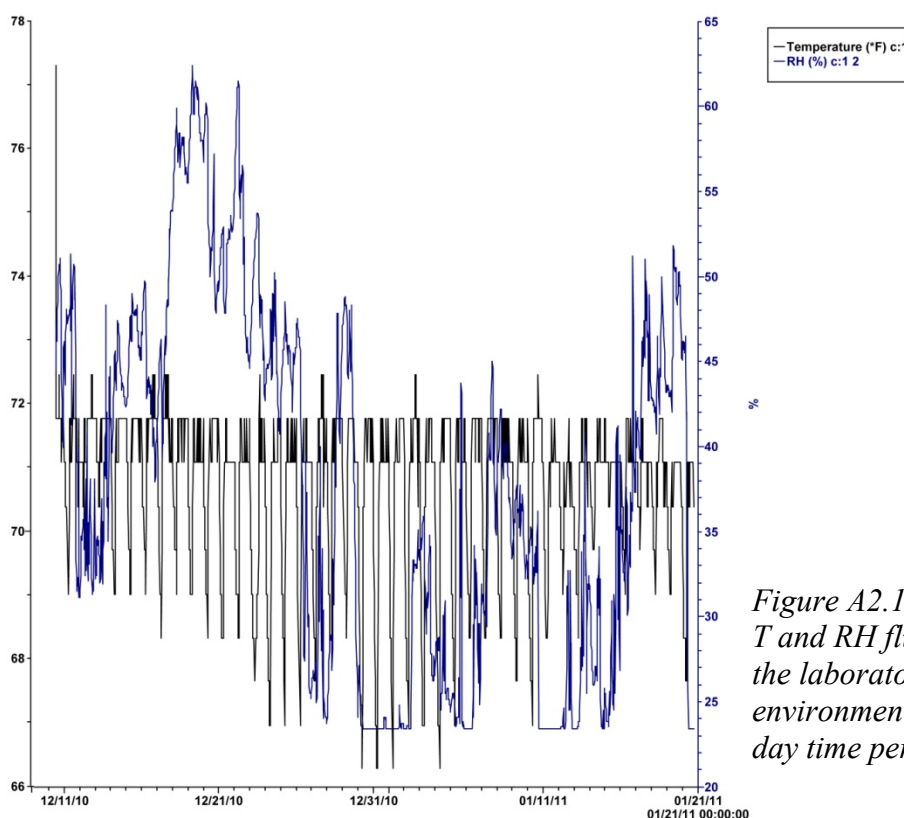


Figure A2.1 Graph of the *T* and *RH* fluctuations in the laboratory environment over a 40-day time period

Appendix 3: Results

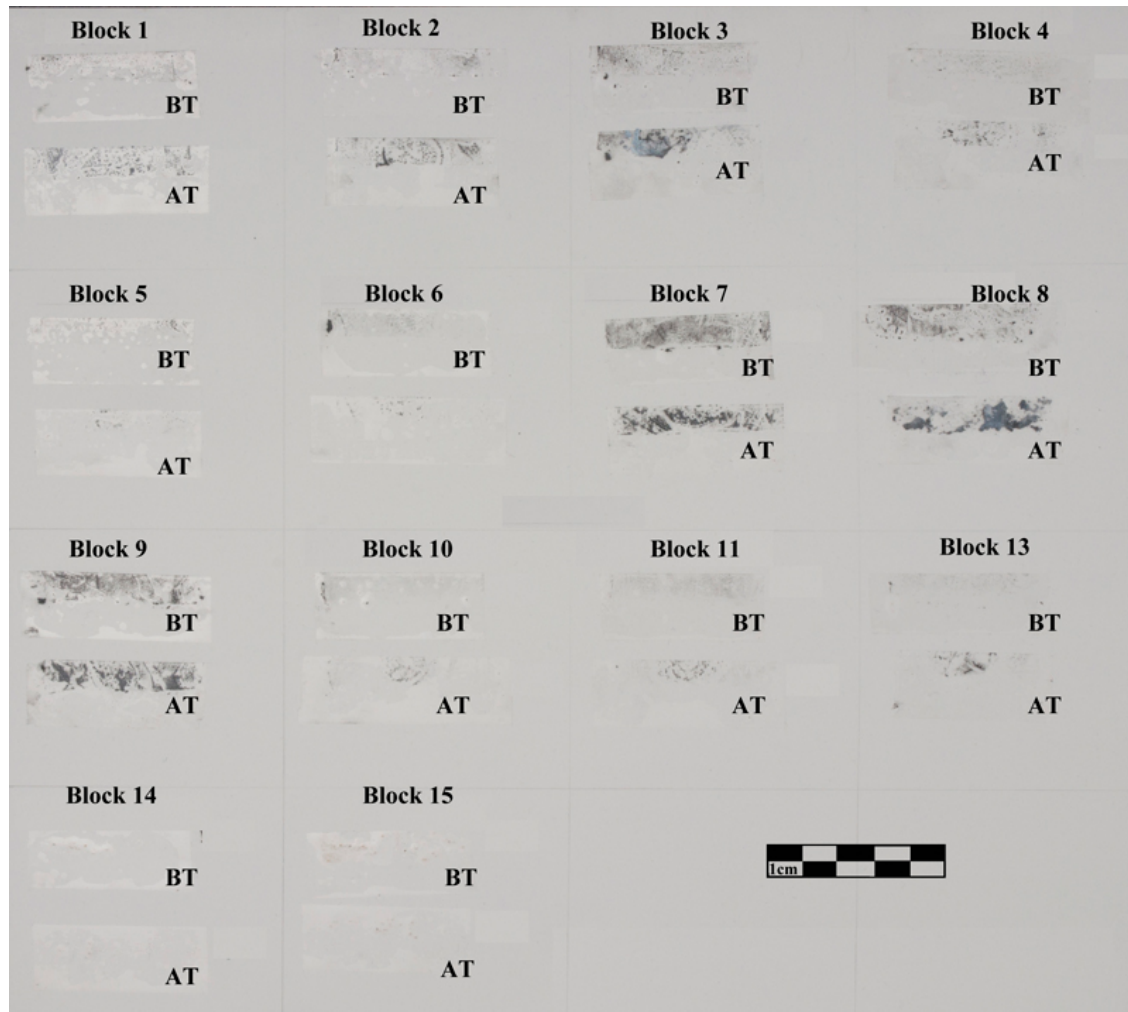


Figure A3.1 Results of the Scotch Tape Tests

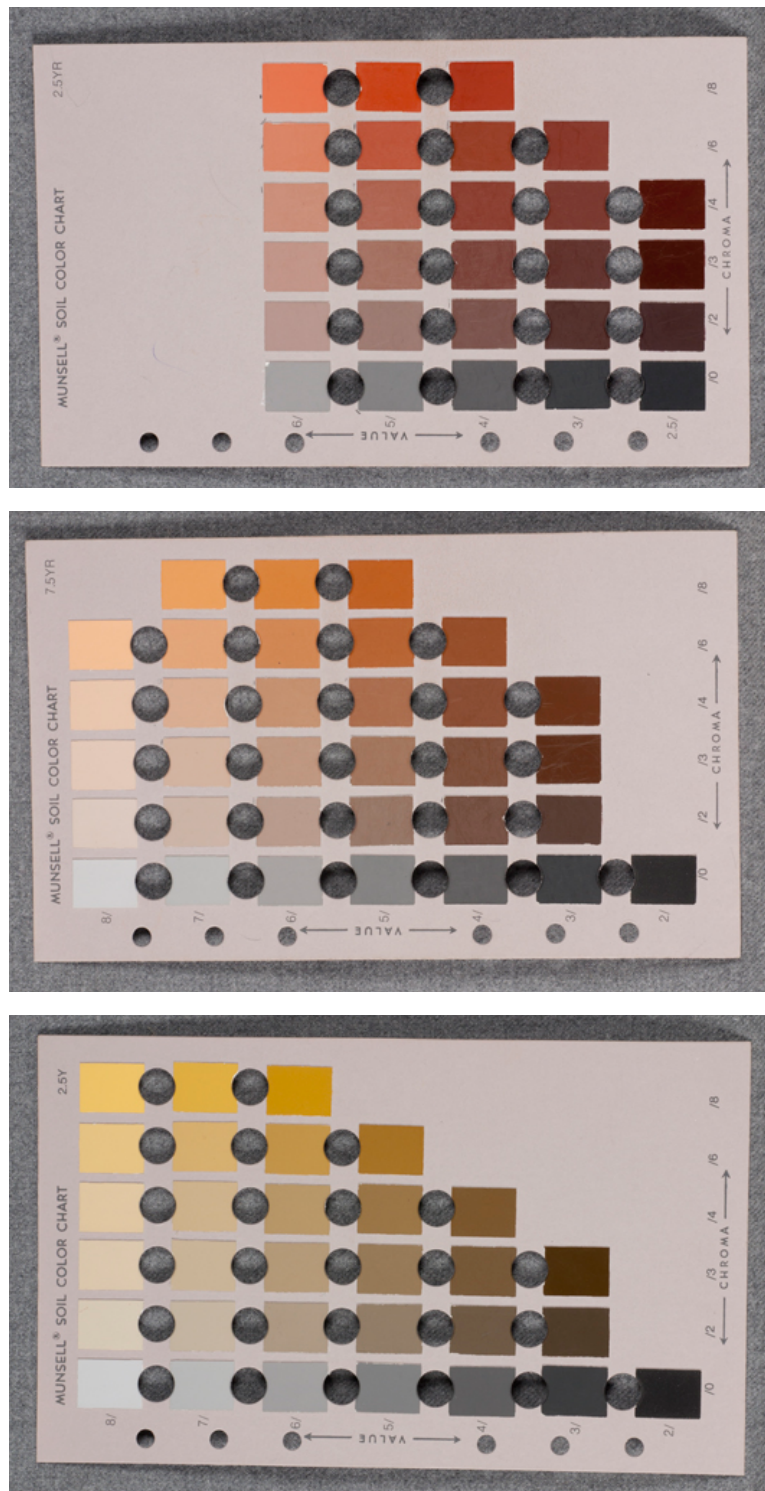


Figure A3.2 Munsell soil charts for comparison. Each of the blocks either maintained the same value/chroma after treatment, or showed some amount of lightening



Block 1 BT



Block 2 BT



Block 3 BT



Block 4 BT



Block 5 BT



Block 6 BT



Block 7 BT



Block 8 BT



Block 9 BT



Block 10 BT



Block 11 BT



Block 13 BT



Block 14 BT

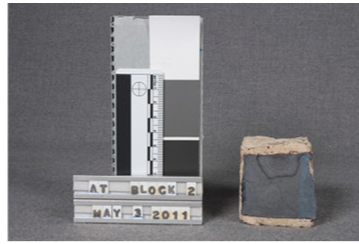


Block 15 BT

Figure A3.3: Sample blocks before treatment



Block 1 AT



Block 2 AT



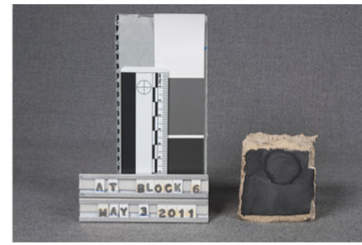
Block 3 AT



Block 4 AT



Block 5 AT



Block 6 (control)



Block 7 AT



Block 8 AT



Block 9 AT



Block 10 AT



Block 11 AT



Block 13 (control)



Block 14 AT



Block 15 (control)

Figure A3.4 Sample blocks, following consolidation (note that blocks 6, 13, and 15 were left unconsolidated as control samples)

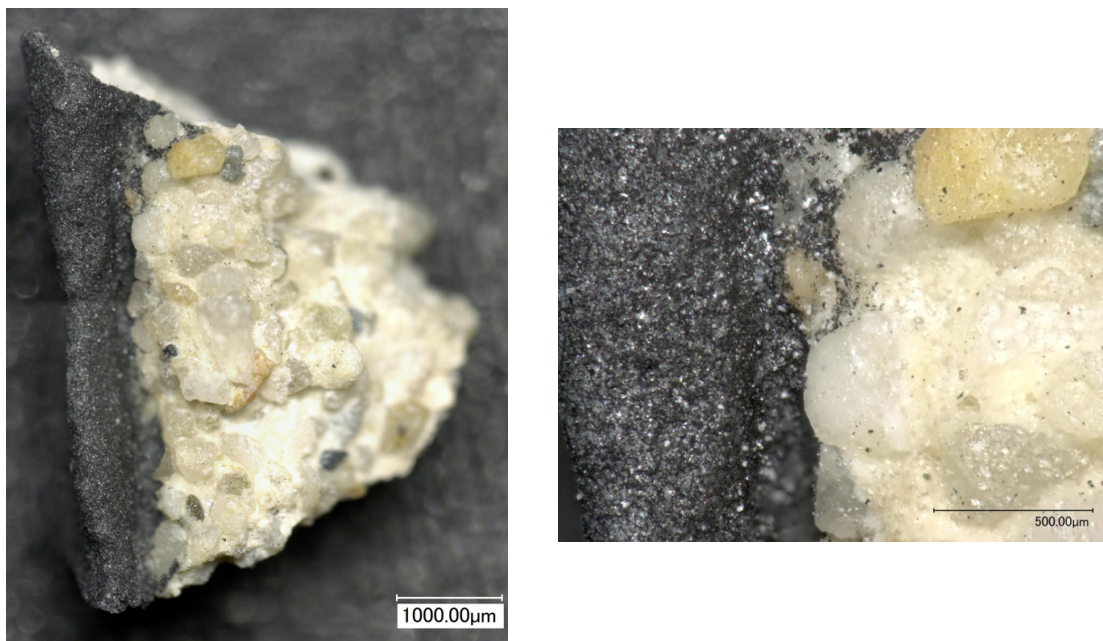


Figure A3.5 Digital micrograph of block 4, before treatment (image on left was taken at 100x, image on right, 200x)

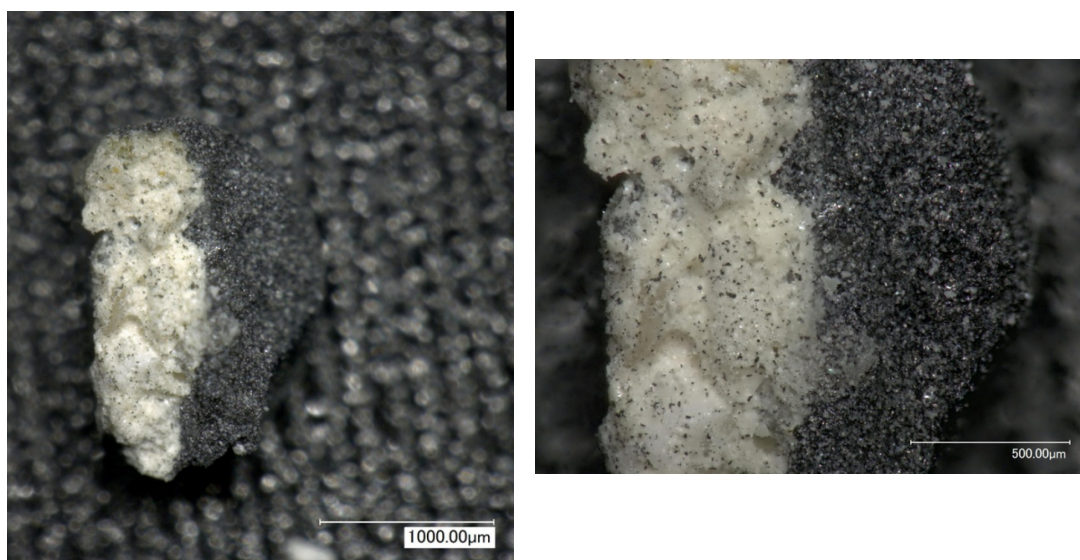


Figure A3.6 Digital micrograph of block 4, after treatment (image on left was taken at 100x, image on right, 200x)

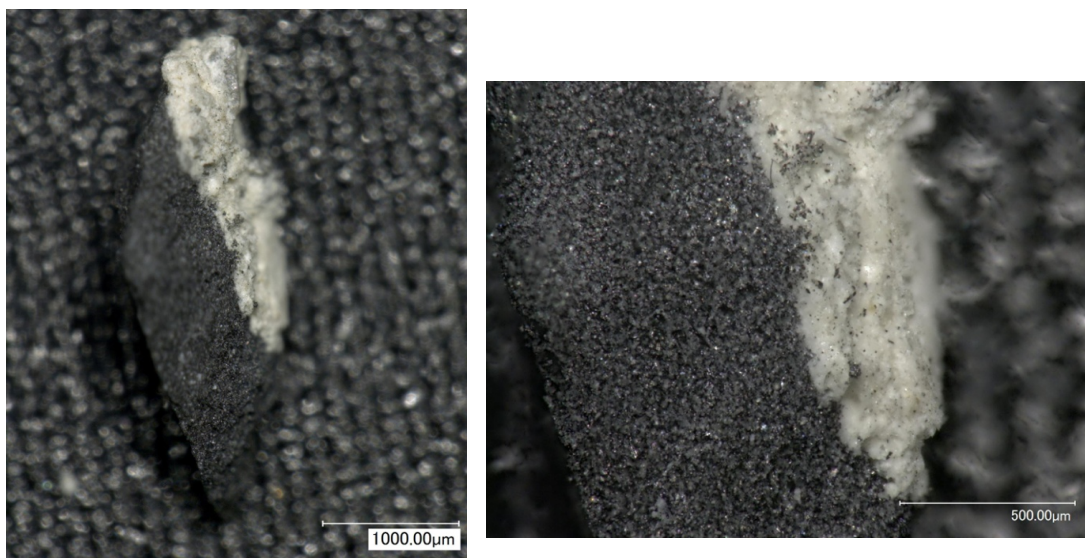


Figure A3.7 Digital micrograph of block 10, before treatment (image on left was taken at 100x, image on right, 200x)

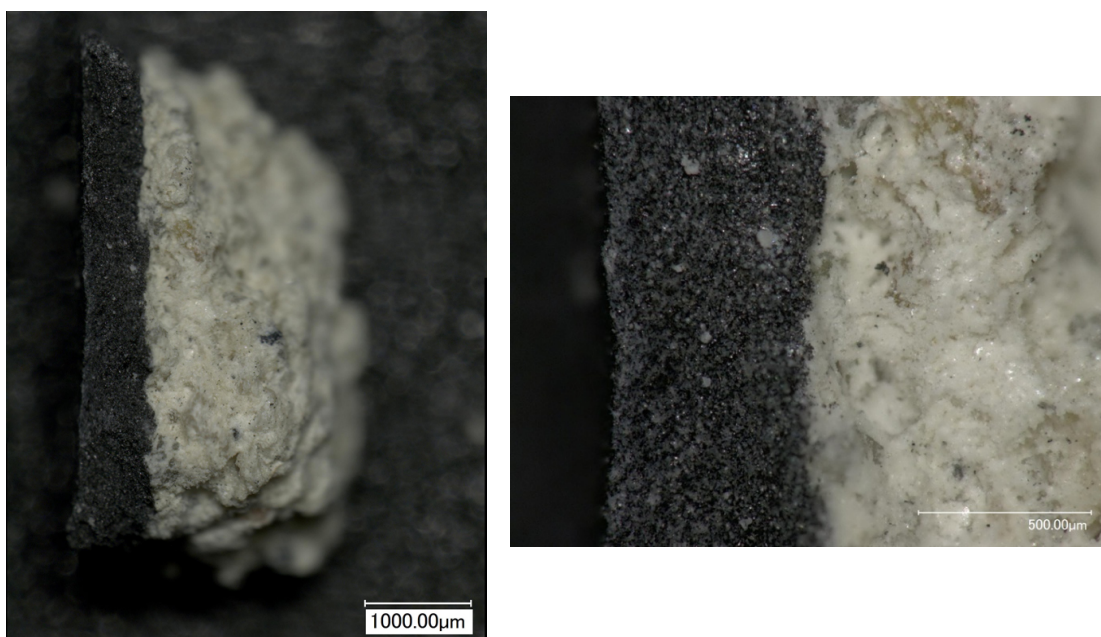


Figure A3.8 Digital micrograph of block 10, after treatment (image on left was taken at 100x, image on right, 200x)

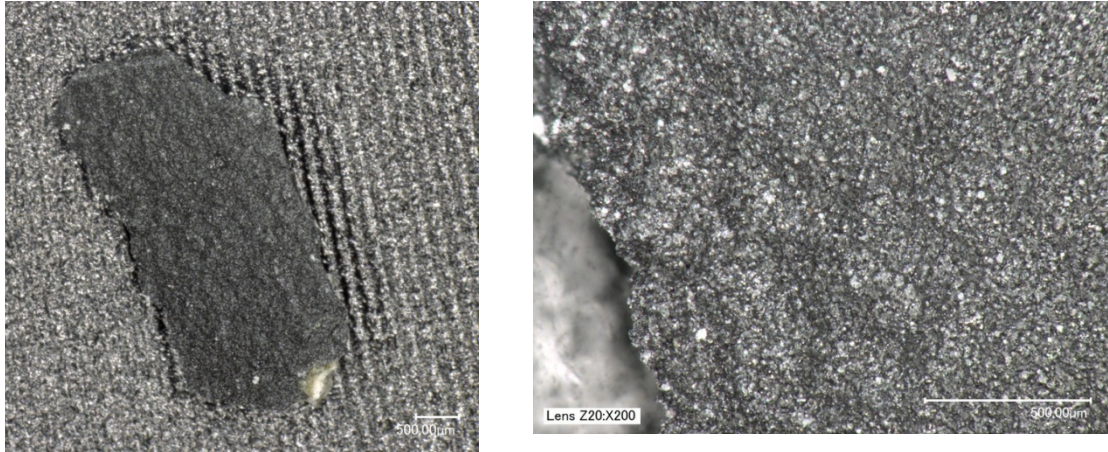


Figure A3.9 Digital micrograph of block 10, before treatment (image on left was taken at 100x, image on right, 200x)

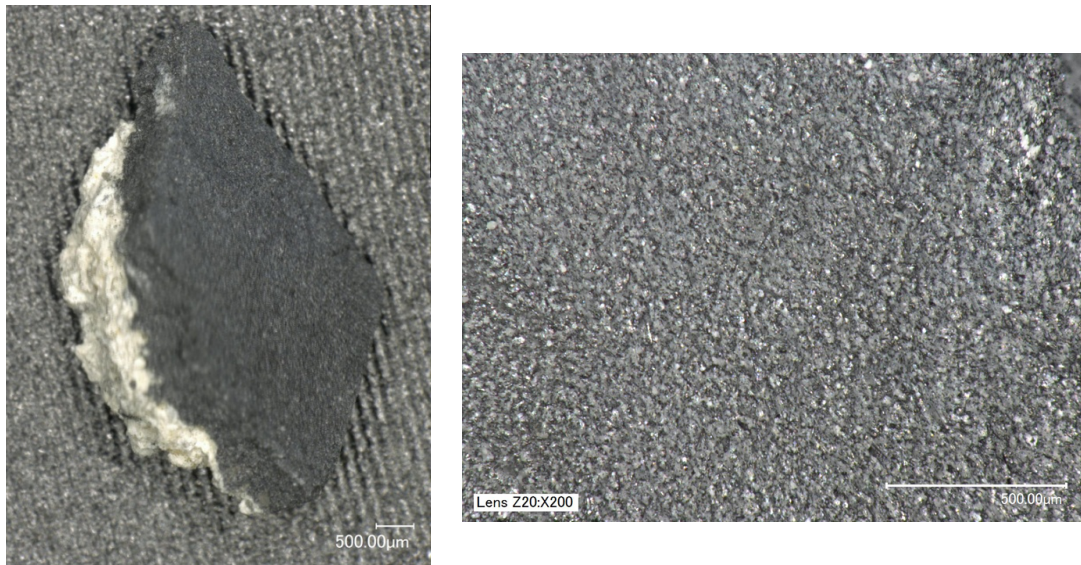


Figure A3.10 Digital micrograph of block 10, after treatment (image on left was taken at 100x, image on right, 200x)

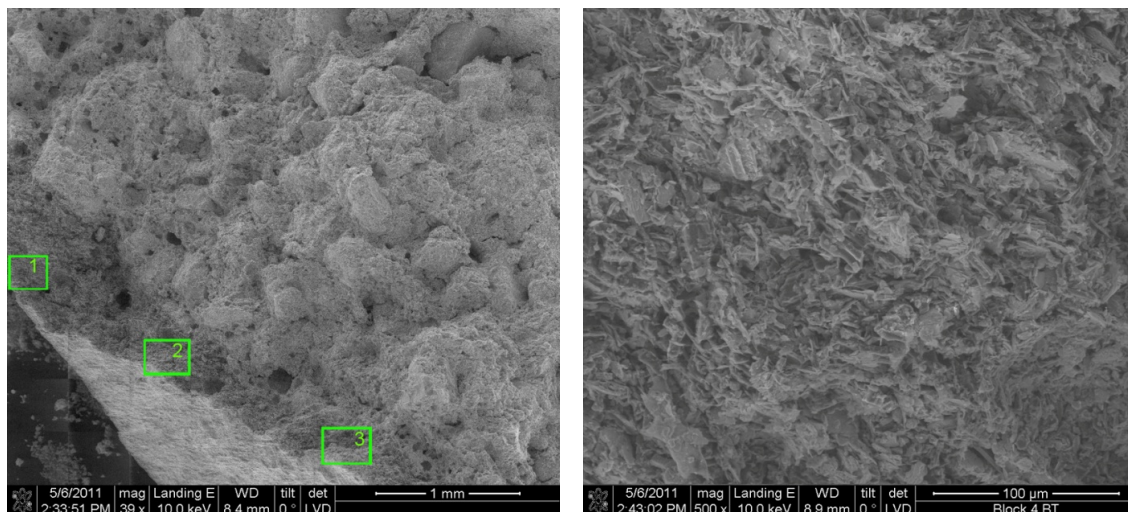


Figure A3.11 Scanning electron micrograph of block 4 before treatment. The image on the left highlights the regions of the paint layers imaged, the image on the right shows a representative micrograph, of area 2

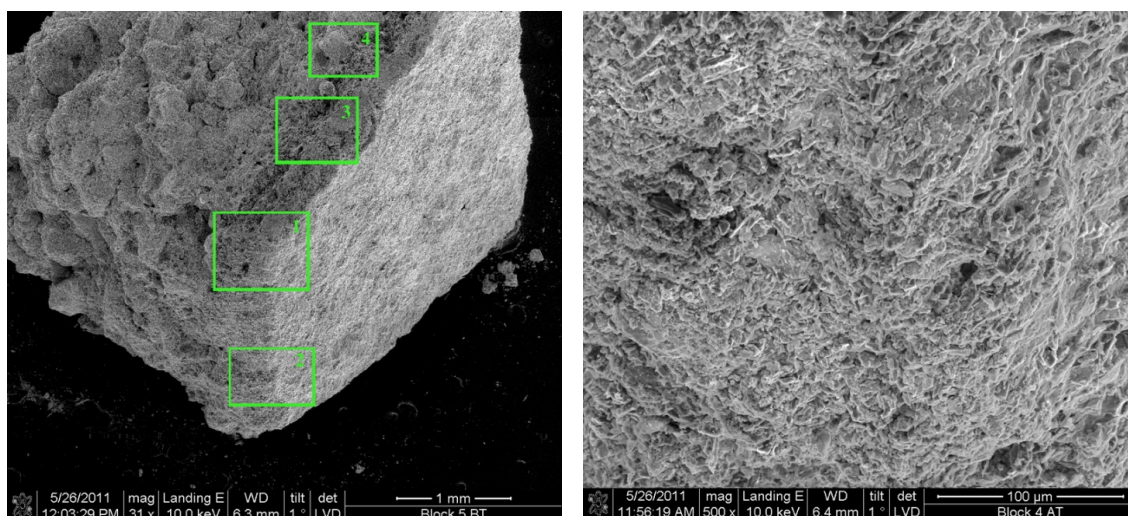
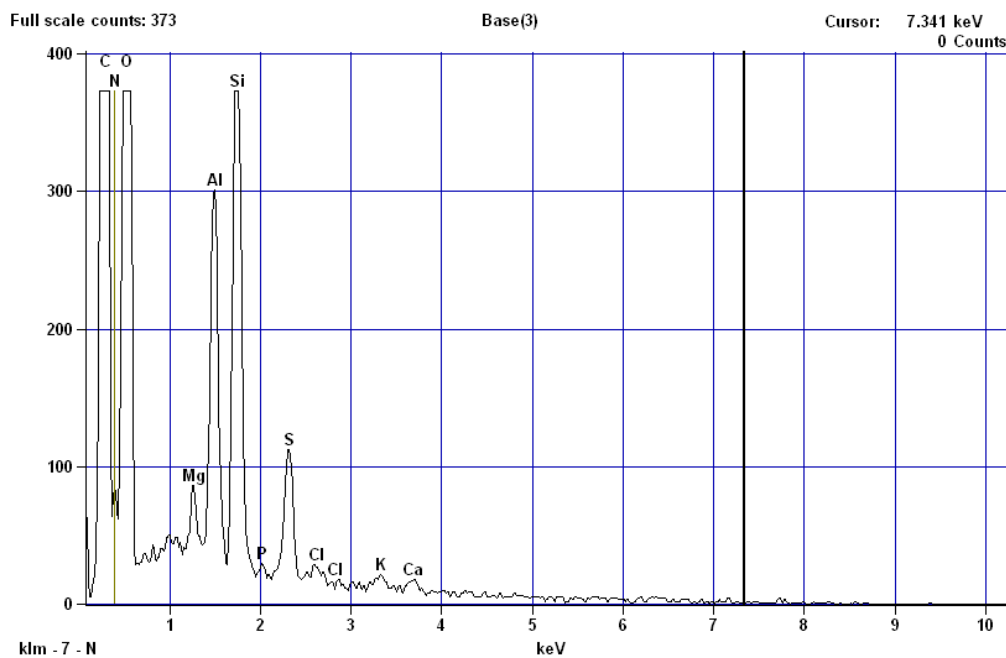
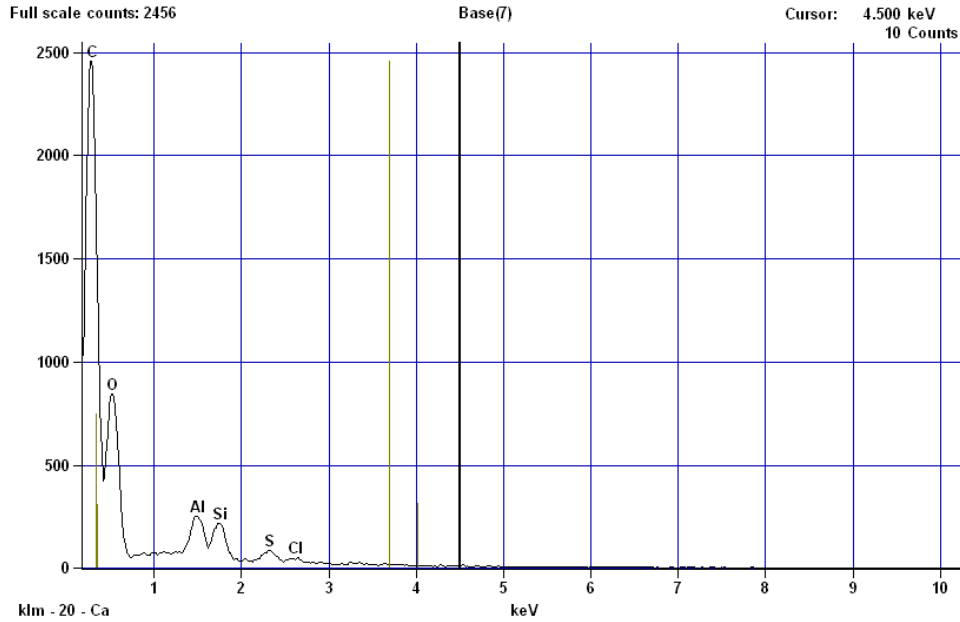


Figure A3.12 Scanning electron micrograph of block 4 after treatment. The image on the left highlights the regions of the paint layers imaged, the image on the right shows a representative micrograph, of area 2



<i>Element</i>	<i>Net</i>	<i>Int.</i>	<i>ZAF</i>	<i>Norm.</i>	<i>Norm.</i>	<i>Atom %</i>
<i>Line</i>	<i>Counts</i>	<i>Cps/nA</i>		<i>Wt. %</i>	<i>Wt. % Err</i>	
<i>C K</i>	17621	734.208	1.911	55.75	+/- 0.48	65.07
<i>N K</i>	411	17.125	5.189	3.93	+/- 1.65	3.93
<i>O K</i>	9677	403.208	3.027	29.40	+/- 0.50	25.76
<i>Mg K</i>	332	13.833	1.351	0.33	+/- 0.04	0.19
<i>Al K</i>	2325	96.875	1.288	2.62	+/- 0.13	1.36
<i>Si K</i>	3865	161.042	1.215	4.83	+/- 0.15	2.41
<i>P K</i>	29	1.208	1.247	0.05	+/- 0.05	0.02
<i>S K</i>	1119	46.625	1.193	1.89	+/- 0.13	0.83
<i>Cl K</i>	159	6.625	1.243	0.33	+/- 0.06	0.13
<i>K K</i>	126	5.250	1.234	0.36	+/- 0.07	0.13
<i>Ca K</i>	144	6.000	1.211	0.51	+/- 0.09	0.18
<i>Total</i>				100.00		100.00

Figure A3.13 Spectrometry readings from SEM-EDS analysis on Block 5, before treatment



<i>Element</i>	<i>Net</i>	<i>Int.</i>	<i>ZAF</i>	<i>Norm.</i>	<i>Norm.</i>	<i>Atom %</i>
<i>Line</i>	<i>Counts</i>	<i>Cps/nA</i>		<i>Wt.%</i>	<i>Wt.% Err</i>	
<i>C K</i>	13915	579.792	2.028	58.55	+/- 2.94	68.19
<i>O K</i>	8127	338.625	2.955	30.08	+/- 0.78	26.30
<i>Al K</i>	2937	122.375	1.284	4.11	+/- 0.28	2.13
<i>Si K</i>	2652	110.500	1.222	4.15	+/- 0.17	2.07
<i>S K</i>	1028	42.833	1.194	2.16	+/- 0.16	0.94
<i>Cl K</i>	365	15.208	1.245	0.95	+/- 0.15	0.37
<i>Total</i>				100.00		100.00

Figure A3.14 Spectrometry readings from SEM-EDS analysis on Block 5, after treatment

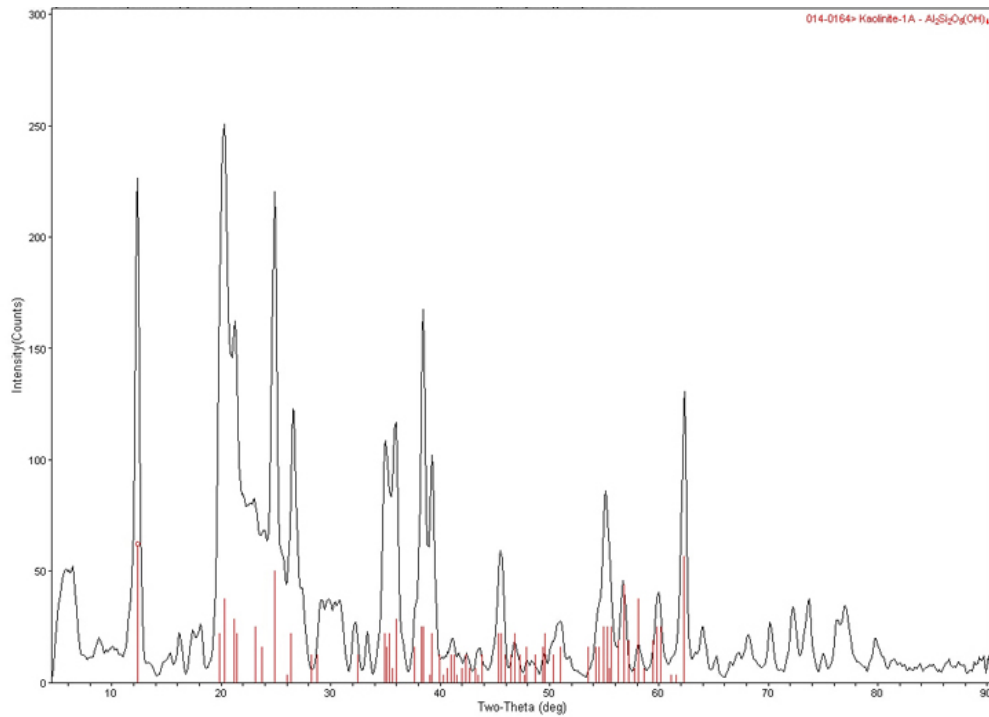


Figure A3.15 X-ray diffraction reading from the paint layer of Block 5, before treatment, showing kaolinite, the main clay component of the paint layer

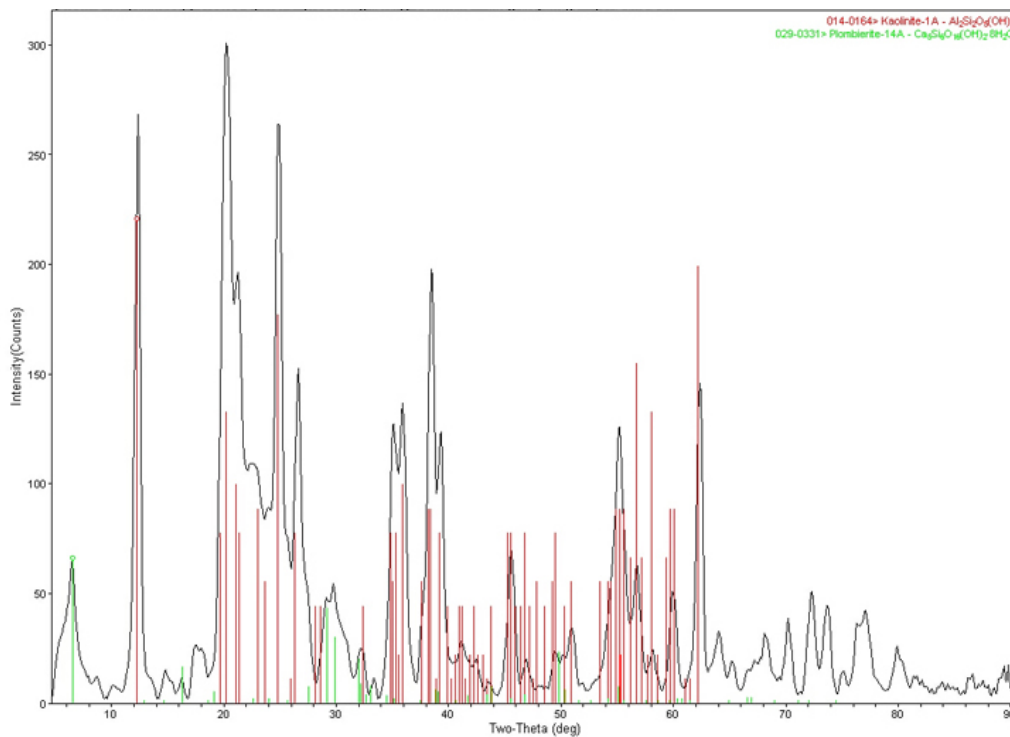


Figure A3.16 X-ray diffraction reading from the paint layer of Block 5, after treatment, showing kaolinite, and the formation of plombierite following consolidation

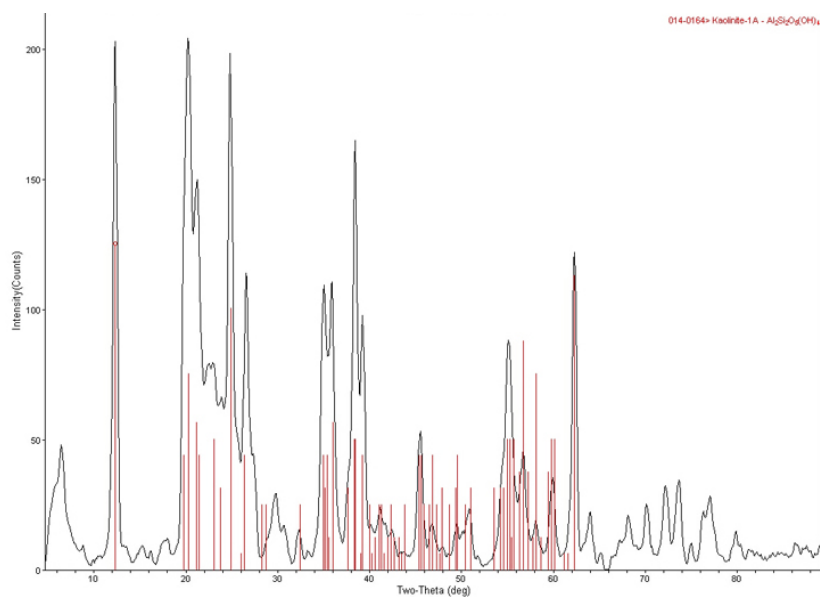


Figure A3.17 X-ray diffraction reading from the paint layer of Block 10, before treatment, showing kaolinite, the main clay component of the paint layer

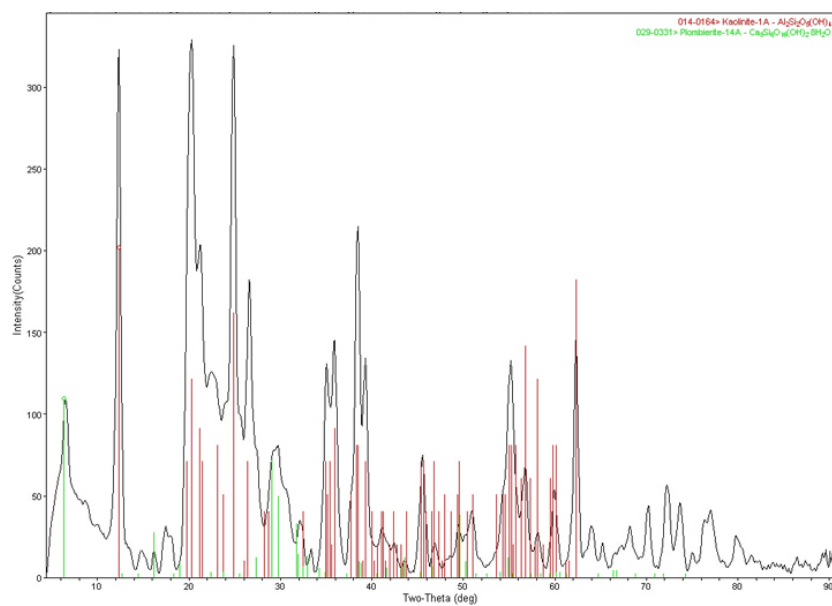


Figure A3.18 X-ray diffraction reading from the paint layer of Block 10, after treatment, showing kaolinite, and the formation of plombierite following consolidation

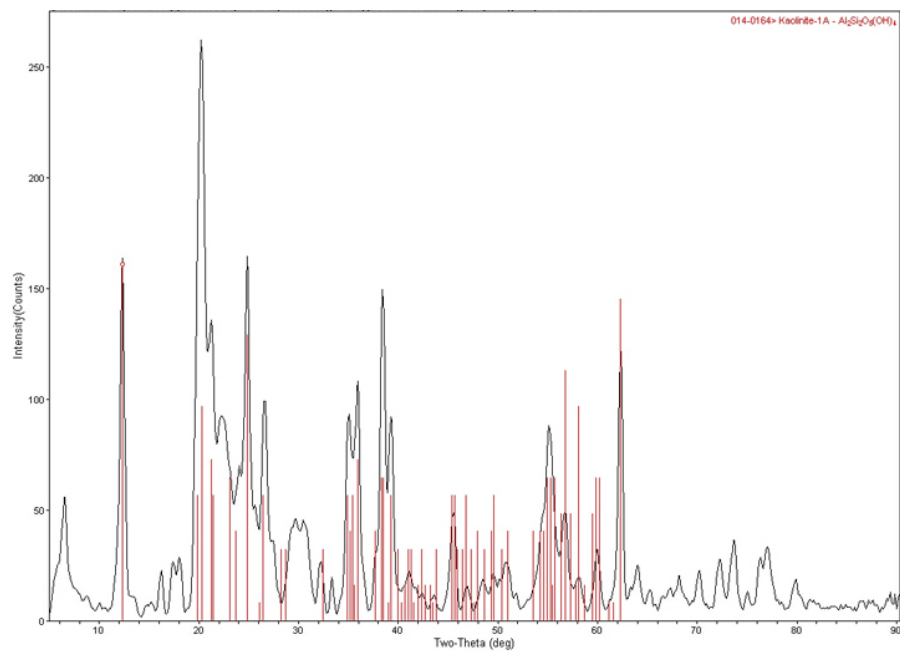


Figure A3.19 X-ray diffraction reading from the paint layer of Block 11, before treatment, showing kaolinite, the main clay component of the paint layer

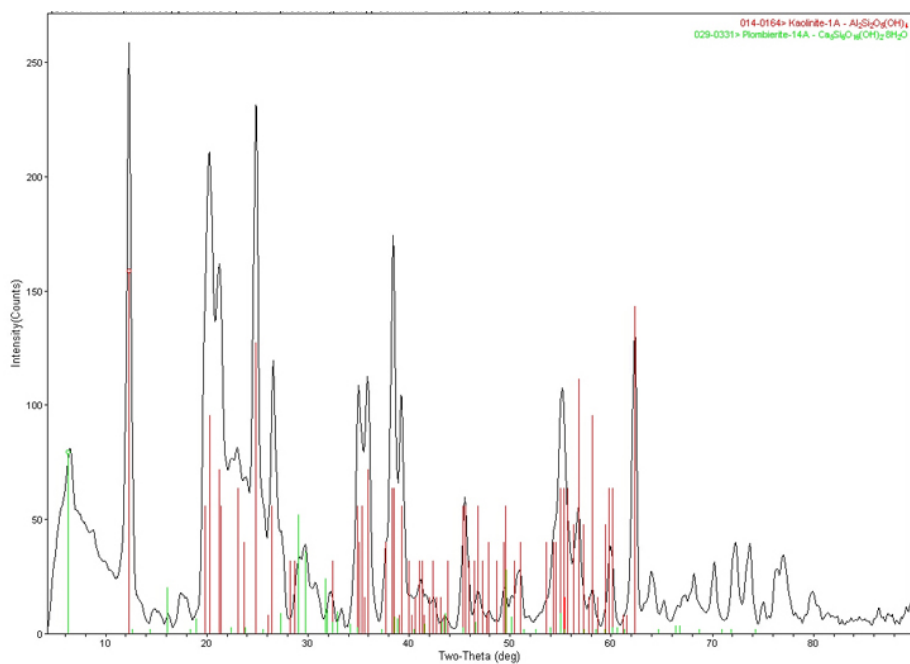


Figure A3.20 X-ray diffraction reading from the paint layer of Block 11, after treatment, showing kaolinite, and the formation of plombierite following consolidation

Appendix 7: Discussion

Table A7.1: Analysis of analytical techniques for determining consolidative efficacy

Test	Test for	Advantages	Disadvantages
XRD	Identify crystallization and/or carbonation	Identify any changes in materials following application of consolidant	Access to machinery
Binocular Microscopy	Visual changes, surface properties	Provides information beyond regular visual examination	Not able to identify significant changes in this case
Adhesion	Cohesiveness of surface being consolidated	Simple test, easily accessible	
Photography	Color changes, visual changes	Provides permanent record, to be referenced in the future	May not be able to detect slight visual changes
SEM	Changes on nanometer scale	Provides perspective unattainable with other instrumentation	Time-consuming
UV/Vis/NIR spectroscopy	Color shifts	Provides objective analysis of color shift on surfaces	Spot size (1cm) can be limiting on small samples
Munsell color charts	Color shifts	Easy to use, access	Not as accurate as other color measurement systems
pH strips	pH changes	Easy to use	Not as accurate as other devices, could damage water-sensitive surface
pH meter	pH changes	Relatively easy to use, more difficult to access	Requires large amount of water for accurate reading
Water absorption test	Hygroscopicity	Relatively easy to implement	Destructive, standardization slightly difficult, hard to interpret when completely absorbed
Colorimetry	Records exact shifts in coloration		Access
Mercury Porosity	Records porosity of	Accurate, commonly-applied test in	Access, requires specific sample size

Test	Test for	Advantages	Disadvantages
XRD	Identify crystallization and/or carbonation	Identify any changes in materials following application of consolidant	Access to machinery
	sample	architectural conservation	for machine
Vapor transmission	Determines vapor transmission, providing indication of porosity	Accurate, commonly-applied test in architectural conservation	Access, requires specific machine

Appendix 8: Materials Information

SOURCE OF MATERIALS

caLoSiL

IBZ Freiberg

Halsbrücker Str. 34

09599 Freiberg, Germany

phone: +49.3731.200.155

www.ibz-freiberg.de

Charcoal (47800)

Kremer Pigments Inc.

247 West 29th Street

New York, NY 1001

212.219.2394

www.kremerpigments.com

EMD colorpHast pH strips

Fisher Scientific

2000 Park Lane Drive

Pittsburg, PA 15275

800.766.7000

www.fishersci.com

Epoxicure epoxy hardener

Buehler

41 Waukegan Road

Lake Bluff, IL 60044

847.295.6500

www.buehler.com

Kaolin (58250)

Kremer Pigments Inc.

247 West 29th Street

New York, NY 1001

212.219.2394

www.kremerpigments.com

Leco microid diamond compound

Leco Corp

3000 Lakeview Ave.

St. Joseph, MI 49085

269.985.5496

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CaLoSiL Technical Information*

CaLoSiL is a solvent based stone, plaster or masonry strengthener on a colloidal calcium hydroxide base. CaLoSiL is used to achieve strengthening by formation of calcium carbonate.

CaLoSiL contains ethanol, propanol or 2-propanol as alcoholic solvents. A special product based on pentan. After saturation of stone or plaster with CaLoSiL, the solvent evaporates and solid calcium hydroxide is formed. That converts into calcium carbonate by reaction with atmospheric carbon dioxide.

The most important property parameters of CaLoSiL are:

- It is a white, opal solution with a density of 0.8g/cm³ containing stable dispersed calcium hydroxide nano particles.
- Deposition of between 15 and 50 g/L Ca(OH)₂ depending on the product type
- Single component system
- Alkaline, flammable solution
- Reliable and easy to use
- No by-products that damage the stone

*adapted from Technical Information Sheet (no liability of the producer can be derived from the contents of this information sheet)

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