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Performance Evaluation of Commercial Nanolime as a Consolidant for Friable Lime Based Plaster

Abstract

This thesis focuses on the performance evaluation of commercial nanolime as a consolidant for friable historic lime based plaster such as found at Mission San Jose de Tumacácori, a Spanish Colonial mission site near Tucson, Arizona. The church's façade was originally finished with a polychromatic painted on fired brick and adobe. Though generally stable over time, the exterior plaster at Tumacácori became friable and detached after repeated weathering cycles of high diurnal temperature swings and precipitation concentration during monsoon season in the summer. As friable stucco is vulnerable to loss, consolidation should be considered a first priority in the conservation plan for the Tumacácori's façade.

Derived from an older limewater method, nanolime is a relatively recent material created by synthesizing nanoscale calcium hydroxide particles and obtaining stability through using alcohol solvents. CaLoSiL®, produced by IBZ-Salzchemie GmbH&Co. KG, was selected for performance testing as a consolidant for friable plaster studying its effect on enhancing grain cohesion, durability to weathering, and impact on aesthetic character. ASTM and RILEM testing methods were employed including splitting tensile strength, porosity by liquid nitrogen immersion, water vapor permeability, color change, frost resistance, and optical and scanning electron microscopy. Ultimately, the analytical findings of this thesis will be used as a recommendation for future conservation of the Tumacácori façade.

Keywords

consolidation, calcium hydroxide, calcium carbonate, nanotechnology, NPS

Disciplines

Historic Preservation and Conservation

Comments

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PERFORMANCE EVALUATION OF COMMERCIAL NANOLIME AS A
CONSOLIDANT FOR FRIABLE LIME BASED PLASTER

Jean Jang

A THESIS

in

Historic Preservation

Presented to the Faculties of the University of Pennsylvania
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Table of Contents

<i>Acknowledgement</i>	<i>ii</i>
<i>Table of Contents</i>	<i>iii</i>
<i>List of Figures</i>	<i>vii</i>
<i>List of Tables</i>	<i>viii</i>
<i>List of Charts</i>	<i>ix</i>
CHAPTER 1. Introduction	1
CHAPTER 2. Mission San José de Tumacácori.....	4
2.1 Materials and Construction Techniques of Spanish Colonial Architecture	4
2.2 Materials at the Mission San José de Tumacácori	7
2.3 Preservation of Stucco (exterior lime plaster).....	9
2.4 Current Condition.....	10
2.4.1 Climate.....	12
2.4.2 Deterioration Mechanisms.....	14
CHAPTER 3. Literature Review – Study and Testing of Nanolime for Conservation	15
3.1 Limewater and Nanolime	15
3.2 Patents and Commercial Nanolime Products	19
3.3 Characterization of Nanolime Consolidant	21
3.4 Consolidant Evaluation.....	24
3.5 Scientific Studies of Nanolime on Plaster and Wall Painting Consolidation	28
3.5.1 Effectiveness.....	28
3.5.2 Compatibility	29
3.5.3 Other Findings	30
3.6 Conclusion	31

CHAPTER 4. Methodology	33
4.1 Introduction	33
4.2 Historical Material Analysis	34
4.2.1 Method	34
4.2.2 Observations.....	35
4.3 Facsimile Sample Preparation	37
4.3.1 Mock Up	39
4.3.2 Ingredients.....	40
4.3.3 Curing	42
4.4 Consolidation	44
4.4.1 Application Technique.....	44
4.4.2 Consolidant.....	47
4.5 Testing Techniques.....	50
 CHAPTER 5. Laboratory Testing	 52
5.1 Splitting Tensile Strength	52
5.1.1 Method	52
5.1.2 Procedure	53
5.1.3 Calculation	55
5.2 Porosity.....	56
5.2.1 Method	56
5.2.2 Procedure	58
5.2.3 Calculation	59
5.3 Permeability.....	60
5.3.1 Method	60
5.3.2 Procedure	60
5.3.3 Calculation	62
5.4 Color change	64
5.4.1 Method	64
5.4.2 Procedure	64

5.4.3 Calculation	65
5.5 Frost Resistance	66
5.5.1 Method	66
5.5.2 Procedure	66
5.5.3 Calculation	67
5.6 Analytical Analysis	68
5.6.1 Sample Preparation – Thin-section	68
5.6.2 Optical Microscopy.....	68
5.6.3 Scanning Electron Microscopy.....	69
5.7 Statistics.....	72
5.8 Photography	74
 CHAPTER 6. Observations.....	 76
6.1 Splitting Tensile Strength	76
6.2 Porosity.....	77
6.3 Permeability.....	79
6.4 Color Change	82
6.5 Frost Resistance	86
6.6 Analytic Observation.....	88
6.6.1 Petrographic Analysis	88
6.6.2 SEM analysis	91
 CHAPTER 7. Conclusions and Recommendations	 92
7.1 Conclusions	92
7.2 Recommendations for Future Research	93
7.2.1 Long Term Performance	93
7.2.2 Color Change and Application	94
7.2.3 Durability and Frost Resistance	94
7.2.4 Thermal Expansion	95
7.2.5 Compatibility	95

7.2.6 On Site Evaluation	96
<i>Bibliography.....</i>	<i>97</i>
<i>APPENDIX A : Geology and Climate Data</i>	<i>109</i>
<i>APPENDIX B : Technical Information of CaLoSiL ®</i>	<i>116</i>
<i>APPENDIX C : Data Set</i>	<i>123</i>
<i>APPENDIX D : Photographs of All Facsimile Samples</i>	<i>141</i>
<i>INDEX.....</i>	<i>167</i>

List of Figures

<i>Figure 2.1 – Morphological Change of Calcium Hydroxide (prismatic to platelike).</i>	5
<i>Figure 2.2 - SEM photomicrographs of crystal evolution of Calcium Hydroxide:(top)after hydration, (bottom)after two months of aging (Elert et al., 2002).</i>	6
<i>Figure 2.3 – Geological Survey of Arizona, expanded window highlighting various limestone deposit near Santa Rosa Foothill area (The Arizona Geological Survey, 2011. Web).</i>	8
<i>Figure 2.5 – NPS Inventory & Monitoring Eco-Regional Networks with Sonoran Desert highlighted; Alaska, Pacific Islands, US Virgin Islands, and Puerto Rico area not represented in this figure, Reproduced by the Author (Program Brief. Inventory and Monitoring, 2015).</i>	13
<i>Figure 3.1 – TEM image of CaLoSiL® E25 (Pesce et al., 2013).</i>	22
<i>Figure 4.1 – Lubricated Cylinder Molds.</i>	38
<i>Figure 4.2 – Lubricated Disk Molds.</i>	38
<i>Figure 4.3 – Lubricated Cube Molds.</i>	39
<i>Figure 4.4 – Photographic Recording of Consolidation Processes.</i>	46
<i>Figure 4.6 – Controlled Environment Curing Chambers.</i>	50
<i>Figure 5.1 – Instron Testing Machine.</i>	53
<i>Figure 5.2 – Loading Unit of the Machine</i>	54
<i>Figure 5.3 – Splitting Behavior of the Sample</i>	55
<i>Figure 5.4 - Set up for Porosity Test using Liquid Nitrogen.....</i>	57
<i>Figure 5.5 – Water Vapor Transmission Test Chamber.</i>	61
<i>Figure 5.6 – Copystand with All Equipment Set for Photographs.....</i>	75
<i>Figure 5.7 – Sample Tray.</i>	75
<i>Figure 6.1 – Deterioration Pattern Observed from Frost Resistance Test.</i>	86
<i>Figure 6.2 – Open pore structure and ground mass of the control sample, approximately 200 µm below the surface (top in PPL, bottom in XPL, mag.10x).....</i>	89
<i>Figure 6.3 - Open pore structure and ground mass of the consolidated sample, approximately 200 µm below the surface (top in PPL, bottom in XPL, mag.10x).</i>	90

List of Tables

<i>Table 3.1 – Commercially Available Nanolime Consolidants.....</i>	<i>21</i>
<i>Table 3.2 – Conservation Principles and Performance Goal Comparison.....</i>	<i>27</i>
<i>Table 4.1 – Principal Component Proportion (Acid Digestion Analysis Result).....</i>	<i>36</i>
<i>Table 4.2 – Type, Dimension, Number of Facsimile Samples.....</i>	<i>37</i>
<i>Table 4.3 – Amount of Ingredients and Mixing Method Used For Each Batches.</i>	<i>42</i>
<i>Table 4.4 – Sample Labeling System.</i>	<i>44</i>
<i>Table 4.5 – Water Immersion Test Result and Actual Amount of Consolidant Used.....</i>	<i>45</i>
<i>Table 4.6 – Manufactured Date of the Products.</i>	<i>48</i>
<i>Table 5.1 – Information from Different Signal Detection.</i>	<i>70</i>
<i>Table 5.2 – Sample Type and ESEM Evaluation.....</i>	<i>71</i>
<i>Table 6.1 – Splitting Tensile Strength Test Result.....</i>	<i>77</i>
<i>Table 6.2 – Liquid Nitrogen Test Result.</i>	<i>79</i>
<i>Table 6.3 – Average Condition of the Testing Chamber (Desiccator).</i>	<i>80</i>
<i>Table 6.4 – Average of the Sample Size.....</i>	<i>81</i>
<i>Table 6.5 – Water Vapor Transmission Test Result.....</i>	<i>81</i>
<i>Table 6.6 – Color Change Value of Samples (before-after).</i>	<i>85</i>
<i>Table 6.7 – Frost Resistance Result.</i>	<i>87</i>
<i>Table 7.1 – Summarized Test Results and Statistical Confirmation.....</i>	<i>92</i>

List of Charts

<i>Chart 4.1 – Gravimetric Chart of the Existing Exterior Plaster Aggregate.....</i>	<i>36</i>
<i>Chart 4.2 – Gravimetric Comparison of Original and Facsimile Sample Sand.</i>	<i>41</i>
<i>Chart 4.3 – Particle Size Distribution.</i>	<i>48</i>
<i>Chart 6.1 – Splitting Tensile Strength.</i>	<i>76</i>
<i>Chart 6.2 – Porosity.</i>	<i>78</i>
<i>Chart 6.3 – Proportion of Open and Impervious Pores.</i>	<i>78</i>
<i>Chart 6.4 – Average Weight Change of Cohorts.....</i>	<i>80</i>
<i>Chart 6.5 – Retained Bulk Volume Percentage after 4 Freeze-Thaw Cycles.</i>	<i>87</i>

CHAPTER 1. Introduction

This thesis examines the performance of commercial nanolime as a consolidant for friable historic lime-based plaster such as that found at Mission San José de Tumacácori, a Spanish Colonial mission near Tucson, Arizona. Located within the Tumacácori National Historical Park with two earlier mission sites in Arizona, the preservation and conservation of the church has been overseen by the National Park Service since 1916. Designated a National Monument in 1908, it was among the first Spanish Colonial structures to be recognized as having national significance.

Mission San José de Tumacácori is a hybrid structure utilizing both Native American and Spanish construction traditions with locally available materials such as earth sand, cobblestones and lime. Especially lime related materials and techniques were highly developed in Spanish construction by the time of the construction. Applied on both interior and exterior surfaces of the adobe structure, plasterworks were often painted or stained for polychromatic effect.

While lime-based materials generally display great stability over time, recurring impact of various weathering agents – moisture infiltration, temperature fluctuation, UV radiation, salt crystallization, and acid rain – can cause lime-based plaster to deteriorate. Particularly on the exterior plaster at Mission San José de Tumacácori, repeated moisture infiltration during monsoon season and high diurnal temperature swings are major weathering agents that have resulted in friability of a loss of inter-granular cohesion. Although it is a slow process, as historic exterior plaster becomes loose and friable it becomes vulnerable to further loss of rare original painted surfaces and eventually even the plaster itself detaches from its substrate and fails simultaneously exposing the vulnerable adobe below. However friability often is one of multiple

conditions observed on the stucco, including detachment, cracks and delamination, flaking, and voids between the brick structure and plasterwork.

In the case of Tumacácori, consolidation of the fragile stucco should be considered as a first priority as this is required before any other treatments such as reattachment can be performed.

Nanolime is a relatively recently developed material used in consolidation, and deacidification. Derived from an older limewater method, nanolime is synthesized at the nanoscale as calcium hydroxide particles in alcohol for suspension stability. As a particle size range of 50 nm to 300 nm is smaller than the pore size range of porous and carbonate based building materials, research has shown that nanolime can be an effective, deep penetrating consolidant for various limestones, lime-based mortars, lime-based plasters and wall paintings. Additionally, as nano particles are more stable in short-chain aliphatic alcohols such as ethanol, iso-propanol, or n-propanol, various concentration of particles (5 g/L, 25 g/L, or 50g/L) are available for the desired consolidating effect.

Currently two commercial product lines are available internationally, CaLoSiL® and Nanorestore®. For the thesis, the CaLoSiL® products, produced by IBZ-Salzchemie GmbH&Co. KG, available through the North American regional distributor, Talas, were used. After consulting with Dr. Gerald Ziegenbalg, the director of the IBZ, ethanol based low concentrated nanolime products, E-5 and E-25, were selected for the experiment and applied following the manufacturer's technical instructions.

As destructive analysis is inevitable to confirm the efficacy of the nanolime consolidant on improvement of mechanical strength, samples of different size and shape were created to

replicate friable stucco at Tumacácori. To comprehensively assess the performance of the nanolime consolidant on lime-based plaster, a series of laboratory analysis was conducted following testing methods established by ASTM and RILEM standards.

The evaluation program was designed to examine the performance of nanolime based on consolidant selection criteria including efficacy of enhancing grain cohesion, compatibility to original materiality, durability to weathering, and impact on aesthetic character. In consideration of time and available equipment, this thesis conducted laboratory testing including splitting tensile strength, porosity using liquid nitrogen, permeability, color change, frost resistance, and analytical analysis using optical microscopy and Environmental Scanning Electron Microscopy (ESEM). All testing results were confirmed statistically using a paired t-test.

Ultimately, the analytical findings of this thesis will be used as a basis to establish comparative data for future research on nanolime. Furthermore, the results of this thesis will help providing recommendations for future conservation to preserve fragile lime-based plaster at Mission San José de Tumacácori and other historic structures using similar building technology or having similar patterns of weathering.

CHAPTER 2. Mission San José de Tumacácori

2.1 Materials and Construction Techniques of Spanish Colonial Architecture

The materials and construction techniques at the church are largely representative of Spanish Colonial architecture, missionary culture, and the available local raw materials. The Jesuits used sun-dried adobes and mud mortar while the Franciscans favored kiln-dried brick and lime mortar (Kennedy, 1993). However in reality, the mission construction was a conglomeration of traditional Native Americans and Spanish building construction. Adobe was used for the core structure while fired bricks and lime were used for the façade and bell tower.

Lime related materials and techniques were highly developed in Spain by the time of construction. As long as limestone was available nearby, lime could be obtained locally using a very cheap and accessible production method. To obtain lime as a building material, limestone, a sedimentary rock composed of calcium or magnesium carbonate, is first burned at temperatures between 925 °C and 1340 °C to make quicklime. The quicklime is then slaked, a process of soaking quicklime in water.

Traditionally the slaked lime was left to mature for several months to years under water (Elert et al., 2002). During the aging process, calcium hydroxide particles undergo a significant size reduction and a morphological change, from large prismatic to small platelike portlandite crystals (Elert et al., 2002). The morphological change is essential to the quality of lime particles as it

ultimately results in increased plasticity, water retention, and workability (Elert et al., 2002). However, because slaked lime, calcium hydroxide, is chemically unstable and highly reactive to carbon dioxide, it is recommended to store under shallow water to prevent unnecessary chemical reaction before use.

Figure 2.1 – Morphological Change of Calcium Hydroxide (prismatic to platelike).

2 μ m

2 μ m

Figure 2.2 - SEM photomicrographs of crystal evolution of Calcium Hydroxide: (top)after hydration, (bottom)after two months of aging (Elert et al., 2002).

The aged lime is then mixed with aggregate and more water to form mortar or plaster. Once it is applied to the desired place, final hardening of lime occurs and lime-based materials obtain mechanical and physical properties as a building material through carbonation. The carbonation is a two part process, a carbon dioxide diffusion in water and a chemical reaction forming calcium carbonates (Van Balen and Van Gemert, 1994).

The excellent plasticity, adhesion, workability, hardening, protective behavior, and aesthetics allowed lime to be employed in various architectural applications (Toniolo, 2011). Most commonly, lime was used in mortar and plaster, both as a mixture of binding medium, aggregate, water and additives.

2.2 Materials at the Mission San José de Tumacácori

Just like other frontier missions, the Mission San José de Tumacácori was built entirely of materials that could be found or made on site (Steen and Gettens, 1962). The foundation was constructed of cobblestones, gathered from the river a quarter mile away and the walls were laid with adobe bricks and adobe mortar (Steen and Gettens, 1962). The bricks were fired about a hundred yards south of the site. Various sizes and forms of adobe and bricks were identified by the Historic American Building Survey (HABS) team in 1937.

The church building's interior and exterior was plastered using locally acquired lime (Steen and Gettens, 1962). Jeremy Moss strongly believes that the source of the lime was from the mountain ranges (Santa Rita, San Cayetano, and Patagonia) to the east of the park where a variety of igneous, metamorphic, volcanic, and sedimentary rocks are found (Graham, 2011; Powell et al., 2005). Rich deposits of limestone around the Santa Rosa foothills and Montosa Canyon are also confirmed through historic geological survey maps (Figure 2.3, APPENDIX A).

Figure 2.3 – Geological Survey of Arizona, expanded window highlighting various limestone deposit near Santa Rosa Foothill area (The Arizona Geological Survey, 2011. Web).

Stratigraphically, the plaster on Tumacácori's façade consists of three layers; a scratch coat, an intermediate coat, and a finishing coat. A three coat process is a typical plastering method. As a first layer, a scratch or rough-cast coat would be laid out by hand or paddle. The layer later would be covered with a brown or intermediate coat in which the thickness varies up to 10 mm depending on the surfaces to be covered and the desired profile (Bass and Porter, 2013). A

finishing coat is a thin layer that ranges from 0.5 to 1 mm of which is usually whitewash or another coating (Bass and Porter, 2013). Though the particle size distribution of the aggregate varied, it was reported that the original plaster contained less than 10 % clay content and 20 – 24 % lime in total (Crosby, 1985). The stucco was painted or sometimes stained using inorganic pigments and colorants to create exterior polychromatic effects. The Mission San José de Tumacácori appears to have used both. (Chan, 2015)

2.3 Preservation of Stucco (exterior lime plaster)

In addition to supporting restoration of the church, Superintendent Pinkley prioritized stabilization of exterior plaster with a general focus on the non-façade walls (Chan, 2015). As the exterior plaster of the west and east walls were rapidly deteriorating, many documented and undocumented repairs have been conducted.

In early 1935, NPSX, a compound of “vinyl resin in acetone and toluene,” was applied to portions of the adobe and lime stucco of the exterior and interior of the mission (Crosby, 1985; Weiss, 1995). However, continuous deterioration of the adobe was observed and finally replaced in 1947 (Crosby, 1985). Attempts were made to find a more permanent synthetic preservative, but were without satisfactory results (Chan, 2015). For example, chemical consolidants were used in 1935 and continued to be used in the 1950s and 60s, such as “Daracone” (a silicone-based water proofing product) and “Daraweld” (a polyvinyl acetate copolymer dispersion in water) was used up to 1970-71 (Crosby, 1985). Due to successive conservation campaigns on the exterior walls by the 1950s, Superintendent Earl Jackson doubted if any portions of original plaster still existed on the church (Moss, 2008).

Unlike other exterior walls where a little evidence of the original fabric is left, the south for main façade of the church has retained relatively large amounts of original fabric. This is exceptional as the lower face consisting of the columns, niches, and the entrance arch and pediment had to be rebuilt in order to be structurally stable while the restoration campaign was underway in the early 20th century.

Among miscellaneous repairs, few consolidation campaigns of the façade were recognized in the records. In summary, major recorded consolidation campaigns on the façade used NPSX on the east jamb of the door arch by Martius in 1935, various testing with ammonium carbonate poultices on the door arch intrados in 1982, and consolidation of an unidentified location occurred using PVA (Porter and Bass, 2013).

2.4 Current Condition

According to a recent assessment of Tumacacori's façade in 2015 by the Architectural Conservation Research Center at the University of Pennsylvania, approximately 316 square feet of 2200 square feet historic plaster was estimated to remain on the exterior of the Tumacacori's south facing façade. Despite the difficulty of distinguishing between the historic and repair plasters, the façade has approximately 14% of original stucco (Architectural Conservation Research Center, 2015).

Generally, where weather exposure is greatest, loss of stucco and surface erosion are observed. These conditions are found on the projecting areas of moldings and centers of columns, having direct exposure to sunlight and rain, and the base of the wall and horizontal surfaces where water collects. As no structural connections between the wall and roof, and cracks penetrating

the entire wall were observed at the southwest and southeast corners of the façade, structural failure may be serious. Lastly in terms of finishes, there have been many inconsistent approaches and poorly integrated repairs to the exterior façade, which aesthetically overpowers the surviving historic decorated plaster (Bass and Porter, 2013).

As the historic stucco on the façade generally received less maintenance (Crosby, 1985) it was greatly impacted by the adjacent impermeable repairs, causing the extant historic materials to deteriorate (Bass and Porter, 2013). The current conditions of the original fabric include overall detachment, cracking and delamination of historic plasters and finished surfaces, flaking coatings, and voids behind plasterwork (Bass and Porter, 2013).

Therefore, it is necessary that a treatment program for the exterior façade be developed to preserve the stucco and historic finishes that are becoming more fragile over time. To be able to establish a comprehensive conservation plan, different objectives should be considered including development of treatments for removal of failed repairs, conservation of edging profile and mixes, loss compensation, stabilization of detaching plaster, and reattachment of flaking finishes and spalling historic undercoat plaster (Bass and Porter, 2013).

However, it should be noted that the treatment for the friable stucco needs to be considered as the most imperative within a future conservation program as the fragile stucco of the façade may result in further losses or damage. Acknowledging the scarcity of the historically significant fabric, and the means and method of consolidation should be a first priority.

2.4.1 Climate

As the building exterior interacts with the surrounding environment, understanding the local weather and climate is integral to understanding deterioration and to recommending appropriate treatment.

The climate data is generated from the Tumacácori NM station located within the boundary of Tumacácori National Historic Site which is identified as COOP: 028865.¹ Though it is a volunteer operating station, the collated data is rated very reliable. The station, as a part of a network of the National Weather Service (NWS) Cooperative Observer Program (COOP), has measured the climate data since 1946. The COOP program produces the data set called summary of the day, which is manually integrated measured data, including daily maximum and minimum temperatures, observation-time temperatures, daily precipitation, daily snowfall, and snow depth and NWS measurement (Davey et al., 2007).

In 1988 the National Park Service created the Inventory and Monitoring (I&M) program in order to understand the present and future of natural resources and collectively manage the 270 national parks (*Program Brief. Inventory and Monitoring, 2015*). According to natural resources, 32 eco-regional networks were created.

The Mission San José de Tumacácori is a part of the Sonoran desert I&M network (SODN). The Sonoran desert network occupies approximately 260,000 km² (100,387 mi²) and 11 national parks in the southwestern United States. This network is characterized as having mild winters and hot summers, with year round high diurnal temperature swings. It is typically free of frosts but has the intense monsoon season in July and August (Davey et al., 2007).

¹ The station is located at 31.5677 ° North, -111.0497° West and elevation of 995.8 meters.

Figure 2.4 – NPS Inventory & Monitoring Eco-Regional Networks with Sonoran Desert highlighted; Alaska, Pacific Islands, US Virgin Islands, and Puerto Rico area not represented in this figure, Reproduced by the Author (Program Brief. Inventory and Monitoring, 2015).

According to the 30-year summary of measured data from 1981 to 2010, the hottest month at Tumacácori was June with an average maximum daily temperature of 96.8 °F (36 °C) and the temperature often exceeded 105 °F (40 °C) during the hottest time. Daily temperature swings between day and night could be as great as 15 °C or more (Davey et al., 2007).

Recent studies found the climate pattern over 10 years in the network has already shifted beyond the historical range of variability, including more intense storms, floods and droughts (Monahan and Fisichelli, 2014). These extreme weather events could have serious consequences for degraded materials and especially the surface finishes.

2.4.2 Deterioration Mechanisms

Plaster and wall paintings made with slaked lime are generally very stable over time. However as a sacrificial layer they are expected to deteriorate over time, being affected by different mechanisms including environmental weathering (Toniolo, 2011). Plaster degradation may be caused by loss of cohesion between the matrix and aggregate, loss of adhesion to the substrate and between the layers, lime leaching, formation of shrinkage fissures, and soluble salts and pollutants (Henry and Stewart, 2012).

The deterioration mechanisms may vary depending on sites and even on different locations in the same building. For example, although the plastering of the Mission San José de Tumacácori was applied stratigraphically in the same manner, the interior plaster mostly underwent salt crystallization whereas the exterior plaster deteriorated due to the constant exposure to the elements and pollution. As in 1952, it was confirmed that the environment caused the disintegration of the façade's plaster above the main entrance arch as it collapsed after a year of heavy rain (Chan, 2015). Piero Baglioni explains this phenomenon as "chemical corrosion," which is a process of losing binder that holds aggregate or pigment together (Baglioni, 2006).

CHAPTER 3. Literature Review – Study and Testing of Nanolime for Conservation

This chapter examines the technical literature on mineral consolidants, and especially lime-based methods applied to carbonate-related materials and investigates development of nanolime consolidant as nanotechnology adopted to cultural heritage conservation.

Recognizing the historic and cultural significance of the exterior plaster at the church of Mission San José de Tumacácori, this thesis argues that the plaster should not be replaced but consolidated in order to retain its material authenticity and remedy the friable surface condition. Though deterioration is most often the result of a combination of different weathering mechanisms and agents such as moisture infiltration, temperature fluctuation, solar radiation, salt crystallization, acid rain and microflora, the main weathering agents for the exterior plaster at the San José de Tumacácori are moisture and temperature in combination with an underbound original plaster.

3.1 Limewater and Nanolime

Analyzing and solving problems using nanotechnology is a growing interest in heritage conservation. Since nano-scale physics was introduced in 1959 (Feynman, 1959), nanotechnology has been developed extensively during the past half century. Nanotechnology in architectural conservation includes synthesizing nanomaterials for treatment, including consolidants and protective coatings, which are 100 nm or smaller, and using devices that can provide the ability to analyze those materials. SEM is a typical analytical device that allows us to visualize material behavior in micro- to nano-scale (Doehne, 2006). By synthesizing nanoparticles of oxide and hydroxide from alkaline earth metals, nanomaterials have been proposed and used for the

preservation of immovable and movable art works (Bonini et al., 2013). The first nanomaterial used in conservation was nanolime (Baglioni and Giorgi, 2013).

Nanolime is derived from limewater, which should not be confused with limewash, which is a diluted form of slaked lime used as an historic water-based paint. Suggested by Vitruvius (Hansen et al., 2003), together with waxes and linseed oil, limewater is considered a historic treatment method used to replace natural cementing components (Winkler, 1997). Produced from slaked lime or a mixture of lime putty and water, limewater is a true solution of calcium hydroxide obtained as a clear liquid after letting lime particles settle out of solution. Introducing limewater to degraded carbonate-related materials was believed to be a natural and compatible consolidation methodology. Because the introduced lime component undergoes a carbonation process and produces a similar cementing matrix as original lime binder, the consolidated materials should possess similar physical and chemical properties over time. Based on its compatibility, the use of limewater was advocated as a traditional and natural inorganic consolidation method (Moncrieff and Hempel, 1971; Peterson, 1981; Simpson and Brown Architects, 2002). The most successful case reported is known at Wells Cathedral in England which was treated using Baker's 'lime treatment' from 1975 to 1986 (Caroe, 1985). Despite its reported success, limewater has not displayed overall good performance when used elsewhere. Some researchers have suggested that the success may be largely superficial or not dependent on the treatment alone (Price, 1984). Conclusive evidence of limewater consolidation was insufficient until recently (Fidler, 1995).

Later researches have shown that 1 liter of a saturated limewater contains 1.8 g of calcium hydroxide at around 25 °C (Hansen et al., 2003). Due to a low solubility and a particle size larger

than most pores, limewater consolidation was limited to a superficial consolidation to a depth of 2 mm (Price et al., 1988). Additionally a large amount of water continuously introduced during 30-40 of repeated applications was considered to activate other deterioration agents, such as soluble salts (Drdácky and Slížková, 2012) and microorganisms (Brajer and Kalsbeek, 1999). Especially for consolidation of wall paintings, the limewater consolidation method was considered to have adverse effects on water- and pH- sensitive pigments and binding media (Brajer and Kalsbeek, 1999).

After successive failures in finding adequate improvement using limewater consolidation, the method lost favor and various organic and inorganic consolidants supplanted this traditional method. For compatible consolidation of porous, calcareous stone and plaster, the use and effect of a range of inorganic consolidants including biological deposition of calcium carbonate, barium hydroxide, artificial calcium oxalate and tartrate were reviewed by a group of researchers (Hansen et al., 2003). Due to their different chemical reactions, each method could prove to be the most effective option under specific conditions. For example, barium treatments are effective for the deterioration caused by the formation of gypsum (calcium sulphate dehydrate), while ethyl silicate and methyl silicate are effective for fragile salt contaminated wall paintings (Brajer and Kalsbeek, 1999). However, a lack of sufficient and standard evaluation methods have prevented conservators from thoroughly understanding the properties and behaviors of the different consolidants.

When alternative aqueous-based consolidants were not suitable, synthetic resins such as acrylate, vinyl, silicone or epoxy polymers (resins) were used (Brajer and Kalsbeek, 1999). Eventually by the 1960s synthetic products became the most dominant consolidants for historic

building materials (Mora et al., 1984; Dei and Salvadori, 2006; Baglioni et al., 2015). Fast and high adhesive power, high weather resistance, hydrophobicity, and presumably reversibility were seen as advantages of using synthetic polymers (Horie, 1987). However later examinations verified synthetic, organic polymers were hardly physico-chemically compatible with historic lime-based materials and accelerated degradation phenomena in short periods (Chelazzi et al., 2013). The most common adverse impacts are excessive modification of the water kinetics, formation of a hard superficial layer, insufficient depth of impregnation, and excessive color change (Ferreira Pinto and Delgado Rodrigues, 2014).

For a long time evaluation relied on applicator experience, and scientific methods of testing lime plaster in situ is rarely specified by standards or in the literature (Peterson, 1981). As more guidelines for preservation were established during 20th century, the significance of treatment evaluation was recognized and emphasized. As preservation treatments aim to recover lost mechanical properties that historic material once possessed without significant alteration to other properties, finding the best material or method can be difficult. Especially, since consolidation, like many other treatments, is considered a non-reversible intervention, the performance should be investigated prior to its use.

To overcome drawbacks of limewater and synthetic polymer consolidants, such as low efficacy and incompatibility, nanotechnology in the form of naolime was embraced as a possibly effective and compatible inorganic consolidant. The low solubility of calcium hydroxide in historic limewater was improved by using short-chain aliphatic alcohols such as ethanol, iso-propanol or n-propanol (Giorgi et al., 2000); however commercial alkaline hydroxide powders can still have mean particle sizes of several microns which are still too large for the paint surface where surface

pores are smaller (Baglioni and Giorgi, 2006). Therefore, nanotechnology was applied to physically reduce the particle size of calcium hydroxide, allowing the material to be drawn into the substrate through capillary action.

3.2 Patents and Commercial Nanolime Products

The two earliest patents related to nanolime dispersion were filed during the late 1990s. The patent in colloidal dispersion of calcium hydroxide in hydrocarbon medium was filed by French research group, Institut Fransais du Petrole in 1995 and the first nanolime synthesizing method patented by CSGI of Italy in 1996.

Although various synthesizing methods of nanolime have been designed since (Giorgi et al., 2000; Salvadori and Dei, 2001; Nanni and Dei, 2003; Rodgriguez-Navarro et al., 2005; Ciliberto et al., 2008; Daniele et al., 2008; Liu et al., 2010; Nasillo et al., 2011; Daniele and Taglieri, 2012; Taglieri et al., 2013; Rodgriguez-Navarro et al., 2013; Poggi et al., 2014; Taglieri et al., 2014; Taglieri et al., 2015), researchers agree there are two basic methods for producing nanolime particles. One mechanically breaking the calcium hydroxide particles into nanoscale particles, while the other produces nanolime using a homogeneous phase or heterogeneous phase synthesizing method (Rodriguez-Navarro et al., 2013).

Currently two product lines of nanolime consolidants are commercially available in the global market, CaLoSiL[®], produced by IBZ-Salzchemie GmbH&Co. KG of Germany, and Nanorestore Plus[®], developed by CSGI and distributed by CTS of Italy. Though both use a phase synthesis method, Nanorestore Plus[®] and CaLoSiL[®] use slightly different methods. Particles of Nanorestore Plus[®] are obtained by homogeneous-phase reaction of sodium hydroxide (NaOH)

and calcium chloride (CaCl_2) in supersaturated water and other organic solvents (Ambrosi et al., 2001a), whereas CaLoSiL[®] products are synthesized directly from alcohol solvents (Baglioni et al., 2015).

All commercial nanolime consolidant products are listed in Table 3.1 as per the 2015 CaLoSiL[®] product catalog and CSGI website. Both product lines offer a range of options of solvents and nanolime concentrations. CaLoSiL[®] offers 8 different products for consolidation purposes using 3 different solvent types (ethanol, iso-propanol or n-propanol) and 3 nanolime particle concentrations (5 g/L, 25 g/L or 50 g/L), and Nanorestore Plus[®] offers 4 different products using 2 solvents (ethanol, or iso-propanol) and 2 nanolime concentration (5 g/L or 10 g/L). Though more options were offered previously, as seen in Table 3.1, both companies now tend to focus on nanolime consolidants that use ethanol solvents and have nanolime concentrations lower than 25 g/L.

Table 3.1 – Commercially Available Nanolime Consolidants.

CaLoSiL®-	Solvent	Concentration of nanolime (g/L)	Nanorestore Plus® -	Solvent	Concentration of nanolime (g/L)
E-5	ethanol	5	Ethanol 5	ethanol	5
-	-	-	Ethanol 10	ethanol	10
E-25	ethanol	25	-	-	-
E-50	ethanol	50	-	-	-
IP-5	iso-propanol	5	Propanol 5	iso-propanol	5
-	-	-	Propanol 10	iso-propanol	10
IP-25	iso-propanol	25	-	-	-
NP-5	n-propanol	5	-	-	-
NP-25	n-propanol	25	-	-	-
grey	ethanol	25	-	-	-

3.3 Characterization of Nanolime Consolidant

According to the Material Safety Data Sheet of ethanol based CaLoSiL®, the products are calcium hydroxide particles and alcohol display a very low viscosity. Depending on the concentration, the products contains 0.1 % to 20 % of nanolime particles and 75 % to 90 % alcohol and have a color of transparent white to murky white.

Generally synthesized particles of commercial nanolime have a size range of 50 nm to 300 nm. However, due to different synthesizing methods, Nanorestore Plus® particles are usually in a range between 100 nm to 300 nm and CaLoSiL® particles between 50 nm to 250 nm (Baglioni et al., 2015). Due to the more homogeneous and smaller particle sizes found in CaLoSiL®, better consolidation was achieved with CaLoSiL® products (Arizzi et al., 2015). Particles are crystalline

and appear as faceted hexagonal platelets in 120 ° inner angle with a thickness of a few nanometers (Ambrosi et al., 2001 a). Because of micron-sized hexagonal plate particles, nanolime is stable for longer time and has a great capacity to absorb water (Baglioni et al., 2015).

Figure 3.1 – TEM image of CaLoSiL® E25 (Pesce et al., 2013).

Although ideal particle size distribution could be obtained through a different synthesis process, the nano calcium hydroxide is generally highly unstable in water because of its tendency to aggregate in water (Giorgi et al., 2010). Whereas in short chain alcohol solvents, the nano calcium hydroxide obtains a kinetically stable dispersion (Giorgi et al., 2010). The kinetic stability of the dispersion is generally proportional to the thickness of the hydrophobic layer on the calcium hydroxide particles with adsorbed alcohol, which is enhanced by n-propanol, ethanol, and isopropanol (Ambrosi et al., 2001 b).

Using alcohol solvents also improves the consolidation process (Giorgi et al. 2000). Colloidal dispersion of nanolime in alcohol can achieve a slower rate of agglomeration, a reduced tendency for a white film to form on surfaces (Hansen et al. 2003), and a better depth of penetration because of lower surface tension (Baglioni and Giorgi, 2006).

Alcohol is a generally non-toxic solvent. However the consolidation work should be conducted in a well ventilated environment free of oxidizers, heat, sparks, or flames. Because of low flashing points ranging 12-15 °C (Division of Organic Chemistry, 2016), solvents like ethanol, iso-propanol, and n-propanol are highly flammable as liquid and vapor.

As materials possess different internal structure, the application method should be determined based on pore structure and the consolidating environment of the materials. Generally, to avoid fast evaporation of alcohol, a damp, cold condition is favorable for nanolime application (D'Armada and Hirst, 2012). Different application methods can be used including dipping, spraying, pouring, immersion, vacuum impregnation, injection, or brushing on Japanese paper (D'Armada and Hirst, 2012; Baglioni et al., 2015). However, Licchelli's research group found brushing applications appear to perform better than immersion methods on bio-calcareous stone (Licchelli et al., 2014).

After alcohol solvents evaporate, carbonation of nanolime takes place in a similar way to traditional lime-based building materials in the presence of atmospheric carbon dioxide and decreasing moisture.

Because the nanolime works through carbonation, several factors were identified as influencing the performance of nanolime: temperature, relative humidity, amount of free water within the pores of the substrate, particle crystallinity, size, surface area, and the nature of the solvents (Chelazzi et al., 2013). Among all, the performance of nanolime consolidants can be especially sensitive to relative humidity and carbon dioxide content in the air. As calcium hydroxide sets in a slightly humid environment, the fast evaporation of alcohol solvents can leave the particles un-carbonated. Studies have revealed that the relative humidity also influences crystallinity, agglomeration, and mineralogy of calcium carbonates (Lopez-Arce et al., 2010; Lopez-Arce et al 2011; Lopez-Arce, 2013). A relative humidity between 75-90 % allows faster formation of calcium carbonate and larger particles of higher crystallinity (Gomez-Villalba et al., 2011) in comparison to that between 33-54 % relative humidity (López-Arce et al., 2011).

3.4 Consolidant Evaluation

As interest in the use of nanolime consolidants grows, researchers have been trying to characterize the behavior of nanolime consolidants and to find better application methods for their optimal performance. Quantitative and qualitative analyses have been used to confirm the efficacy and the behavior of the consolidant in various porous materials and to explore potential use of nanolime consolidants. As various concentrations and solvents are offered by the manufacturers, laboratory testing must be conducted depending on the application conditions and researcher's intent.

Meanwhile, having guidelines and standards are significant for the evaluation of materials especially in the application of a consolidant. Ideally, consolidation should improve the internal

cohesion without affecting other physical properties of the substrate (Ferreira Pinto and Delgado Rodrigues, 2014). The success of the consolidation should be analyzed based on four conservation principles; effectiveness, compatibility, durability, and reversibility (Sassoni et al., 2016).

The effectiveness of any consolidant is determined by whether the consolidation improves the internal cohesion of the material. As a measurable concept, this includes measuring mechanical improvement of the consolidated material and penetration depth of the consolidant. Different methods can be used for this purpose, including measurement of flexural strength, shear bending, compressive strength, tensile strength, drilling resistance, resistance to scotch tape peeling or ultrasound velocity measurements. Although achievement of uniform increased strength is ideal, the consolidating effect is likely to be higher on the surface and lower within the internal substrate. When a consolidant diffuses evenly throughout a material, improvement of compressive strength is achieved. Whereas, when a consolidant deposits closer to the surface, tensile strength is increased (D'Armada and Hirst, 2012).

The compatibility of consolidant is evaluated by investigating the consolidant's impact on other properties of the substrate. As a building assembly of different materials interacts with the environment, systematic performance should be maintained. Depending on the site, slight modifications to the current microstructural and physical properties may be desirable when consolidated (Sassoni et al., 2016). However other changes such as permeance reduction may accelerate the deterioration of the material and the building.

Durability and reversibility/retreatability ultimately determine long term performance. A long term performance of the consolidant itself, as well as performance of the consolidated materials under environmental weathering processes should be evaluated. Although reversibility

was once a stated objective in conservation, retreatability is now considered a more realistic goal. Some organic resin based consolidants can be removed by dissolution in solvents but it is unlikely to be completely removed from the pores and the substrate is likely to be damaged during the removal procedure (Crosby, 1985; Sassoni et al., 2016). Therefore instead of reversibility, retreatability, which is the possibility to retreat the substrate with either the same or a different consolidant in the future (Scherer and Wheeler, 2009), should be considered in evaluation of any consolidant.

Parameters for consolidation can be found in ASTM E2167 – 01 - Standard Guide for Selection and Use of Stone Consolidants. As more complex and various consolidants are available, following the guidelines and testing standards allows comparisons to be made between a variety of consolidants and their behavior to the substrate (Searls and Wessel, 1995). Although the current ASTM standard for consolidant selection is limited to stone substrates, as consolidating conditions can be similar in porous architectural elements, consolidation objectives for plasters are reviewed based on the ASTM E2167 – 01.

Table 3.2 – Conservation Principles and Performance Goal Comparison.

Conservation principles	Performance goal (ASTM E2167)	Description
Effectiveness	Depth of penetration (6.1.1)	Penetrate at least through the weathered layer
	Consolidating ability (6.1.2)	Increase mechanical properties – compressive strength, flexural strength, abrasion resistance, erosion resistance
Compatibility	Water vapor transmission (6.1.3)	Minor impact on water vapor transmission rate
	Thermal expansion characteristic (6.1.5)	Minor impact in coefficient of thermal expansion
	Appearance (6.1.6)	Minor changes in texture, hue, value, chroma, lightness, gloss or reflectivity
Durability	Resistance to internal expansive forces (6.1.4)	Resistance to internal expansive forces caused by deterioration
	Soiling resistance (6.1.7)	Not susceptible to collecting airborne particles, gases, and soil
	Durability (6.1.8)	Retain improved properties for extended time
	Water resistance (6.1.9)	Resistant to water dissolution and water erosion
	Biodegradation (6.1.10)	Not susceptible to provide environment to biological growth
Retreatability	-	-

3.5 Scientific Studies of Nanolime on Plaster and Wall Painting Consolidation

3.5.1 Effectiveness

As nanolime is an improved version of traditional limewater, researchers have been trying to evaluate the application and consolidating effect of limewater to compare it to the performance of nanolime. It was widely accepted that 30-40 applications of limewater could consolidate friable stone and plaster. However, a recent study observed that mechanical strength was significantly improved when 160 applications of limewater (approximately 2 g/1L) was conducted in a 1:9 part (by volume) lime mortar (Slížková et al., 2015). It was further proved that a similar degree of increased compressive strength and a two-fold increase in tensile strength could be achieved via 40 applications of CaLoSiL® IP-15, 15 g/1L of nanolime dispersion in isopropanol, over 3.5 days (Dradacky et al., 2009).

Consolidation can be achieved by using either multiple applications of a lower concentration of nanolime or a single application of a high concentration of nanolime (Slížková and Frankeová, 2012). Mechanical strength of the consolidated materials was increased when a larger number of applications was conducted (Moreau et al., 2010). The high concentrated nanolime (CaLoSiL® E-50) has an ability to increase bending strength 54 %, compressive strength 73 % even after 2 applications, while the lower concentration of nanolime (CaLoSiL® E-25) increase bending strength 20 % and compressive strength about 50 %. However, consolidation with a higher percentage of nanolime can more often result in uneven distribution within the internal structure of the materials and usually remains concentrated on the surface (Costa and Rodrigues, 2012; Slížková and Frankeová, 2012).

As seen in Table 3.2, the performance of nanolime consolidants can be evaluated by examining the depth of penetration. Despite the small particle size of nanolime, the consolidant did not penetrate deeply into the substrate (Campbell et al., 2011). It was determined that nanolime consolidants reached at 60 μm to 90 μm of depth for *Alberse* stone and at 60 μm for *Gallina* stone when consolidating phase was satisfactory (Dei and Salvadori, 2006). Later on various stone types, a slightly improved depth of penetration was observed ranging from 300 μm to about 1 mm (Daniele and Taglieri, 2011).

Though in this thesis the use of nanolime was reviewed as a consolidant for only stone, lime mortars, and wall painting, researchers have also investigated its use in paper, canvas, and wood deacidification (Rodriguez-Navarro et al., 2013). Recently, feasibility of using nanolime consolidant was tested on portland cement based materials (Barberena-Fernández et al., 2014).

3.5.2 Compatibility

Nanolime consolidants do not appear to change other physical properties of the material consolidated. No significant increase in the weight or density has been reported (Booth, 2012). However as shown by Jornet and Romer, porosity of lime mortar decreases as the binder to aggregate ratio increases (Moreau et al., 2010). Therefore, the degree of porosity modification is more obvious when the consolidating materials have a low lime to aggregate ratio and when then number of applications increases (Moreau et al., 2010). For example, 25 g/L nanolime to limestone after 6 cycles resulted 2.9 % decrease in absolute porosity and 5.8 % in relative porosity (Slížková and Frankeová, 2012). Whereas, on Portland limestone, a coarse bioclastic material in the UK that has a larger percentage of small pores, 10 applications of E-25 resulted in 14 % to 19 %

porosity reduction and approximately a 40 % increase in permeability reduction (Campbell et al., 2011).

Meanwhile, uneven penetration can cause a white haze to develop because of the strong optical property of lime as a white material. The white haze, which is a surface whitening effect, has been reported as a drawback of nanolime (Booth, 2012). Since hazing can alter the appearance of an original color scheme, monitoring of application is necessary when nanolime is applied to a surface that contains colored surfaces. Therefore, many researchers have tried to quantify the whitening effect caused by the consolidant (López-Arce et al. 2013).

3.5.3 Other Findings

In addition to understanding the behavior of nanolime consolidants to historic material, its behavior to previously treated substrates can be essential in determining a proper application method. In the presence of acrylic copolymers, nanolime showed an increase in mechanical strength; however water vapor permeability was reduced due to the hydrophobicity of the copolymers (Carretti, 2013).

A group of researchers tried to compare the consolidating behavior of a mixture of limewater and 5% ethyl silicate to a nanolime alone (Borsoi et al., 2013 b). Although the mixture of limewater and ethyl silicate resulted in a greater increase in mechanical strength, it was concluded that nanolime alone showed more ideal behavior as a compatible but effective consolidant with an adequate increase in mechanical strength, and a deeper and more even penetration (Borsoi et al., 2013 b). However, the use of ethyl silicate can be beneficial when it is used with the nanolime consolidant and the mixture of nanolime and ethyl silicate can achieve

further stability of consolidated materials (Ziegenbalg et al., 2010; Maryniak-Piaszczyński et al., 2012; Ziegenbalg and Piaszczyński, 2012; Borsoi et al., 2013 a).

Nanolime can be successfully used in a humid environment (Macchia et al., 2014) and consolidation using a commercial nanolime may have a moderate effect on the deterioration of historic materials caused by salt crystallization (Giorgi et al., 2010; Zornona-Indart et al., 2012; Ruffolo et al., 2014). To enhance the consolidation efficiency of the nanolime, it is recommended to identify salts and treat them accordingly using barium hydroxide nanoparticles (Giorgi et al., 2010), or alcoholic dispersion of strontium hydroxide (Gregorio, 2010).

3.6 Conclusion

Many researches agreed that the nanoparticles of calcium hydroxide restore cohesion of lime based materials without significantly altering overall physical and chemical compatibility. For even penetration and consolidating effect, using 2 cycles of 25 g/L ethanol or 25 g/L iso-propanol nanolime dispersion is generally recommended (Slížková and Frankeová, 2012). Despite the availabilities of other solvents, researchers appear to prefer the use of CaLoSiL® E-25 (Slížková and Frankeová, 2012; Borsoi et al., 2016). However, the ultimate consolidating effect highly depends on the mortar's binder to aggregate ratio and pore size distribution (Moreau et al., 2010; Slížková and Drdácáký, 2014). Therefore basic understanding of a material's microstructure seems necessary to determine the application of nanolime consolidant.

Despite many efforts to evaluate nanolime consolidants using highly technical tools, the evaluation seems inconclusive without accelerated or real time durability tests. For lime-based materials, nanolime also allows the use of other lime-based treatments such as grouting, mortar

fills, and limewashes, ultimately creating a totally material-compatible treatment regime (Maryniak-Piaszczyński and Ziegenbalg, 2010).

CHAPTER 4. Methodology

4.1 Introduction

To better understand significant properties and possible decay mechanisms of the original plasters at the Mission San José de Tumacácori, the evaluation began with characterization of the existing original exterior plaster. Following the literature review on previous condition and conservation efforts at the church, mortar analysis was conducted. Previously collected bulk samples and prepared thin sections were available through the Architectural Conservation Laboratory (ACL) at the University of Pennsylvania. Fallen plaster fragments collected during site visits in summer 2015 were used for mortar analysis to identify the aggregate's grain size distribution, the binder to aggregate ratio, and to confirm plaster characteristics described in previous research.

The results from the analysis were then applied to the recreation of plaster replication for laboratory testing. A lack of sufficient original material for testing required facsimile samples. These samples were created following ASTM C305 – 14 - Standard Practice for Mechanical Mixing of Hydraulic Cement Pastes and Mortars of Plastic Consistency. After 28 days of curing, the facsimile samples reached full carbonation and were ready for consolidation treatment. Consolidation means and methods were determined after reviewing the technical literature on nanolime and other consolidants. Overall, facsimile samples were prepared to be treated in a controlled environment to introduce the least variables.

The literature on the evaluation of nanolime consolidants and ASTM guidelines for consolidation testing were reviewed to determine the shape, size, and number of the facsimile samples. Despite various relevant tests that have been conducted in other research, tests were

designed based on available equipment and time. Ultimately performance was evaluated according to three criteria: compatibility, durability, and aesthetics. Each criterion was considered in terms of a set of critical properties: strength and color change.

4.2 Historical Material Analysis

4.2.1 Method

The physical characteristics of the existing original exterior plaster at Tumacácori were investigated to provide information for recreating plaster samples for consolidant performance evaluation, this was also beneficial in understanding the original matrix of the existing exterior plaster.

This part included two phases of analysis: gravimetric analysis using the fragmented samples collected over the summer 2015, and microscopic and petrographic confirmation using the previously prepared thin sections (Chan, 2015). Two samples were collected from two different locations, and both were confirmed as original plaster from the south facing façade of the church.

For the first phase, a simple acid digestion method and sieve analysis were used to confirm the approximate weight proportion of the different fractions. As this method uses hydrochloric acid to break down the binder and isolate the aggregate, the result can often give inaccurate results if acid-sensitive aggregates exist as well as soluble silicates (Teutonico, 1988; Schnabel, 2009). However, knowing that lime was the binder and the aggregate contained little to none calcareous minerals in the Tumacácori's plaster, this method was considered reliable for gross characterization.

The second phase of analysis was conducted using thin-section petrography. Although the previous research by Jocelyn Chan included brief description of the plaster substrate her scope was mainly focused on the painted surfaces of the exterior plaster. This phase of analysis was to produce further information on the plaster substrate with a particular interest in binding medium. A transmitted light microscope at the ACL as well as Quanta 600 FEG ESEM at the Singh Nanotechnology Center were used for the purpose.

4.2.2 Observations

The bulk sample examined represents the current weathered condition of the exterior plaster at the church. The sample showed very low strength and high friability. The sample was snap-able by hand with little pressure. When it was rubbed, surface grains disaggregated easily. The Mohs hardness also indicated that the sample registered less than 2.

Bulk color and streak color were measured using the Munsell Soil Color Charts (New Windsor: GretagMacbeth, 2000) under natural light and determined as 7.5YR/1/8. However, in order to establish reference color data in comparison to facsimile samples, the color from surfaces of the bulk sample and aggregate after acid digestion test was measured using a handheld Konica Minolta Spectrophotometer CM-2500d.

After acid digestion the coarse and fine fractions were calculated and the acid soluble content determined by weight as shown in Table 4.1. This confirmed the petrographic analysis results from the previous research, which suggested that the scratch or lower layer of exterior plaster was composed of 20 % to 25 % of binder (lime) (Chan, 2015). Approximately 3 % of fine impurities by weight were observed which was considered negligible.

Table 4.1 – Principal Component Proportion (Acid Digestion Analysis Result).

	Total sample	Soluble	Aggregate	Fine
Mass (g)	24.93	4.59	19.48	0.86
Percent to total sample (%)	100	18.4	78.1	3.5

Acid soluble components of the sample showed an extreme reaction to the initial 100 mL of 14 % solution of hydrochloric acid and continued with another 150 mL of the solution. This observation of extreme reaction to hydrochloride acid indicates the component has a carbonate component, presumably lime:

The coarse fraction was then isolated for sieve analysis to determine aggregate size distribution. As plotted in Chart 4.1, the aggregate is well graded.

Chart 4.1 – Gravimetric Chart of the Existing Exterior Plaster Aggregate.

4.3 Facsimile Sample Preparation

The facsimile samples were moulded in three different shapes to be used for different testing. Shape, size and number of the samples were determined according to corresponding ASTM standards for each property test. As Table 4.2 suggests, shapes of samples included cylinders, disks, and cubes. In order to avoid having less samples than needed and to reject not qualified samples, more samples were prepared than were required.

It should be noted that the consolidated* column in Table 4.2 was not tested in the scope of this thesis due to time constraints. This set of consolidated* samples was prepared for future research based on longer cure time. As the only variation between consolidated and consolidated* samples is curing duration, the result of this thesis would benefit in establishing this correlation.

Table 4.2 – Type, Dimension, Number of Facsimile Samples.

Shape/ type	Material	Size	Control	Consoli dated	Consoli dated*	Total	Testing parameter
Cylinder	PVC pipe	2" Dia. 4" H.	6	6	6	18	-Splitting tensile -Depth of penetration
Disk	PVC pipe	2" Dia. 1" H.	6	6	6	18	-Water vapor permeability -Porosity -Color change -Surface morphology
Cube	Wood	2" x 2" x 2"	3	3	3	9	-Frost resistance

Each set of molds was cleaned and then lubricated with mineral oil until they reached full saturation. Full saturation was determined when the molds started to reject absorbing more mineral oil.

Figure 4.1 – Lubricated Cylinder Molds.

Figure 4.2 – Lubricated Disk Molds.

Figure 4.3 – Lubricated Cube Molds.

4.3.1 Mock Up

Plaster by definition is a mixture of binder, aggregate, and water. To produce nearly identical samples throughout, the same formulation of 1 part binder to 5 parts aggregate to 1.3 parts water by volume was prepared under the same mixing procedures.

Samples were designed to have a lower binder to aggregate ratio that is the formulation was lean with more sand than originally used. This was done to create a friable mortar that simulated the weathered plaster found on the church today. The mortar analysis result in Table 4.1 indicates the weathered original plaster at the church contained approximately 1 part binder to 4 parts aggregate by weight, thus, the binder to aggregate ratio was adjusted to have lower cohesive strength (i.e., friability). The amount of water was also predetermined through workability tests. This was to introduce minimum water to prevent samples from shrinking while acquiring sufficient plasticity of the mixture. It was considered that an adequate workability or

plasticity was achieved when one could form a ball of the mixture by hand but the shape was breakable with a little pressure.

4.3.2 Ingredients

To recreate samples as close to the existing finish layer at the church, Type S hydrated lime and a local sand obtained from Tumacácori National Historical Park were used. Graymont Super Limoid's Mason's Lime is a dolomitic hydrated lime product defined as Type S according to ASTM C206 and C207.

Slaked lime putty was the traditional binder used during the Spanish Colonial period in the region and it usually obtained locally (Chan, 2015). At Tumacácori, the source of lime appears to have originated within the foothills and drainages on the west side of the Santa Rita Mountains, specifically from the area around Montosa Canyon (Graham, 2011). The lime was slaked on site as suggested by the lime kiln at the site. Recently the binder of the plaster was confirmed as a high-calcium, nonhydraulic lime with less than 5 % of Magnesium compounds (Highbridge Materials Consulting, Inc., 2014). However, owing to its limited availability Type S hydrated lime was used for the facsimiles. Although slaked lime and Type S hydrated lime possess almost identical chemical composition of calcium compound, their crystal morphology can vary based on the soaking period. Additionally it was considered using dolomitic lime could benefit identification of nanolime consolidant later on.

As change in color is one of objective that this thesis seeks, aggregate was chosen in consideration of grading and general color. Since it was difficult to find matching sand from the sand library at the ACL, local site sand was used for the facsimile samples. The color and grading was confirmed according to the mortar analysis result. In order to produce the same texture in

the facsimile samples particles larger than 2.36 mm (0.0937 in) were removed by sieving using ASTM sieve No.4 and No.8 to match the original aggregate used.

Chart 4.2 – Gravimetric Comparison of Original and Facsimile Sample Sand.

As lime gains plasticity during mixing, to obtain uniform properties throughout, samples were made using the determined ratio and ingredients above with a mechanical mixer, Hobart C-100, following the procedure specified in ASTM C305 – 14 - Standard Practice for Mechanical Mixing of Hydraulic Cement Pastes and Mortars of Plastic Consistency. Because capacity of the mixing bowl is limited to 5 qt, it was determined to separate batches by sample types/tests. As shown in Table 4.3, each batch yielded a different amount yet the same ratio of ingredients. Each batch was mixed mechanically following the procedure in the ASTM standard; however it should be noted that batch no. 3 was split up for mechanical mixing and then combined and completed by hand mixing in a larger container.

Table 4.3 – Amount of Ingredients and Mixing Method Used For Each Batches.

	Ratio	Batch 1	Batch 2	Batch 3
Type S Lime	1	1200mL	300mL	600mL
Aggregate	5	6000mL	1500mL	3000mL
Water	1.3	1600mL	400mL	800mL
Mold	-	Cylinder	Disk	Cube
Mixing method	-	Mechanical + Manual	Mechanical	Mechanical

4.3.3 Curing

Curing occurred using three procedures – wet curing, dry curing, and weathered surface simulation – in sequential order.

Wet curing allows the samples to set in the presence of moisture. Ultimately carbonation is a reaction of calcium hydroxide to carbon dioxide in air, however lime mortar needs some moisture to set (Lea, 1970). The two stage carbonation process of lime putty was provided in *Section 2.1 Materials and Construction Techniques of Spanish Colonial Architecture*.

Carbonation process of brucite ($Mg(OH)_2$), however is a more complicated chemistry. As the hydration and carbonation process is processed at a much slower rate than portlandite ($Ca(OH)_2$), depending on the moisture content of the material, as well as carbon dioxide and moisture content of the air, resulting compounds include periclase (MgO), brucite, magnesite

(MgCO_3), and a variety of hydroxycarbonates (i.e., hydromagnesite ($\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2 \cdot 4\text{H}_2\text{O}$), nesquehonite ($\text{Mg}(\text{HCO}_3)(\text{OH}) \cdot 2\text{H}_2\text{O}$), artinite ($\text{Mg}_2(\text{CO}_3)(\text{OH}) \cdot 3\text{H}_2\text{O}$), or dypingite ($\text{Mg}_5(\text{CO}_3)_4(\text{OH}) \cdot 5\text{H}_2\text{O}$)) (Hartshorn, 2012).

Once all the samples were prepared in designated molds, samples were covered with plastic wrap not touching any of the sample surfaces and stored in an indoor space that has a controlled environment of average 23.6 °C temperature and 48 % relative humidity.

During wet curing, disk samples and cylinder samples were laid vertically with their round shape surfaces facing top and bottom to help retain shape. After seven days in wet curing, the facsimile samples were introduced to the dry curing procedure. This process was simply conducted by removing the plastic wrap. To allow full carbonation from all surfaces of the samples, cube samples were demolded while disk and cylinder samples were laid horizontally. Curing of the samples was considered complete after 28 days of wet and dry procedures as per ASTM and to allow sufficient time to complete the thesis.

After allowing 28 days of curing, simulated weathering was applied by lightly brushing the sample surfaces with a natural bristle brush until they displayed the desired degree of surface friability. By removing surface concentrated lime laitance the samples were prepared to receive the nanolime consolidant much like the original plaster on site.

The labeling system was organized according to the sample types (disk/cylinder/cube), curing duration (no treatment/curing for 28 days/curing for more than a year) and sample number (1-6), as suggested in Table 4.4. Marking on the physical surfaces of the samples was avoided; instead predesigned contact sheets were printed and used for the purpose of identification.

Table 4.4 – Sample Labeling System.

	Cylinder	Disk	Cube
Control	A1-A6	D1-D6	G1-G3
Thesis	B1-B6	E1-E6	H1-H3
Post thesis	C1-C6	F1-F6	I1-I3

Overall comparison in terms of porosity, color, grading of aggregate between facsimile samples and original exterior plaster was provided in APPENDIX C.

4.4 Consolidation

4.4.1 Application Technique

To avoid the consolidation treatment accumulating on the contact surface or forming a lime concentrated film on the surfaces during evaporation, samples were placed on a wire rack that has a 3/4 inch gap between wires during consolidation. The full application process was conducted in the laboratory under a controlled temperature of 18.6 ± 1.0 °C and relative humidity of 42 ± 7 %.

The general amount of consolidant required to treat the various samples for each application to saturation was predetermined by the results of liquid water absorption via total immersion test. By allowing the facsimile samples to be immersed into a water bath until no further weight gain was observed, the maximum amount of consolidant needed was calculated. As pure water has a density of 1 g/ml at 4 °C, weight gain by water absorption was considered equal to the volume of pores that could be filled with an equal volume of consolidant. However because untreated plaster samples were susceptible to total immersion liquid water, the actual

amount of consolidant was adjusted as needed. Particularly, as consolidation proceeded, the samples took slightly less consolidant than expected.

Table 4.5 – Water Immersion Test Result and Actual Amount of Consolidant Used.

	Cylinder	Disk	Cube
Water absorption (ml)	47	8.5	30
Applied amount of consolidant (ml)	40 – 50	8 – 10	28 – 30

Each cycle of applications was conducted using a 1 inch wide natural bristle brush. A predetermined amount of evenly dispersed consolidant was poured into a 50 ml polypropylene tri-cornered beaker and the brush was dipped into the consolidant and applied to the samples. Consolidant was applied to the curved face of the cylinder first, to the top and bottom circular faces of the disks, and to all faces of the cubes. After applying the consolidant, the excess was immediately blotted and the samples placed in a humid environment that was created by using a plastic wrap tent. Since nanolime consolidants use a short-chain alcohol as a solvent, when evaporation occurs too rapidly, nanolime particles can be pulled up as alcohol evaporates. Thus, to mitigate the rapid evaporation rate of ethanol and allow the nanolime particles to sufficiently penetrate into the sample, treated samples were covered with a plastic wrap tent. This was also to avoid superficial carbonation, which may cause a white haze to form on the surface (Peterson, 1981). At least 24 hours of slow evaporation was allowed between each application cycle.

<p>a. Consolidation of the samples started with removing loose particles by light surface brushing.</p>
<p>b. Nanolime product was applied to the top and bottom surfaces of the disk samples by allowing product to be absorbed via brushing.</p>
<p>c. Excess nanolime on the sample surfaces was immediately blotted.</p>

Figure 4.4 – Photographic Recording of Consolidation Processes.

4.4.2 Consolidant

The selected commercial nanolime consolidant used in this thesis was CaLoSiL[®] produced by IBZ-Salzchemie GmbH&Co. KG and obtained through the North American distributor, Talas. The selection was made after consulting with Dr. Gerald Ziegenbalg, the director of the IBZ in consideration of accessibility to products in the United States. Research suggests the solvent carriers (ethanol, iso-propanol, or n-propanol) have a little influence on the performance of the consolidant (Ziegenbalg et al., 2010; Slížková and Frankeová, 2012; Pesce, 2013). However, as ethanol based nanolime seems to penetrate quickly and uniformly than others because of a lower molecular weight (D'Armada and Hirst, 2012), CaLoSiL[®] E-5 and CaLoSiL[®] E-25 were chosen for the thesis.

For an accurate evaluation, using fresh nanolime products has been recommended. During the thesis research it was discovered that the nanolime obtained were older than additional product obtained from the manufacturer. This was initially of some concern as some researchers have described performance of the commercial nanolime as a function of product age by suggesting use within 3-5 months unless refrigerated (Ziegenbalg et al., 2010; D'Armada and Hirst, 2012; John Fidler, per.comm., April 3, 2016; Catherine Myers, per.comm., January 28, 2016). However, it was confirmed by the manufacturer that the products obtained in the US were manufactured after 2013, when an improved synthesizing process was introduced and the consolidating quality can be insured by taking an additional shaking step for even dispersion prior to use (Ziegenbalg, per.comm., January 5, 2016, April 11, 2016).

Following Table 4.6 is showing a list of information of obtained nanolime products.

Table 4.6 – Manufactured Date of the Products.

Product	Size	Obtained from	Date Written on the Container
CaLoSiL® E-5	1L	Talas, US	April 17, 2015
CaLoSiL® E-25	500mL	Talas, US	October 4, 2013
CaLoSiL® E-25	1L	IBZ- Salzchemie GmbH&Co. KG, Germany	May 16, 2016

The consolidation process was applied with 1 application of pre-consolidation with a low concentrated nanolime, CaLoSiL® E-5, followed by 2 applications with a higher concentration of nanolime, CaLoSiL® E-25, followed by 28 days of curing.

Chart 4.3 – Particle Size Distribution.

Chart 4.3 was reproduced by the author based on the particle size distribution data obtained from the manufacturer. Nanolime particles in ethanol generally range between 50 nm and 250 nm. A better consolidating effect was expected from a multiple applications of CaLoSiL® E-25. However as the lower concentration of the product has a higher concentration of the finer particles, greater depth of penetration of nanolime was expected by pre-consolidation using CaLoSiL® E-5.

As discussed earlier in *Section 3.3 Characterization of Nanolime Consolidant*, relative humidity can affect the carbonation rate and agglomeration of nanolime (Lea, 1970; Gómez-Villalba et al. 2011; Lopez-Arce et al, 2010; Lopez-Arce et al 2011; Lopez-Arce, 2013) and slow drying and curing in slightly damp conditions optimizes carbonation of the consolidant (Henry and Stewart, 2012). Therefore the samples were damp cured after treatment in a humid environment chamber. Three chambers in total were used to cure samples by specimen type. To maintain moisture content in the chamber in a range of 60 ± 10 % relative humidity, moisture was provided by filling a bottom shelf with water, whereas to keep humidity from increasing higher than 70 %, the door of the chamber was partially opened.

Figure 4.5 – Controlled Environment Curing Chambers.

4.5 Testing Techniques

The objective of laboratory based evaluation and analysis was to determine the properties and performance of friable lime plaster and to assess to what extent the nanolime consolidant improved the surface cohesion without altering critical properties. Following standardized guidelines, the commercial nanolime consolidant was evaluated based on its compatibility with the original plaster. The testing matrix was designed based on previous technical literature on evaluation of masonry consolidants in general and nanolime specifically.

Performance of the consolidant was evaluated by degree of increase in strength. Physical Compatibility was determined through porosity/permeability, water vapor transmission, and

color change while chemical compatibility was observed via depth of penetration and morphological analysis using transmitted light microscopy and scanning electron microscopy on thin sections and cross sections. Durability was measured using frost resistance.

CHAPTER 5. Laboratory Testing

5.1 Splitting Tensile Strength

5.1.1 Method

Sample strength was measured as splitting tensile strength of cylindrical specimens. Also known as the Brazilian test, the method was invented by Fernando Carneiro (Fairbairn and Ulm, 2002). By using cylindrical specimens subjected to compressive forces, the method provides a simple and inexpensive yet reliable way to measure compressive and calculate tensile strength (Schork et al., 2012). The splitting tensile strength was determined by applying a diametral compressive force along the length of the sample at a constant rate. Generally, the splitting tensile strength is greater than direct tensile strength but lower than flexural strength. As a typical stress-based fatigue performance, flexural strength is the stress developed in a specimen just before it cracks or breaks in a flexural test (Mandal et al., 2016; *Flexural Strength*, 2016). Tested with the three point loading method, the strength is reported as modulus of rupture, or Young's modulus.

Cylindrical samples of 2" diameter and 4" in height were tested using an Instron Electromechanical Testing Machine - Model 4206 at the Laboratory for Research on the Structure of Matter (LRSM) at the University of Pennsylvania. The use of the machine as well as the interpretation of the testing results were performed under the supervision of Dr. Alex Radin at the Mechanical Testing Service Facility.

Figure 5.1 – Instron Testing Machine.

5.1.2 Procedure

The procedure and calculations followed ASTM C496/C496M – 11 - Standard Test Methods for Splitting Tensile Strength of Cylindrical Concrete Specimens.

Using a digital caliper, three diameters and two lengths of each cylindrical sample were measured. The diameter and length of the samples were determined to the nearest 0.01" by averaging three diameters and to the nearest 0.1" by averaging two lengths. The sample was then loaded on the stage horizontally, and centered at the midpoint. The upper loading unit had a rounded tip 1/4" in diameter and 4" in length. In order to hold the sample in place negligible amount of preloading was applied.

Although the ASTM standard specifies the use of thin plywood bearing strips on the top and bottom of the specimen to distribute the applied load, this procedure was rejected. Because the length of loading the upper loading blade covered the total length of the cylindrical sample, plywood strips were not needed to distribute the load. Additionally it was determined that testing could be disturbed by the plywood strips absorbing the load.

Constant rate of load was applied until failure was observed. The failure was determined when the maximum load was reached. Often fracture was evident when it failed, as further loading can lead to a false result, apparent fracture was not necessarily observed during the test.

Figure 5.2 – Loading Unit of the Machine

Figure 5.3 – Splitting Behavior of the Sample

5.1.3 Calculation

The following is the calculation used to determine the splitting tensile strength of each samples.

$$T = \frac{2P}{\pi ld}$$

Where:

T = splitting tensile strength (psi)

P = maximum applied load (lbf)

l = length (in)

d = diameter (in)

5.2 Porosity

5.2.1 Method

Various direct and indirect measuring methods are available to examine porosity and porosimetry of building materials. In particular, water absorption (Maryniak-Piaszczyński and Ziegenbalg, 2010; Maryniak-Piaszczyński et al., 2012; Bengtsson, 2012; Deahne and Herm, 2013) and mercury intrusion methods have been favored in previous technical researches (Moreau et al., 2010; Booth et al., 2012; Slížková and Frankeová, 2012; López-Arce et al., 2013; Rodríguez et al., 2013; Barberena-Fernández et al., 2014; Ruffolo et al., 2014; Arizzi et al., 2015; Slížková et al., 2015). Although the mercury intrusion method allows accurate measure of the total porosity and pore size distribution it is highly hazardous and was rejected as the method of choice in this thesis. Water absorption was also avoided because the friable characteristics of the samples rendered them vulnerable in water.

Ultimately, the apparent porosity of specimens was measured using liquid nitrogen. The liquid nitrogen method follows ASTM C830 – 00 - Standard Test Methods for Apparent Porosity, Liquid Absorption, Apparent Specific Gravity, and Bulk Density of Refractory Shapes of Vacuum Pressure. As liquid nitrogen is very inert and stays cold in a liquid state at 77 K (-195.79 °C or -320 °F), the method was useful in measuring the porosity of friable plaster samples. Additionally this method was considered fast and more accurate than water absorption, affordable, and less hazardous than mercury intrusion.

Figure 5.4 - Set up for Porosity Test using Liquid Nitrogen.

The experiment was conducted at the Merck High Throughput Experimentation Laboratory at the Chemistry Department at the University of Pennsylvania, with assistance of the lab director, Dr. Simon Berritt. The equipment and tools used included a Satorius electronic balance with an under-hook, a lab timer, a Swiss Boy lab jack, a custom made work station, a Dewar container that has an opening wider than the width of the samples, an AWG Gage-22 copper wire, and plastic zip ties.

5.2.2 Procedure

The procedure and calculation of this method generally followed ASTM C830 – 00 - Standard Test Methods for Apparent Porosity, Liquid Absorption, Apparent Specific Gravity, and Bulk Density of Refractory Shapes of Vacuum Pressure. The test started with drying the disk samples (D and E series) in a drying oven at 60 °C until the weight was consistent. As excessive drying temperature can alter microstructure of the lime based samples (Boutouil and Levacher, 2002), the temperature of the drying oven was carefully monitored. Dried samples were then placed in a desiccator and cooled at room temperature.

The proper immersion time was predetermined using dummy samples that had the same shapes as the testing cohorts. The immersion test was performed in 5 minute increments to 30 minutes. Ultimately 10 minute immersion was selected, when suspended samples gained the most weight. To reduce abrupt change in temperature of the samples when they were introduced to liquid nitrogen, samples were suspended for 10-20 seconds prior to immersion. As the specific gravity of the liquid nitrogen can changed during the procedure due to evaporation, or contamination with foreign material, the condition of the liquid nitrogen was monitored during the entire process. All measuring was conducted on the samples using a hanging device made of a plastic tie.

5.2.3 Calculation

The apparent porosity was determined using the following calculation suggested in the ASTM

C830 standards:

$$\text{Volume of open pores (cm}^3\text{)} = \frac{(W - S)}{\text{density of liquid}}$$

$$\text{Volume of impervious portions (cm}^3\text{)} = \frac{(D - S)}{\text{density of liquid}}$$

$$P (\%) = \frac{W - D}{W - S} \times 100$$

Where:

P = apparent porosity (%)

W = saturated weight (g)

D = dry weight (g)

S = suspended weight (g)

5.3 Permeability

5.3.1 Method

The water vapor transmission and permeance test measures the amount of water vapor that flows through two parallel surfaces of a material with a known thickness during a unit of time. This method uses the flow of water vapor that results from different unit vapor pressure between air facing and water facing surfaces of the samples. Water vapor may move via pores and voids of the sample. The obtained data allows the analysis of the behavior of vapor water in the samples. A reduction in permeability could influence behavior of original material as well as the entire building assembly and cause water entrapment and subsequent decay, thus change in permeance is undesirable. This method was used to determine whether consolidation might cause a change in permeance.

Samples used for the test were disks, 2" in diameter and 1" in height.

5.3.2 Procedure

This test followed ASTM E96/E96M – 16 - Standard Test Methods for Water Vapor Transmission of Materials. The disk samples were dried in a drying oven at 60 °C until a consistent weight was achieved. Dried samples were then placed in a desiccator and cooled at room temperature for an hour. The circumference of disk samples was lined with 1" Scotch® Super 88 Premium Vinyl Electrical Tape to prevent leakage along the circumference of the samples when mounted in their containers. The samples were set on the inner rim of a 100 ml polypropylene tri-cornered beaker containing cotton balls soaked in 30ml of deionized water. By using water soaked cotton balls, this prevented having liquid water directly in contact with the sample's test area or

condensation on the bottom face of the sample. To allow water vapor transmission only through two parallel surfaces of the samples, airtight testing assemblies were created by sealing the gap between the sample and beaker with heated paraffin wax.

The assembled beakers were then placed in a desiccator equipped with hygrometers. To maintain a constant relative humidity of $50 \pm 2\%$ in the standard, the bottom pan of the desiccator was filled with anhydrous calcium sulfate desiccant. The assembly was weighed every 10 minutes for the first 30 minutes, every hour for the next 6 hours and every 24 hours following from the initial start time until the 21st day of the cycle was completed.

Figure 5.5 – Water Vapor Transmission Test Chamber.

5.3.3 Calculation

The rate of water vapor transmission is calculated as follows:

$$WVT = \frac{G}{t} A = (G/t) / A$$

Where:

WVT = rate of water vapor transmission ($g/h \cdot m^2$)

G = weight change (g)

t = time during which G occurred (h)

A = test area (cup mouth area, sample area) (m^2)

Permeance of the samples were determined as follows:

$$Permeance = \frac{WVT}{\Delta p} = \frac{WVT}{S(R_1 - R_2)}$$

Where:

Δp = vapor pressure difference ($mm\ Hg$)

S = saturated vapor pressure at test temperature ($mm\ Hg$)

R_1 = relative humidity at the source expressed as a fraction

R_2 = relative humidity at vapor sink expressed as a fraction

Saturated vapor pressure is calculated as follows:¹

$$e_s = 6.11 \times 10^{\left(\frac{7.5 \times T}{237.3 + T}\right)}$$

Where:

e_s = saturated vapor pressure (mb)

T = air temperature (°C)

The conversion of unit of millibars (mb) to millimeters of mercury (mmHg) as follows:

$$P_{mmHg} = 25.4 \times P_{inHg} = \frac{25.4}{33.8639} \times P_{mb}$$

Where:

P_{mmHg} = vapor pressure (mmHg)

P_{inHg} = vapor pressure (inHg)

$P_{mb} = e_s$ = vapor pressure (mb)

When the test specimen is homogeneous and has a thickness no less than 1/2" average permeability is:

$$\text{Average Permeability} = \text{Permeance} \times \text{Thickness}$$

¹ Saturated vapor pressure and unit conversion calculation formula are each based on "Vapor Pressure," <http://www.srh.noaa.gov/images/epz/wxcalc/vaporPressure.pdf>. (accessed April 18, 2016)
"Pressure Conversion," <http://www.srh.noaa.gov/images/epz/wxcalc/pressureConversion.pdf>. (accessed April 18, 2016)

5.4 Color change

5.4.1 Method

As lime plaster often is pigmented or finished with a decorative layer, aesthetic changes and especially white hazing is an undesirable change often resulting from consolidation. To assess the impact of the consolidant on the appearance of the plasters, color change was measured and evaluated. Since the color measurement could be biased from sources such as viewer, light source, surface texture and test area, in order to reduce possibilities of errors, a handheld colorimetric spectrophotometer, a Konica Minolta Spectrophotometer CM-2500d, was used to obtain the colorimetric data. The data was obtained under daylight illuminant of D65 in the CIE L*a*b color system at a 10 degree angle of observation.

Before and after consolidation measurements of the disk samples were used for the analysis and the data was graphically depicted using color data software *SpectraMagic NX*.

5.4.2 Procedure

The color data was measured before treatment and after 28 days of curing of treatment application. However it should be noted that the number of color measurements was not equal. Specifically, the color data from before treatment was obtained from the center of the top surface, whereas the color data after treatment was measured from 3 random spots of the disk samples including the center of the top surface that was previously measured. Ultimately, 3 readings from the after treatment were averaged for the comparison purpose.

SpectraMagic NX provided the calculated value of color difference, chroma, white index, yellow index, and brightness. Calculations for the evaluation followed guidelines, ASTM D2244 –

15a - Standard Practice for Calculation of Color Tolerances and Color Differences from Instrumentally Measured Color Coordinates, and ASTM E313 – 15 - Standard Practice for Calculating Yellowness and Whiteness Indices from Instrumentally Measured Color Coordinates.

5.4.3 Calculation

Color difference is calculated as follows:

$$\Delta E = \sqrt{[(\Delta L)^2 + (\Delta a)^2 + (\Delta b)^2]}$$

Where:

ΔE = color difference

ΔL = the difference in the luminosities

ΔE = the difference in the green – red scale

ΔE = the difference in the blue – yellow scale

Equation for the whiteness index as follows:

$$WI = Y + (WI, x)(x_n - x) + (WI, y)(y_n - y)$$

Where:

WI = whiteness index

Y, x, y = the luminance factor and the chromaticity coordinates of the specimen

WI, x and WI, y = numerical coefficients ²

x_n and y_n = the chromaticity coordinates for the CIE standard illuminant and source used

² Coefficients given in Table 3 in ASTM E313 – 15 Standard Practice for Calculating Yellowness and Whiteness Indices from Instrumentally Measured Color Coordinates.

5.5 Frost Resistance

5.5.1 Method

Long term performance of the consolidant was evaluated by its resistance to freeze and thaw cycling. The frost resist test measures a materials' performance during freezing and thawing cycles and indirectly analyzes durability. Although Mission San José de Tumacácori does not exist in a freezing environment, the test was conducted to determine general resistance to stress cycling.

2" cube samples of control (G series) and consolidated (H series) samples were used for the testing.

5.5.2 Procedure

The test generally followed guidelines outlined in RILEM V.3 – Frost Resistance with some modification. Modification included change in sample dimensions, performance of longitudinal fundamental resonance frequency, thawing temperature, and the number of cycles and weighing. Especially, as the standard was created based on stone materials, plasters are inherently more vulnerable to the type of extreme weathering environment, and measurement of apparent volume could only be conducted after 4 cycles.

The 2" cube samples were dried in a drying oven at 60 °C until a consistent weight was achieved. The samples were transferred to a desiccator and cooled at room temperature. To aid weighing procedures later on, samples were loosely tied with plastic zip ties. The samples were placed in a wire basket to allow the samples not to touch each other and avoid damage from handling. For the initial 6 hours, the prepared samples were placed in a container that allowed

the dry samples to be fully immersed in deionized water at 20 °C. After 6 hours the samples were removed from the water bath and weighed in the air and in the water. Each cycle was considered complete after 6 hours of freezing in the freezing cabinet at -15 ± 2 °C followed by 6 hours of thawing in the water bath at 20 ± 2 °C. The testing was conducted for a total of 8 cycles, however, measurement was only conducted after 4 cycles due to disintegration of samples during measurement after 8 cycles.

5.5.3 Calculation

Remaining bulk volume of the samples after n cycles is determined as follows:

$$V = Ma_n - Me_n$$

Reduction of volume of the samples in percentage after n cycles is calculated as follows:

$$V \text{ in } \% = \frac{[(Ma_0 - Me_0) - (Ma_n - Me_n)]}{(Ma_0 - Me_0)} \times 100$$

Where:

n = number of cycles

Ma_0 = mass of the specimen in the air after 6 hours of immersion

Me_0 = mass of the specimen in the water after 6 hours of immersion

Ma_n = mass of the specimen in the air after n cycles

Me_n = mass of the specimen in the water after n cycles

5.6 Analytical Analysis

5.6.1 Sample Preparation – Thin-section

Two cylinder samples saved from the splitting tensile strength test were sent to National Petrographic Service, Inc., in Houston, Texas, to create thin-sections. Two samples, one control and one consolidated, were considered most representative of the cohorts, based on splitting tensile strength, texture and appearance. In order to aid analysis, an entire section from the surface to the core was made in 50 x 76 mm (2"x3") slides. As the cylinder samples were made to have 2" diameter, a full circular section was able to be conveyed in a larger slider. To better identify pore structure in the cross section, the samples were vacuum-impregnated with a blue epoxy resin which has an approximate refractive index of $n_D = 1.54$. No staining or microprobe polishing was requested. For better visibility under optical microscopes the thin sections were requested to be permanently cover slipped. In the meantime the billets that were epoxy impregnated and left after thin sectioning were saved and became useful specimens for the SEM-EDS element mapping.

5.6.2 Optical Microscopy

Optical and petrographic analysis was conducted on thin sections to examine internal structure and mineralogical behavior of the samples of the consolidant. As the major interest was on the effect of the nanolime as a consolidant, rather than the aggregates, the analysis was focused on identifying and differentiating the groundmass of the specimens, namely the paste and the voids in terms of alteration before and after consolidation.

The analysis was conducted in number of sessions to confirm findings and observation. After preliminary visual analysis by the author, the thin sections were brought to the Penn Museum's Center for the Analysis of Archaeological Material and examined by Dr. Marie-Claude Boileau using a compound transmitted Zeiss AX 10 microscope. The thin sections were also examined by Professor Frank Matero in the Architectural Conservation Laboratory on a Nikon Aplanaphot-2 microscope that is retrofitted to generate a pseudo-dark field that allows for a thin-section to be viewed as if it was in reflected light (Chan, 2015) and a Leica MZ 16a stereomicroscope with a transmitted light setting. For final confirmation, the thin sections were viewed under microscope after SEM-EDS element mapping.

5.6.3 Scanning Electron Microscopy

Using tools that allow investigation at the nanoscale level were essential in this thesis, as nanolime consolidant is composed of nanoscale particles. Therefore, a microscopic study of the consolidating product and the possible changes from consolidation was conducted using Environmental Scanning Electron Microscopy (ESEM) and the consolidant's depth of penetration using Energy-dispersive X-ray Spectroscopy (SEM-EDS). The ESEM is a powerful analytical technique that can capture images on topographic, morphologic, compositional and crystalline structural information of the material.

By using electron beams instead of using visible transmitted or reflected light, the scanning electron microscope detects different reactions of the sample to the beams and raster scans the signal of emitted electrons and photons from the sample. The relation between type of information and signal is suggested in Table 5.1 as follows:

Table 5.1 – Information from Different Signal Detection.

Signal	Information
Secondary Electrons	Topographical analysis
Primary Backscattered Electrons	Compositional analysis
X-rays	Elemental analysis
Auger Electrons	Compositional analysis
Cathodoluminescence	Internal characteristics

The investigation was performed using a FEI Quanta 600 FEG Mark II Environmental Scanning Electron Microscope facilitated at the Singh Center for Nanotechnology at the University of Pennsylvania. The obtained information was further analyzed with the XT Microscope Control Software and the TEAM™ EDS Analysis System for the SEM. The equipment was operated under the Low Vacuum mode with the backscattered electrons detector, the Large Field Detector (LFD), and the EDX detector plugged in. Using the LFD would allow to use samples that have wet and nonconductive nature and image samples in gaseous atmosphere, by using water vapor. The setting used for the examination was 10.00 Kv of high voltage, 0.53 Torr of chamber pressure. Magnification and the spot size varied depending on the interests.

In this research three types of electronic reactions of primary backscattered electrons, secondary electrons, and X-rays were examined and the X-rays analysis was supplemented by SEM-EDS elemental mapping. Depending on the purpose of the analysis, physical samples and billets saved from thin-sectioned samples prepared as explained in Table 5.2 were used. Each control and consolidated representative samples from cohorts were selected.

Table 5.2 – Sample Type and ESEM Evaluation.

Sample	Purpose	Source detection
Disk	<ul style="list-style-type: none"> · Surface topography · Morphological change 	<ul style="list-style-type: none"> · Secondary Electrons · Primary Backscattered Electrons
Billet	<ul style="list-style-type: none"> · Depth of penetration · Nanolime consolidate deposit 	<ul style="list-style-type: none"> · Primary Backscattered Electrons · X-rays

The equipment was operated by the author under guidance of Jamie Ford, a staff scientist of the Nanoscale Characterization Facility at the University of Pennsylvania.

Measuring Depth of Penetration

The Elemental Mapping and Linescan functions that TEAM™ software offers were used to determine the depth of penetration. Elemental data and images of the flat surface of the billet samples were first obtained using the Multifield Analysis function in the software. The multifield analysis allowed data to be obtained at the identical setting. Despite powerful imaging ability, analysis takes a longer time to obtain higher resolution images across a 2" long section, therefore the decision was made to analyze in lower magnification on a series of lower magnification images. As a result, a total of 19 images in 64x50 resolution were captured with a dwell time of 1000 μ s at the magnification of 75x. Images were manipulated using Adobe Photoshop CC 2015.

Once the images were obtained, the software's built-in function of Linescan was used to quantify the amount of calcium every 50 μ m across the 2" section.

5.7 Statistics

A paired t-test was used to statistically determine the significant difference between the average values of unconsolidated and consolidated sample cohorts for each test. This was based on the statistical evaluation of the null hypothesis assuming the mean of two paired samples was equal. The null hypothesis could be accepted or rejected via calculation. Though the calculation was conducted using a t-Test: Paired Two Sample For Means on Microsoft Excel add-in, Data Analysis ToolPak, mathematical calculation follows below.

$$S_D = \sqrt{\frac{\sum d^2 - \frac{(\sum d)^2}{n}}{n - 1}}$$

Where:

S_D = standard deviation

d = difference in value

n = sample size

$$t_{calculated} = \frac{\bar{d}}{\frac{S_D}{\sqrt{n}}}$$

Where:

$t_{calculated}$ = calculated t value

$\bar{d}$ = mean value of d

The calculated t value was compared with the tabulated t value at 95 % confidence level at 5 degrees of freedom. If the calculated t value is bigger than the tabulated t, the null hypothesis was rejected and there was significant mean difference between the two paired samples.

$$t_{calculated} > t_{tabulated} (95\%)$$

As consolidation can either significantly decrease or increase the given properties of facsimile samples, t value was specifically compared with t value of two-tailed reference.

For interpretation purposes, the p-value that was provided via Data Analysis ToolPak was also seen. The p-value is the probability of obtaining results or the significance level of the test. The p-value ranges from 0 to an absolute value of 1, where 1 indicates 100 % probability. Therefore at 95 % confidence level, when the p-value is less than 0.05 the null hypothesis is rejected.

5.8 Photography

Overall photographic recording of the samples was conducted. The equipment used included a copy stand with two mounted quartz tungsten halogen lamps, a DSLR camera Canon 450D, a light shed, and a sample tray. The copy stand was equipped with a non-reflective baseboard, a height adjustable camera arm with two lighting units mounted with a width of 47" at an angle of 45 degrees from the center of the baseboard. A scale card, a QP101 calibration card, and a X-Rite Colorchecker card were placed on the sample tray.

The camera setting was fixed at ISO 100, an aperture of 11 F with a time setting of 1/60 throughout the recording process. The lighting was only provided by two halogen lamps at the copy stand, which maintains 300 W intensity and 3200 K color temperature. Samples were photographed individually to provide comparison of the top face between samples rather to record samples from different angles. Photographs were saved as RAW format and only lens distortion and white balance were adjusted in Photoshop CC 2015 for comparison purpose. A complete set of photographs of the samples during the consolidation process is provided in APPENDIX D.

Figure 5.6 – Copystand with All Equipment Set for Photographs.

Figure 5.7 – Sample Tray.

CHAPTER 6. Observations

6.1 Splitting Tensile Strength

Nanolime consolidation resulted in increased splitting tensile strength of the friable lime plaster samples. The average splitting tensile strength of the control cohort and consolidated cohort is provided in Table 6.1. Chart 6.1 compares the mean value of the splitting tensile strength of the control samples (A1-A6) and consolidated samples (B1-B6). One application of E-5 and 2 applications of E-25 showed approximately 45 % increase in splitting tensile strength after a minimum of 28 days of curing of the nanolime consolidant.

The change is also confirmed statistically significant. The two-tailed p-value from the paired t-test is 0.0165, which is lower than the value of 0.05. This rejects the null hypothesis that two mean values are identical, which confirms there was an improvement in splitting tensile strength.

Chart 6.1 – Splitting Tensile Strength.

Table 6.1 – Splitting Tensile Strength Test Result.

	Control (A)	Consolidated (B)
Mean of Maximum Load (lbf)	86.51	125.10
Mean of Splitting Tensile Strength (psi)	451.27	654.74
Standard deviation of Splitting Tensile Strength (psi)	90.48	99.79

6.2 Porosity

Liquid nitrogen is a lighter material than water. At 68 °F (20 °C), when water has a specific gravity of 1, specific gravity of liquid nitrogen (N₂) is 0.808. Though detailed pore distribution cannot be measured using this method, it allowed to distinguish pervious and impervious portion of the sample.

Nanolime consolidation appears to have had little to no impact on the pore structure of the lime plaster samples. As shown in Chart 6.2, the mean porosity value of the control cohort and consolidated cohort was almost identical, but the standard deviation was slightly increased in the consolidated cohort. The same patterns were seen in Chart 6.3, which compares the volume of open pores and impervious pores.

No obvious change in pore structure was observed from the test. The two tailed p-value of the porosity, volumetric change in open pores and impervious pores were each 0.76, 0.50, 0.53, which were larger than 0.05. Therefore the null hypothesis was accepted. This implied that the result was statistically not significant at 95 % confidence level, and the change in the pore system was negligible.

Chart 6.2 – Porosity.

Chart 6.3 – Proportion of Open and Impervious Pores.

Table 6.2 – Liquid Nitrogen Test Result.

		Control (D)	Consolidated (E)
Porosity (%)	Mean	22.75	22.55
	Standard Deviation	0.73	1.65
Volume of Open Pores (cm ³)	Mean	8.57	8.60
	Standard Deviation	0.24	0.72
Volume of Impervious Portions (cm ³)	Mean	29.12	29.53
	Standard Deviation	0.85	1.37

6.3 Permeability

Water vapor transmission was continued for a total of 21 days with the testing chamber controlled to maintain an average temperature of 20.7 ± 2.1 °C and a relative humidity of 50.6 ± 4.5 %.

As seen in Chart 6.4, the weights of the samples increased for approximately 24 hours and equilibrated between 24 and 48 elapsed hours. Once equilibrium was reached, the weight of all the samples continued to decrease to the end of the test. The decreasing slopes in Chart 6.4 depict the average weight decline rate of the control and consolidated cohorts. These appear to be almost identical suggesting no change in permeability between the treated and untreated samples.

Chart 6.4 – Average Weight Change of Cohorts.

The following Table 6.3 presents the average temperature and relative humidity of the testing chamber, which was recorded at 20.7 °C and 50.6 %. At 20.7 °C, the saturation vapor pressure was 18.31817 mmHg. The relative humidity of the dish (R_2) was 100 %, the testing chamber's relative humidity (R_1) was 50.6 %.

Table 6.3 – Average Condition of the Testing Chamber (Desiccator).

	Temperature (°C)	Relative Humidity (%)	S (mmHg)	$R_1 - R_2$
Average condition	20.7	50.6	18.31817	0.49

The average surface area and thickness of the control and consolidated cohorts were identical at 0.00207 m² and 0.01817 m.

Table 6.4 – Average of the Sample Size.

	Control (D)	Consolidated (E)
Average surface area (m ²)	0.00207	0.00207
Average thickness (m)	0.01817	0.01817

Table 6.5 presents the calculated value of water vapor transmission, permeance, and average permeability of each samples. Due to the equilibration period during the first 12 hours, the weight change value was obtained from the difference between measurements taken at 428 elapsed hours and 48 elapsed hours. Though the actual weight change value is negative, for the purpose of evaluation, the value was converted to an absolute value.

Table 6.5 – Water Vapor Transmission Test Result.

		Control (D)	Consolidated (E)
WVT ($g/h \cdot m^2$)	Mean	1.62E-05	1.59E-05
	Standard Deviation	5.03E-07	8.92E-07
Permeance	Mean	1.81E-06	1.77E-06
	Standard Deviation	5.61E-08	9.93E-06
Average Permeability	Mean	3.28E-08	3.22E-08
	Standard Deviation	1.02E-09	1.80E-09

The paired t-test was conducted to evaluate statistical significance of water vapor transmission, permeance and average permeability between the control and consolidated cohorts. The two-tailed p-value of all three tests were identical as 0.329884, which is larger than 0.05 of the confidence level. Therefore, the difference between two cohorts is statistically not significant which indicates the nanolime consolidant did not impact the water vapor transmission of the plaster samples.

6.4 Color Change

While a number of articles reported a white hazing effect from the nanolime consolidant, most of them examined the degree of whitening effect through visual inspection. Acknowledging the possibility of white hazing from nanolime consolidation, researchers have attempted to incorporate different aspects of color data to quantify degree of color change including whitening, yellowing, and brightening. However, this has been limited to the colorimetric modification degree of the stone materials consolidated with nanolime (Zornoza-Indart et al., 2012; López-Arce et al., 2013).

The results of color evaluation using spectrophotometry measurements are provided in the Table 6.6. The table shows color evaluation of each sample before consolidation and 28 days after consolidation as well as that of each cohort. For evaluation purposes, the samples before consolidation treatment were set as the target and the very same samples after consolidation were set as the sample. Therefore, the value provided in Table 6.6 shows the degree of spectrophotometric change based on the readings conducted on the samples before consolidation. The detailed information regarding each color measurement can be found in the APPENDIX C.

Based on Table 6.6, the color difference data was analyzed in two phases, firstly, color changes between the before and after consolidation treatment and secondly, color changes in relation to the natural behavior of the lime binder.

The data obtained from the unconsolidated samples, labeled as D series, appeared to have slight spectrophotometric changes. A slight increase in total color (ΔE_{SCI}) was observed without evidence of gloss change (value difference between ΔE_{SCI} and ΔE_{SCE}), while the

chroma ($\Delta Tint$), the white index (ΔWI), and the brightness (ΔB) parameters were decreased. Especially the white index was decreased up to a value of -18.14. The brightness also decreased but not as great as the white index. Meanwhile the yellow index value was increased slightly.

The consolidated samples of series E and F appeared to have barely increased in value of total color (ΔE_{SCI}), chroma ($\Delta Tint$), and brightness (ΔB). Any glossy texture or film forming was not detected in terms of visual inspection or the value difference between ΔE_{SCI} and ΔE_{SCE} . However, the increase in white index (ΔWI) and the decrease in yellow index (ΔYI) were observed. The trend of change in the white and yellow index was very different from the trend observed from the unconsolidated samples, which must be the result of introducing nanoparticles of lime to the samples.

According to the before-after treatment observations of facsimile samples series D, E, and F, spectrophotometry patterns showed a direct relationship between white index and brightness whereas an inverse relationship between white index and yellow index. Though 28 days is a limited window to rationalize the color changing pattern over time, the general trend of change observed from the testing can be summarized as follows.

Lime based plaster samples lost the whiteness and brightness but became yellowish after curing was completed. Based on observation and known properties of the samples, yellowing could be the result of samples revealing the incomplete carbonated binding medium while losing surface calcium carbonate particles, or aging of calcium carbonate particles. Meanwhile, the consolidated samples' increased value in white index and brightness, and decreased value in yellow index indicate the spectrophotometric change caused by the nanolime consolidant. Although the absolute value of the change was slight in comparison to unconsolidated samples,

it was clear that nanolime consolidation can cause the surface to become whiter. It was also statistically confirmed that the color change in terms of white index, yellow index, and brightness between consolidated samples and unconsolidated samples is significantly different.

However, it should be also noted that while the nanolime consolidant may have only a slight modification on whiteness of the surface, as the lime binder tends to become darkened over time, the whitening effect can be better seen in comparison to aged lime based plaster to consolidated plaster. Nevertheless the final appearance is similar to the original appearance of the decorated plaster.

Table 6.6 – Color Change Value of Samples (before-after).

Before	After	ΔE_{SCI}	ΔE_{SCE}	$\Delta Tint$	ΔWI	ΔYI	ΔB
D1	Control_D1_MEAN	1.93	1.88	-0.94	-5.09	1.19	-3.19
D2	Control_D2_MEAN	3.74	3.5	-0.41	-10.12	1.57	-6.61
D3	Control_D3_MEAN	0.85	0.89	0.39	2.42	-0.54	1.51
D4	Control_D4_MEAN	5.29	5.11	-0.83	-11.04	0.97	-9.22
D5	Control_D5_MEAN	6.50	6.47	-1.60	-18.14	3.44	-11.17
D6	Control_D6_MEAN	6.34	6.46	-1.15	-15.70	2.47	-10.44
MEAN_D(1-6)	MEAN_D(1-6)	2.46	2.41	-0.64	-6.17	1.01	-4.28
E1	Consolidated_E1_MEAN	2.47	2.55	3.30	12.29	-5.25	3.29
E2	Consolidated_E2_MEAN	1.15	1.11	-0.03	1.65	-1.16	-0.95
E3	Consolidated_E3_MEAN	2.77	2.74	1.31	13.75	-4.39	4.45
E4	Consolidated_E4_MEAN	2.13	2.07	0.18	-0.56	-1.10	-2.64
E5	Consolidated_E5_MEAN	0.82	0.72	-0.53	-1.61	0.33	-1.37
E6	Consolidated_E6_MEAN	2.54	2.59	0.62	8.09	-1.70	4.59
MEAN_E(1-6)	MEAN_E(1-6)	0.90	0.93	0.69	5.13	-2.00	1.23
F1	Consolidated_F1_MEAN	0.72	0.7	-1.38	0.04	0.53	-0.28
F2	Consolidated_F2_MEAN	0.46	0.47	0.50	2.22	-1.06	0.41
F3	Consolidated_F3_MEAN	3.21	3.16	-0.46	-5.05	-0.01	-5.18
F4	Consolidated_F4_MEAN	1.95	1.94	1.30	8.88	-2.95	3.15
F5	Consolidated_F5_MEAN	2.65	2.63	0.87	8.33	-1.85	4.73
F6	Consolidated_F6_MEAN	2.07	2.11	1.18	9.76	-3.13	3.49
MEAN_F(1-6)	MEAN_F(1-6)	0.67	0.69	0.28	3.77	-1.30	1.05

6.5 Frost Resistance

The frost resistance test was run for a total of 8 cycles, however the quantitative data was only able to be collected after the 4th freezing and thawing. Therefore the observations provided here are largely visual examination in addition to volumetric calculation.

Both unconsolidated and consolidated facsimile samples showed the same pattern of deterioration as seen in the Figure 6.1. The samples first started to lose their bottom corners and then top corners. The samples eventually became a round ball-like shape and disintegrated in suspension during weighing procedure. Though the consolidated samples lost less material during each cycle, they eventually failed the same as the unconsolidated samples.

Figure 6.1 – Deterioration Pattern Observed from Frost Resistance Test.

As seen in Table 6.7 and Chart 6.5, no apparent improvement in durability by consolidation was observed. Due to a limited number of specimens and by losing one sample from the control cohort, the number of comparable data sets was not sufficient for statistical evaluation. Therefore it is suggested that the evaluation based on the data be used only as a reference point. Chart 6.5 depicts the mean value of volume reduction percentage after 4 freeze-

thaw cycles, which appears to be nearly similar. However, as the standard deviation of the consolidated sample is quite large, the chart implies that there can be an error establishing a relationship between consolidation and frost resistance. It was also proven that the difference of reduction of bulk volume after 4 freeze-thaw cycles between control samples and consolidated samples was not statistically significant.

Table 6.7 – Frost Resistance Result.

	V_0 (g) Volume after 6h immersion	V_1 (g) Remaining volume after 4 cycles	V_1 in % Reduction of volume after 4 cycles
Control_G1	105.55	Failed	n/a
Control_G2	128.14	91.16	28.66
Control_G3	125.37	80.56	35.74
Consolidated_H1	128.19	58.75	54.17
Consolidated_H2	126.58	95.21	24.78
Consolidated_H3	128.53	106.47	17.16

Chart 6.5 – Retained Bulk Volume Percentage after 4 Freeze-Thaw Cycles.

6.6 Analytic Observation

6.6.1 Petrographic Analysis

Petrographic analysis of blue dyed thin sections of both the untreated and nanaolime treated samples clearly revealed a high degree of porosity. In general all the samples displayed poor intergranular contact with voids and separations between the aggregate and a low presence of paste. This was to be expected given the high percentage of aggregate to binder (5:1 by volume) to intentionally produce an underbound and friable plaster. A zone of slightly higher density of paste to aggregate and less discontinuities was observed in all samples prior to treatment probably due to the molding process for the samples which allowed colloidal lime particles to migrate to the surface during drying.

Photomicrographs of the unconsolidation control (Figure 6.2) and the consolidated sample, (Figure 6.3) approximately 200 μm below the surface under plan polarized light (PPL) illustrate pore structure and microtexture of the samples. In photomicrographs, these same samples under cross polarized light (XPL) reveal significant differences and confirm the presence and consolidating behavior of nanolime.

As seen in Figure 6.2, aggregates are poorly bound with the groundmass (paste) and the pores are largely interconnected. The groundmass seem fairly homogenous in color and has defined edges created due to shrinkage, typically found in the lime paste. In Figure 6.3, the texture of the groundmass seems to be less defined. The edges of the groundmass are more rounded and clear perimeters of cloudiness are observed. These perimeter 'halos' are due to the deposition and crystallization of nanolime. Appearing light blue in color under the XPL as indicated by the arrows, nanolime was deposited by filling and bridging the microcracks and lining pores.

Figure 6.2 – Open pore structure and ground mass of the control sample, approximately 200 μm below the surface (top in PPL, bottom in XPL, mag.10x).

Figure 6.3 - Open pore structure and ground mass of the consolidated sample, approximately 200 μm below the surface (top in PPL, bottom in XPL, mag.10x).

Though a petrographic thin section analysis was suggested as a useful tool to examine morphological change and depth of penetration of the nanolime consolidant (Ghaffari, 2012; Daehne and Herm, 2013), the analysis proved to be difficult as a sole tool to determine change in microstructure. Due to the small particle size of the original lime binder and the nanolime consolidant, determination of the each is difficult given the limitations of the optical light microscope. Comparative microfabric morphology clearly suggests a change after consolidation; however additional confirmatory examination should be supplemented by the SEM-EDS, which can map distribution of each elements, especially the Mg in the original dolomitic lime binder.

6.6.2 SEM analysis

By using dolomitic lime binder, calcium and magnesium ions should be present in the groundmass of the prepared samples. When it was determined to use EDS for measuring penetration depth, it was originally considered that elemental mapping would show an increased amount of calcium where nanolime was deposited. However as calcium is a minor element in the samples, the chance to detect calcium within a limited dwell time was practically lower than its presence and not sufficient to make a clear observation.

Alternatively, the penetration depth could be determined by confirming the presence of calcite (CaCO_3) from consolidation across the section. An expertise in distinguishing different morphologies and sizes of calcite (CaCO_3) with ESEM is required for this method. Though it is not easy to distinguish calcite from nanolime and lime binder due to their same nature (Bengtsson, 2012), this method may be more practical as it could be used even when the material has a high calcium lime binder.

CHAPTER 7. Conclusions and Recommendations

7.1 Conclusions

This thesis demonstrated that friable plaster (about 20 % lime binder) can be strengthened by consolidation with ethanol-based nanolime at low concentrations without displaying significant physico-chemical changes. As seen in Table 7.1, results of all testing conducted in this thesis are summarized and provided with the statistical confirmation using a two-tailed p-value from a paired t-test at 95 percent confidence level.

Table 7.1 – Summarized Test Results and Statistical Confirmation.

Testing Parameters	Result	Statistical Confirmation (at 95% confidence level)
Splitting tensile strength	Increased mechanical strength, approximately 45% increase	Significant
Porosity	Less than 1% reduction in porosity due to increased volume of impervious portions	Not significant
Permeability	Approximately 2% of reduction in water vapor transmission, permeance, and average permeability	Not significant
Color change	resulted less change in color value (ΔE), but more change in whiteness (ΔWI) and brightness(ΔB) of the surfaces than unconsolidated cohorts	Not significant
Frost resistance	A failure occurred earlier in unconsolidated cohorts, but the percentage of volume retainage via frost resistance was similar	Not significant

The decision as to whether a nanolime consolidant should be used on historic plasters is dependent on conditions other than measurable property changes, good or bad. Environmental conditions will greatly affect the cure of nanolime and in situ testing must be performed to confirm lab test results.

The results of this thesis provide recommendations for future conservation options for the Mission San José de Tumacácori and other historic structures possessing friable lime plasters and stuccos. Consolidation of friable renders – both exterior stuccos and interior plasters at Mission San José de Tumacácori is the first remedial step of any preservation program. As current investigation confirms, Tumacácori's façade is experiencing a host of complex conditions including structural cracking, delamination, detachment, and friable surfaces. Reestablishment of the stucco surface must precede most other treatments given the fragility of the surface and the necessity to have sound surfaces for subsequent treatments such as grouting and compensation of losses.

7.2 Recommendations for Future Research

7.2.1 Long Term Performance

As with many other lime-based building materials, performance of the nanolime consolidant is associated with the completion of the carbonation process, which may continue for many years. Therefore to understand a long term performance of nanolime consolidant on lime-based plaster, further testing is required on the additional sample sets created for this research. This will allow performance evaluation of the nanolime consolidant after longer curing (carbonation) period.

7.2.2 Color Change and Application

As whitening due to consolidation can alter the appearance of the original painted, or colored surfaces of the historic buildings, further research on nanolime consolidant is recommended to include quantification of color change of pigmented lime-based plaster. White index seems to provide the information that allows the user to determine whether white haze effect is significant or not.

It is also recommended to compare the degree of color change by different application methods, such as treatment through brushing or spraying or capillary rise. (Daehne and Herm, 2013) and powdering painted layer was sufficiently consolidated without alteration of color by brushing nanolime over Japanese paper. (Baglioni et al, 2014) Future research may also focus on comparing whitening behavior via different application methods. This could be beneficial for future conservators determining adequate application methods for lime-based plaster conservation when painted surfaces must be preserved.

7.2.3 Durability and Frost Resistance

Though continuing research is recommended to confirm durability, a modified version of weathering resistance testing needs to be developed for lime-based consolidation. As noted previously plaster is generally vulnerable to extreme environment and temperature fluctuations. Other durability testing such as dry-wet resistance may be more adequate to the given environment at Tumaćacori, where high daily temperature swings and large precipitation during monsoon periods impacts the performance of the building envelope.

In general, thorough investigation on treatment durability is encouraged. Although plaster is a sacrificial layer, knowing the durability of any treatment in terms of weathering resistance could eventually benefit the maintenance cycles and performance of the consolidant.

7.2.4 Thermal Expansion

As the Mission San José de Tumacácori is situated in a hot and dry climate, the performance of the consolidant must be considered in terms of its exposure to high daily temperatures and temperature swings. It was previously observed that the difference in the coefficients of thermal expansion of newly installed Portland cement and lime plaster accelerated the deterioration of the plaster at Tumacácori (Crosby, 1980). Though the nanolime consolidant is chemically identical to that of the original lime binder, is unlikely to have a different thermal expansion coefficient and therefore result in thermal stresses and damage.

7.2.5 Compatibility

The evaluation results of this thesis showed that the nanolime can sufficiently consolidate friable lime-based plaster. However, the composition of plaster and stucco vary depending on the regional tradition and material availability. The dry mixture often contains clay or brick dust in addition to lime, aggregate, and water. Depending on additional needs, various additives could be added to the mixture; to enhance certain properties of the plaster such as strength and durability, or performance and workability, to obtain slower setting time, or to promote air entrainment (Chan, 2015). For example, Giffords explains the use of fermented juice of the prickly pear cactus (nopal) to create a smooth and more durable finish (Chan, 2015). As the practice is found at Mission San Xavier del Bac, a geographical and contextual comparison to Mission San

José de Tumacácori (Chan, 2015), it is possible the technique could have been used at Tumacácori. Additionally, any previous organic consolidants used on the façade should be confirmed.

As Chan recommended previously, analysis such as gas chromatography mass-spectroscopy (GC-MS) or high-pressure liquid chromatography (HPLC) could be utilized to identify any organic components – original or applied later (Chan, 2015). Once the material is identified, further investigation of the compatibility of nanolime to the organic components is recommended.

7.2.6 On Site Evaluation

The commercial nanolime products offer a range of particle concentrations and this can be further customized by diluting to desired concentrations and mixing with other solvents. To obtain the best results in using nanolime consolidation, correct concentrations for the purpose should be determined through further laboratory and on site performance test.

On site evaluation should be conducted with an acknowledgement that carbonation of nanolime consolidants can be very sensitive to the curing environment. Many have reported environments with cooler temperatures and higher relative humidity allow faster and higher carbonation of nanolime consolidants. However, Tumacacori's location is not ideal for nanolime consolidation unless performed in the cooler wetter weather. Different methods may be considered to provide the sufficient environment for nanolime carbonation.

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APPENDIX A : Geology and Climate Data

A1. Geology

A2. Weather and Climate

A1. Geology

Source:

Schrader, Frank C. Geological Map of the Santa Rita and Patagonia Mountains, Arizona [map]. 1:125,000. In *Bulletin 582: Mineral Deposits of the Santa Rita and Patagonia Mountains, Arizona*. Washington, D.C.: U.S. Geological Survey, 1915, plate II.

Legend

A2. Weather and Climate

Source:
 "Tumacacori NM, Arizona - Climate
 Summary." Western Regional Climate
 Center, Accessed April 5, 2016. <
[http://www.wrcc.dri.edu/cgi-bin/
 cliMAIN.pl?az88865](http://www.wrcc.dri.edu/cgi-bin/cliMAIN.pl?az88865)>

U.S. Department of Commerce
 National Oceanic & Atmospheric Administration
 National Environmental Satellite, Data, and Information Service
 Elev: 3267 ft. Lat: 31.568° N Lon: 111.050° W
 Station: **TUMACACORI NM, AZ US GHCND:USC00028865**

Summary of Monthly Normals 1981-2010

Generated on 03/25/2016

National Centers for Environmental Information
 151 Patton Avenue
 Asheville, North Carolina 28801

112

Temperature (°F)																						
Mean							Cooling Degree Days					Heating Degree Days					Mean Number of Days					
Month	Daily Max	Daily Min	Mean	Long Term Max Std. Dev.	Long Term Min Std. Dev.	Long Term Avg Std. Dev.	Base (above)					Base (below)					Max >= 100	Max >= 90	Max >= 50	Max <= 32	Min <= 32	Min <= 0
							55	57	60	65	70	72	55	57	60	65						
1	64.6	32.1	48.3	3.5	2.8	2.3	11	5	1	-7777	0	0	217	273	362	516	0.0	29.5	0.0	15.9	0.0	
2	67.5	34.1	50.8	3.4	2.4	2.3	24	12	4	-7777	0	0	142	186	261	398	0.0	27.5	0.0	10.5	0.0	
3	72.3	37.6	54.9	3.6	2.4	2.7	84	55	24	3	-7777	-7777	86	118	181	315	0.0	30.8	0.0	5.8	0.0	
4	80.0	42.6	61.3	3.5	2.4	2.7	212	165	104	34	5	2	23	36	65	145	0.0	30.0	0.0	1.3	0.0	
5	88.2	49.5	68.9	3.0	2.4	2.5	431	370	282	151	57	34	1	3	8	31	1.4	12.9	31.0	0.0	0.1	
6	96.8	58.7	77.7	2.3	3.2	2.4	682	622	533	383	239	185	0	-7777	-7777	1	8.4	26.4	30.0	0.0	0.0	
7	95.2	66.3	80.8	2.7	1.7	1.8	798	736	643	488	333	272	0	0	0	0	7.4	24.6	31.0	0.0	0.0	
8	92.2	65.3	78.7	1.9	1.5	1.4	736	674	581	426	272	211	0	0	0	0	1.4	21.1	31.0	0.0	0.0	
9	90.2	58.9	74.5	2.1	2.2	1.8	586	526	437	288	150	103	-7777	-7777	-7777	2	0.6	16.1	30.0	0.0	0.0	
10	82.0	47.8	64.9	2.8	2.4	2.0	315	259	179	72	16	7	8	14	27	75	0.0	31.0	0.0	0.5	0.0	
11	72.2	37.6	54.9	3.8	2.3	2.8	83	54	25	3	-7777	-7777	86	117	178	306	0.0	-7777	29.8	0.0	6.5	0.0
12	64.5	31.8	48.2	3.3	2.1	2.1	11	4	1	-7777	0	0	223	279	368	522	0.0	29.0	0.0	15.9	0.0	
summary	80.5	46.9	63.7	3.0	2.3	2.2	3973	3482	2814	1848	1072	814	786	1026	1450	2311	19.2	107.4	360.6	0	56.5	0

Ⓔ Denotes mean number of days greater than 0 but less than 0.05.
 -7777: a non-zero value that would round to zero
 Empty or blank cells indicate data is missing or insufficient occurrences to compute value.

U.S. Department of Commerce
National Oceanic & Atmospheric Administration
National Environmental Satellite, Data, and Information Service
Elev: 3267 ft. Lat: 31.568° N Lon: 111.050° W
Station: TUMACACORI NM, AZ US GHCND:USC00028865

**Summary of Annual Normals
1981-2010**
Generated on 03/25/2016

National Centers for Environmental Information
151 Patton Avenue
Asheville, North Carolina 28801

Freeze Data												
Spring Freeze Dates (Month/Day)												
Temp (F)	Probability of later date in spring (through Jul 31) than indicated(*)											
	.10	.20	.30	.40	.50	.60	.70	.80	.90			
36	5/09	5/04	4/30	4/27	4/23	4/19	4/15	4/11	4/05			
32	4/26	4/17	4/12	4/08	4/04	3/31	3/28	3/22	3/14			
28	4/05	3/29	3/24	3/18	3/14	3/09	3/05	2/28	2/18			
24	3/15	3/07	3/01	2/23	2/15	2/09	2/03	1/27	1/14			
20	2/28	2/13	2/03	1/28	1/18	1/10	1/03	12/26	12/14			
16	2/19	2/05	1/22	1/08	1/03	12/30	12/25	12/19	12/10			
Fall Freeze Dates (Month/Day)												
Temp (F)	Probability of earlier date in fall (beginning Aug 1) than indicated(*)											
	.10	.20	.30	.40	.50	.60	.70	.80	.90			
36	10/16	10/20	10/24	10/27	10/30	11/02	11/05	11/08	11/13			
32	10/25	10/31	11/03	11/06	11/10	11/13	11/16	11/19	11/23			
28	11/04	11/10	11/14	11/17	11/20	11/24	11/28	12/01	12/06			
24	11/15	11/21	11/26	11/30	12/03	12/06	12/10	12/16	12/25			
20	11/27	12/02	12/08	12/13	12/18	12/25	1/01	1/07	1/26			
16	12/05	12/14	12/20	12/25	12/30	1/03	1/08	1/27	2/13			
Freeze Free Period												
Temp (F)	Probability of longer than indicated freeze free period (Days)											
	.10	.20	.30	.40	.50	.60	.70	.80	.90			
36	213	205	200	196	191	187	182	176	168			
32	244	236	230	224	220	215	209	203	194			
28	281	271	264	258	252	246	240	233	224			
24	329	316	306	299	292	285	278	269	258			
20	365	361	352	344	336	330	322	311	297			
16	365	365	365	365	365	365	363	352	334			

* Probability of observing a temperature as cold or colder than the indicated threshold, later in the spring or earlier in the fall than the indicated date
 -4444: year-round risk of frost-freeze
 -6666: parameter undefined: insufficient occurrences to compute value
 -7777: a non-zero value that would round to zero
 blank: missing or insufficient data

APPENDIX B : Technical Information of CaLoSiL®

B1. Technical Leaflet

B2. Material Safety Data Sheet

B1. Technical Leaflet

Technical Leaflet

CaLoSiL®

Colloidal nano-particles
of lime for stone and plaster
consolidation

CaLoSiL® in different concentrations

Properties

CaLoSiL® contains nano-particles of lime hydrate $[\text{Ca}(\text{OH})_2]$ suspended in different alcohols. Typical concentrations are between 5 and 50 g/L. The average particle size is 150 nm. The extremely fine size of the synthetic nano-lime results from its preparation, which is based on chemical synthesis. Ethanol, iso-propanol or n-propanol serve as solvents. Due to the low particle size stable sols are formed which do not sediment for a long time.

CaLoSiL® is a ready-to-use stone and plaster consolidant. Treatment of stone, mortar or plaster with CaLoSiL® results in the formation of solid calcium hydroxide after evaporation of the alcohol, that converts into calcium carbonate in a way similar to traditional lime mortars by reaction with atmospheric carbon dioxide. All alcohols evaporate without any residues so they do not harm the stone or plaster. Chemicals or residues deteriorating stone or mortar are not formed.

CaLoSiL® can be applied using either a flow coating procedure, by dipping, spraying or injection. It is important that the complete weathered zone of the stone down to the sound is treated.

Available types of CaLoSiL / Packaging

CaLoSiL® is available in concentrations between 5 and 50 g/L. The letters behind the name "CaLoSiL®" indicate the used solvent, the numbers give the total calcium hydroxide concentration in g/L. E –stands for ethanol, IP for iso-propanol and NP for n-propanol. For example, E-25 means, 25 g/L calcium hydroxide dispersed in ethanol.

Standard products are:

CaLoSiL® E-5, E-25 and E-50

CaLoSiL® IP-5, IP-15 and IP-25

CaLoSiL® NP-5, NP15 and NP-50

All CaLoSiL® types are available in 500 mL, 1 Liter, 2,5 Liter, 5 Liter and 10 Liter containers.

Properties of formed calcium hydroxide / calcium carbonate

The calcium hydroxide particles formed after evaporation of the alcohol cover the surface of treated cracks, pores or joints. Dense films of calcium hydroxide films are

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formed, depending on the number of treatment cycles and the concentration of the used sols. Typical particles sizes are in the range of few hundred nano-metres. Their detection by means of standard optical microscopy may be difficult, the use of SEM is recommended.

Calcium carbonate formation by reaction with atmospheric carbon dioxide requires the presence of humidity. Depending on the conditions and the amount of calcium hydroxide brought into stone, mortar or plaster carbonations takes place within few days and weeks. After spraying the treated materials with water the carbonation process can be accelerated.

Penetration behaviour

The penetration into mortar, stone or plaster depends on the following factors:

- Characteristics of the CaLoSiL type applied
- Structure and surface characteristics of the materials to be treated,
- Porosity and capillary rise,
- Moisture content of the material
- Air temperature and air humidity during the application

When dense materials are treated with highly concentrated CaLoSiL products (CaLoSiL E-50, CaLoSiL-paste like etc.) the penetration behaviour may be only slow, especially if there are dense surface layers such as gypsum crusts which prevent its penetration.

High moisture content also inhibits penetration so when necessary pre-wetting with ethanol may help to reduce the moisture content of the material.

White haze formation

The formation of a white haze on the surface of the treated material depends not only on the penetration behaviour of CaLoSiL but also on the evaporation conditions of the alcohol, which can re-transport nano-particles back to the surface. In addition if too little time is allowed for carbonation of the nanolime within the treated material it will not be fixed in place and can be transported to the surface. General rules to prevent / reduce the formation of white haze are:

- Start the treatment with low concentrated products, increase the calcium hydroxide concentration step by step
- Avoid the treatment of wet materials, reduce the moisture content by pre-treatment with ethanol or ethanol-water mixtures (1:1).
- In the case of sensitive surfaces try to use CaLoSiL grey, which has a special consistency allowing deep penetration without white haze formation
- Avoid an "oversaturation" of the treated stone, plaster or mortar. Remove all

CaLoSiL which could not penetrate into the treated material for example, with a sponge.

- Test the addition of small amounts of acetone or heptane.

Times

The alcohols evaporate within a few hours. The carbonation process itself requires between few days to several weeks, depending on the amount of calcium hydroxide formed and the environmental conditions (humidity, possibility of carbon dioxide migration).

CaLoSiL® and silicic acid esters

The combination of CaLoSiL with silicic acid esters allows the successful consolidation and strengthening of materials in which pure silicic acid esters do not work satisfactorily alone. In these cases it is recommended to treat the materials with CaLoSiL first (for example E-25 or IP-25) and then apply silicic acid esters after the evaporation of the alcohol. The calcium hydroxide formed from CaLoSiL acts as an adhesion promoter as well as catalyst accelerating the hydrolysis of the silicic acid ester. The final strength is in many cases much higher than can be achieved by single treatment with silicic acid esters. All commercially available silicic acid esters can be used. Detailed information are summarised in a special technical leaflet.

Mixability with other materials

All CaLoSiL®-products can be intermixed. Blending with ethanol, n- or iso-propanol is also possible without any difficulties. However, the addition of water can result in the formation of a gel because of flocculation of calcium hydroxide particularly when the amounts of water is greater than 10% by weight.

Storage

All materials have to be stored between + 5 °C and +30 °C. When CaLoSiL remains in unopened, original containers, storage for at least three months is possible. After that time, agglomeration and sedimentation may occur. The settled particles, however, can be re-dispersed by shaking the closed bottle or by ultrasonic treatment. The properties of the nano-sols remain unaffected.

Safety

CaLoSiL® is flammable/combustible. Keep away from oxidizers, heat, sparks and flames. Avoid spilling, skin and eye contact. Ventilate well, avoid breathing vapours. CaLoSiL® reacts strongly alkaline. Do not breathe vapour or mist. Do not smoke. Keep container closed. Use with adequate ventilation. Wash thoroughly after handling. Keep away from sources of ignition.

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Store in a cool, dry place. Store in a tightly closed container. Further information concerning safety during transport, storage and handling as well as for disposal and ecology can be found in our latest Material Safety Data Sheet.

Before using in large scale we recommend to treat a small test field with CaLoSiL® in order to find out the most favourable application method and the required volumes of CaLoSiL.

The information mentioned above is state of the art. The application of our products and the work using is beyond the range of our influence. Therefore IBZ-Salzchemie GmbH & Co.KG can take no liability from events that result from the information contained in this leaflet.

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B2. Material Safety Data Sheet

Safety Data Sheet CaLoSiL-products based on Ethanol According to EC Directive 91/155/EEC

Date of issue: 20.12.2013

page 1 of 2

Product name: **CaLoSiL-E, CaLoSiL grey, CaLoSiL paste-like (pasty)**

1 Company, identification of the substance and preparation					
Identification of the product:					
Product name:	CaLoSiL-E, CaLoSiL grey, CaLoSiL paste-like,				
Itemnumber:	2- -				
Use of the substance/preparation:	stone strengthener				
Company/ Producer:	IBZ-Salzchemie GmbH & Co.KG				
	Schwarze Kiefern 4				
	Tel.: +49(0)3731 200 155;				
	38249070				
Customs tariff number:	09633 Halsbruecke; Germany Fax: +49(0)3731 200 156				
2 Composition/ information on ingredients					
chemical composition					
specification:	in ethanol dispersed calcium hydroxide				
ingredients:					
calcium hydroxide	0,1 – 20%	ethanol	75 - 90 %		
CAS-No:	1305-62-0	CAS-No.:	64-17-5		
EC-No :	215-137-3	EC-Index-No.	603-002-00-5	EC-No:	200-578-6
Formula Hill:	CaH ₂ O ₂	Formula Hill:	C ₂ H ₆ O		
chemical Formula:	Ca(OH) ₂	chemical Formula:	C ₂ H ₅ OH		
3 Special risks					
<div> </div>					
H225	Highly flammable liquid and vapour.				
H318	causes severe eye damage				
4 First aid measures					
After Inhalation:	Fresh air				
After skin contact:	Wash off with plenty of water. Remove contaminated clothing				
After eye contact:	Rinse out with plenty of water with the eyelid held wide open. Immediately call in ophthalmologist.				
After swallowing:	Immediately make victim drink plenty of water. Call in physician.				
5 Fire-fighting measures					
Suitable extinguishing media:	CO ₂ , foam, powder				
Spezial risk:	Combustible. Vapours are heavier than air. Forms explosive mixtures with air at ambient temperatures. Beware of backfiring. Developments of hazardous combustion gases or vapours are possible in the event of fire. Special protective equipment for fire fighting: Do not stay in dangerous zone without self-contained breathing apparatus.				
Other information:	Cool container with spray water from a save distance. Prevent fire-fighting water from entering surface water or groundwater				
6 Accidental release measures					
Person-related precautionary measures:	Avoid substance contact. Ensure supply of fresh air in enclosed rooms				
Environmental-protection measures:	Do not allow to enter sewerage system; risk of explosion				
Procedures for cleaning/ absorption:	Take up with liquid-absorbent material. Forward for disposal. Clean up affected area.				
7 Handling and storage					
Handling:	Notes for prevention of fire and explosion: Keep away from sources of ignition. Take measure to prevent electrostatic charging.				
Storage:	Tightly, closed in a well-ventilated place, away from sources of ignition and heat. At +5°C to 25°C. Do not use light-weight-metall containers.				
8 Exposure controls/ personal protection					
Name:	Ethanol				
Personal protective equipment:	Protective clothing should be selected specifically fort he working place, depending on concentration and quantity of the hazardous substances handled. The resistance of the protective clothing to chemicals should be ascertained with the respective supplier.				
Respiratory protection:	Required when vapours/ aerosols are generated; Filter A (acc. to DIN 3181) for vapours of organic compounds				
Eye protection:	Required				
Hand protecting grip: in full contact:	Glove material: nitrile rubber; layer thickness: 0.70 mm; Breakthrough time: >480 min				
in splash contact:	Glove material: nitrile rubber; layer thickness: 0.40 mm; Breakthrough time: >120 min				
The protective gloves to be used must comply with the specifications of EC directive 89/686/EEC and the resultant Standard EN374					
Other protective equipment:	Flame-proof and antistatic protective clothing.				
Industrial Hygiene:	Change contaminated clothing. Application of skin-protective barrier cream recommended. Wash hands after working.				
9 Physical and chemical properties					
Form:	liquid	Colour:	white, opal, grey	Odour:	alcohol like
pH-value (50g/l in H ₂ O)	> 12	Melting point:	-114°C	Boiling point:	78°C
Ignition temperature:	425 °C	Flash point:	18°C	Explosion limits:	under: 3,5 Vol.-%; upper: 15 Vol.-%
Vapour pressure:	20°C, 59 hPa	Solubility in Water:	soluble, formation of aqueous calcium hydroxide slurry		

Safety Data Sheet CaLoSiL-products based on Ethanol According to EC Directive 91/155/EEC

Date of issue: 20.12.2013

page 2 of 2

Product name: **CaLoSiL-E, CaLoSiL grey, CaLoSiL paste-like (pasty)**

10 Stability and reactivity

Conditions to be avoided: Warming
Substances to be avoided:
 Risk of ignition or formation: of inflammable gases or with alkali metals, alkaline earth metals, alkali oxides, strong oxidizing agents, halogen-halogen compounds, CrO₃; chromyl chloride, ethylene oxide, fluorine, perchlorates, potassium permanganate/ sulphuric acid, perchloric acid, permanganic acid, phosphorus oxides, nitric acid, nitrogen dioxide, uranium hexafluoride, hydrogen peroxide
 Exothermic reaction: with acids, hydrogen sulfide, light metals, phosphorous, organic nitro compounds
Hazard decomposition products: No information available
Further Information: Unsuitable working materials: various plastics, rubber. Explosible with air in a vaporous/ gaseous state

11 Toxicological Information

Acute toxicity of Ethanol:
 LC₅₀(inhalation, rat): 95.6 mg/l /4 h (external MSDS)
 LD₅₀ (oral, rat): 6200 mg/kg (external MSDS).
Acute toxicity of Ca(OH)₂
 LD₅₀ (oral, rat): 7340 mg/kg (external MSDS).
Further toxicological information
 After inhalation of vapours: irritation symptoms in respiratory tract. Drowsiness, Dizziness, Risk of absorption
 After skin contact: Degreasing effect on skin
 After eye contact: Severe irritations. Risk of serious damage to eyes. Risk of corneal clouding. Risk of blindness.
 After swallowing: Irritations of gastrointestinal tract
 After absorption of large quantities: dizziness, inebriation, narcosis, respiratory paralysis
Further data: The product should be handled with the usual care when dealing with chemicals. Further hazardous properties can not

12 Ecological information

Ethanol: rapid abiotic degradation, Biologic degradation
 Calcium hydroxide: methods for the determination of biodegradability are not applicable to inorganic substances
 Biological effects: Harmful due to pH shift. Forms corrosive mixtures with water even if diluted- Neutralization possible in waste water treatment plants.
 Further ecologic data: do not allow to enter waters, waste water or soil!

13 Disposal considerations

Chemicals must be disposed of in compliance with the respective national regulations. Under www.retrologistik.de you will find country- and substance specific information as well as contract partners..

14 Transport information

Street and railway: ADR, RID UN1170 ETHANOL, 3, II, (D/E)
inland navigation vessel: ADN, **ADNR untried**
Sea IMDG-Code: UN1170 ETHANOL, 3, II EmS: F-E S-D
IATA-DGR: UN1170, Ethanol, 3, II
 Transport instructions are cited after international regulations and the one's used in Germany. Deviations of other countries are not considered.

15 Regulatory information

Labeling according to EC Directives:

Symbol:

Hazard Statements:
 225, 318 Highly flammable liquid and vapour, causes severe eye damage

Precautionary Statements:
 210, 233, 305, 351, 338 Keep away from heat/sparks/open flames/hot surfaces.- No smoking. Keep container tightly closed. Rinse in touch with eyes, rinse immediately with water and consult a doctor. Wear protective gloves/protective clothing/eye protection/face protection. IF IN EYES: Rinse cautiously with water for several minutes. Remove contact lenses, if present and easy to do. Continue rinsing. Get medical advice/attention.

water hazard classification: low water-hazardous
storage class VCI: 3 A

Hazardous Incident (Reporting) Ordinance No.: 7b
 Law for the protection of children and youth attended!

16 Other information

Information: IBZ-Salzchemie GmbH & Co. KG
 Schwarze Kiefern 4, D09633 Halsbruecke, Germany
 phone: +49 (0)3731/200155 Fax: +49 (0)3731/200156
 e-mail: info@ibz-freiberg.de www.ibz-freiberg.de

The information contained herein is based on the present state of our knowledge. It characterizes the product with regard to appropriate safety precautions. It does not represent a guarantee of the properties of the product.

APPENDIX C : Data Set

- C1. Gravimetric Analysis
- C2. Test Results & t-test Results
- C3. Photomicrographs

C1. Gravimetric Analysis

Table 1 – Particle Size Distribution (Sieve Analysis Result)

ASTM Sieve No.	Screen Size(mm)	Mass of sample(g)	Percent sample to total(%)	total mass retained(%)	total mass passed(%)
8	2.360	0.5	2.57	2.57	97.43
16	1.180	4.04	20.77	23.34	76.66
30	0.600	5.78	29.72	53.06	46.94
50	0.300	5.38	27.66	80.72	19.28
100	0.150	2.75	14.14	94.86	5.14
200	0.075	0.78	4.01	98.87	1.13
pan	0.000	0.22	1.13	100	0.00
Total	-	19.45	100	-	-

Table 2 – Color Variance between Tumacacori Bulk Samples and Facsimile Samples

Target	Sample	ΔE_{SCI}	ΔE_{SCE}	$\Delta Tint$	ΔWI	ΔYI	ΔB
TUMA_SAND	TUMA_BULK	17.91	17.90	8.29	50.00	-13.11	17.36
TUMA_BULK	D(1-6)	14.14	14.00	13.40	68.62	-24.13	22.18
TUMA_BULK	E(1-6)	10.60	10.47	11.69	56.08	-21.25	14.82
TUMA_BULK	F(1-6)	11.47	11.36	12.43	59.40	-22.26	16.51
TUMA_BULK	D-F	12.07	11.94	12.51	61.37	-22.55	17.84

C2. Test Results & t-test Results

Table 3 - Splitting Tensile Test Result

sample	d1(in)	d2(in)	d3(in)	ave. d(in)	L1(in)	L2(in)	ave. L(in)	P(max)	T(psi)
control_A1	2.03	2.01	2.01	2.01	4.01	4.03	4.02	75.72	390.16
control_A2	2.03	2.03	2.05	2.04	3.99	4.00	3.99	91.56	473.51
control_A3	2.02	2.03	2.03	2.03	4.00	4.01	4.00	88.48	456.50
control_A4	2.05	2.02	2.02	2.03	4.03	3.98	4.00	64.04	331.58
control_A5	2.05	2.06	2.08	2.06	4.06	4.05	4.06	85.52	455.14
control_A6	2.05	2.07	2.03	2.05	4.04	4.05	4.04	113.74	600.72
consolidated_B1	2.02	2.01	2.02	2.01	4.02	4.05	4.04	96.20	497.65
consolidated_B2	2.01	2.04	2.04	2.03	4.05	4.04	4.04	128.86	673.42
consolidated_B3	2.05	2.05	2.05	2.05	3.99	3.99	3.99	148.78	774.79
consolidated_B4	2.04	2.04	2.06	2.05	4.03	4.07	4.05	140.66	743.05
consolidated_B5	2.03	2.04	2.03	2.03	4.00	3.99	3.99	118.55	612.57
consolidated_B6	2.05	2.05	2.07	2.05	4.09	4.06	4.08	117.53	626.98

Table 4 - Paired T-test (Splitting Tensile Strength)

	Control_A	Consolidated_B
Mean	451.2661	654.7412
Variance	8186.313	9957.295
Observations	6	6
Pearson Correlation	-0.09388	
Hypothesized Mean Difference	0	
df	5	
t Stat	-3.53857	
P(T<=t) one-tail	0.008294	
t Critical one-tail	2.015048	
P(T<=t) two-tail	0.016588	
t Critical two-tail	2.570582	

Table 5 - Porosity Test Result

Sample ID	D (g) Dry Weight	W (g) Saturated weight	S (g) Suspended Weight	Volume of Open Pores (cm ³)	Volume of Impervious Portions (cm ³)	P (%) Porosity
tuma_bulk1	51.3	32.3	57.8	8.1	23.6	25.6
tuma_bulk2	13.2	8.1	15.2	2.5	6.3	28.0
tuma_bulk3	8.8	5.5	10.1	1.6	4.2	27.7
tuma_bulk4	11.1	6.8	12.7	2.0	5.2	27.5
control_D1	62.3	39.4	69.5	8.9	28.4	23.8
control_D2	62.5	39.7	69.4	8.6	28.2	23.3
control_D3	61.8	38.8	68.4	8.3	28.5	22.5
control_D4	64.4	40.4	71.5	8.8	29.7	22.8
control_D5	65.6	41.5	72.5	8.5	29.8	22.2
control_D6	63.9	39.6	70.7	8.4	30.1	21.8
consolidated_ E1	64.5	40.3	72.0	9.4	30.0	23.9
consolidated_ E2	65.8	41.8	72.4	8.1	29.8	21.4
consolidated_ E3	61.8	39.0	68.2	7.9	28.2	21.9
consolidated_ E4	62.7	39.6	70.5	9.6	28.7	25.1
consolidated_ E5	71.3	45.5	77.9	8.3	31.9	20.6
consolidated_ E6	62.7	39.6	69.4	8.3	28.6	22.4
consolidated_ F1	67.2	42.2	74.0	8.4	31.0	21.4
consolidated_ F2	66.3	41.9	73.7	9.2	30.2	23.3
consolidated_ F3	64.2	40.7	71.3	8.7	29.2	22.9
consolidated_ F4	68.7	43.7	76.3	9.4	30.9	23.3
consolidated_ F5	66.5	40.4	73.4	8.6	32.3	21.0
consolidated_ F6	65.6	41.5	72.0	7.9	29.9	21.0

Table 6 – Paired T-test (Volume of Open Pores)

	<i>Control_D</i>	<i>Consolidated_E</i>
Mean	8.572903759	8.597686906
Variance	0.05561109	0.511350753
Observations	6	6
Pearson Correlation	0.907624652	
Hypothesized Mean Difference	0	
df	5	
t Stat	-0.118859663	
P(T<=t) one-tail	0.455007133	
t Critical one-tail	2.015048373	
P(T<=t) two-tail	0.910014267	
t Critical two-tail	2.570581836	

Table 7 – Paired T-test (Volume of Impervious Portions)

	<i>Control_D</i>	<i>Consolidated_E</i>
Mean	29.11606774	29.53118546
Variance	0.722652421	1.864565883
Observations	6	6
Pearson Correlation	0.1118132	
Hypothesized Mean Difference	0	
df	5	
t Stat	-0.666483578	
P(T<=t) one-tail	0.26730845	
t Critical one-tail	2.015048373	
P(T<=t) two-tail	0.534616901	
t Critical two-tail	2.570581836	

Table 8 – Paired T-test (Porosity)

	<i>Control_D</i>	<i>Consolidated_E</i>
Mean	22.75396255	22.55037418
Variance	0.530043034	2.733975348
Observations	6	6
Pearson Correlation	0.390764085	
Hypothesized Mean Difference	0	
df	5	
t Stat	0.327177631	
P(T<=t) one-tail	0.378393547	
t Critical one-tail	2.015048373	
P(T<=t) two-tail	0.756787095	
t Critical two-tail	2.570581836	

Table 9 – Water Vapor Transmission Test Data (Control)

Elapsed hour (h)	control					
	A1	A2	A3	A4	A5	A6
0	0	0	0	0	0	0
0.17	0.01	0.01	0.02	0.01	0.02	0.01
0.34	0.02	0.01	0.03	0.01	0.02	0.02
0.50	0.03	0.01	0.03	0.01	0.03	0.02
1	0.04	0.03	0.04	0.04	0.05	0.05
2	0.07	0.07	0.08	0.08	0.08	0.08
3	0.09	0.08	0.10	0.09	0.09	0.10
6	0.11	0.10	0.13	0.10	0.13	0.12
12	0.10	0.10	0.12	0.12	0.12	0.11
24	0.06	0.05	0.07	0.05	0.07	0.04
48	-0.14	-0.11	-0.11	-0.11	-0.09	-0.13
72	-0.36	-0.33	-0.31	-0.32	-0.30	-0.33
96	-0.60	-0.56	-0.53	-0.53	-0.50	-0.54
120	-0.78	-0.71	-0.69	-0.67	-0.65	-0.70
144	-1.01	-0.95	-0.94	-0.93	-0.87	-0.93
168	-1.22	-1.14	-1.12	-1.11	-1.06	-1.11
192	-1.43	-1.35	-1.33	-1.31	-1.26	-1.32
216	-1.59	-1.49	-1.46	-1.46	-1.40	-1.46
240	-1.79	-1.67	-1.66	-1.62	-1.57	-1.64
264	-2.04	-1.91	-1.90	-1.88	-1.80	-1.88
288	-2.26	-2.10	-2.11	-2.09	-1.99	-2.06
312	-2.44	-2.26	-2.29	-2.25	-2.18	-2.24
336	-2.61	-2.41	-2.45	-2.40	-2.33	-2.42
360	-2.76	-2.55	-2.61	-2.55	-2.48	-2.55
384	-2.90	-2.69	-2.76	-2.70	-2.64	-2.70
408	-3.10	-2.86	-2.93	-2.88	-2.80	-2.85
432	-3.31	-3.05	-3.14	-3.09	-2.98	-3.10
480	-3.72	-3.43	-3.53	-3.47	-3.38	-3.47

Table 10 – Water Vapor Transmission Test Data (Consolidated)

Elapsed hour (h)	consolidated					
	B1	B2	B3	B4	B5	B6
0	0	0	0	0	0	0
0.17	0.02	0	0.01	0.01	0	0.01
0.34	0.04	0.02	0.01	0.02	0.02	0.02
0.50	0.04	0.02	0.02	0.02	0.01	0.03
1	0.04	0.05	0.04	0.03	0.01	0.03
2	0.07	0.07	0.06	0.06	0.05	0.06
3	0.09	0.08	0.07	0.08	0.07	0.08
6	0.13	0.11	0.10	0.10	0.11	0.11
12	0.13	0.14	0.11	0.12	0.14	0.12
24	0.03	0.04	-0.01	0.03	0.07	0.03
48	-0.14	-0.13	-0.21	-0.17	-0.09	-0.15
72	-0.35	-0.32	-0.42	-0.36	-0.26	-0.36
96	-0.55	-0.53	-0.62	-0.57	-0.44	-0.58
120	-0.72	-0.69	-0.81	-0.75	-0.59	-0.76
144	-0.95	-0.89	-1.03	-0.95	-0.77	-0.95
168	-1.16	-1.10	-1.24	-1.16	-0.93	-1.16
192	-1.38	-1.32	-1.47	-1.39	-1.14	-1.37
216	-1.52	-1.45	-1.6	-1.51	-1.24	-1.50
240	-1.69	-1.62	-1.79	-1.70	-1.42	-1.67
264	-1.93	-1.84	-2.04	-1.91	-1.60	-1.92
288	-2.15	-2.04	-2.23	-2.13	-1.78	-2.11
312	-2.33	-2.22	-2.42	-2.33	-1.94	-2.29
336	-2.48	-2.38	-2.58	-2.45	-2.08	-2.45
360	-2.63	-2.54	-2.75	-2.59	-2.22	-2.60
384	-2.79	-2.68	-2.91	-2.75	-2.35	-2.76
408	-2.96	-2.86	-3.08	-2.94	-2.50	-2.91
432	-3.16	-3.05	-3.28	-3.12	-2.68	-3.14
480	-3.56	-3.44	-3.70	-3.52	-3.05	-3.53

Table 11 – Water Vapor Transmission Test Result

	Weight change (g)	Elapsed time (h)	WVT ($g/h \cdot m^2$)	Permeance	Average Permeability
Control_D1	3.58	432	1.72E-05	1.91E-06	3.47E-08
Control_D2	3.32	432	1.59E-05	1.77E-06	3.22E-08
Control_D3	3.42	432	1.64E-05	1.83E-06	3.32E-08
Control_D4	3.36	432	1.61E-05	1.79E-06	3.26E-08
Control_D5	3.29	432	1.58E-05	1.76E-06	3.19E-08
Control_D6	3.34	432	1.60E-05	1.78E-06	3.24E-08
Consolidated_E1	3.42	432	1.64E-05	1.83E-06	3.32E-08
Consolidated_E2	3.31	432	1.59E-05	1.77E-06	3.21E-08
Consolidated_E3	3.49	432	1.67E-05	1.86E-06	3.39E-08
Consolidated_E4	3.35	432	1.61E-05	1.79E-06	3.25E-08
Consolidated_E5	2.96	432	1.42E-05	1.58E-06	2.87E-08
Consolidated_E6	3.38	432	1.62E-05	1.80E-06	3.28E-08

Table 12 – Paired T-test (Water Vapor Transmission)

	Control_D	Consolidated_E
Mean	1.62198E-05	1.59003E-05
Variance	2.5325E-13	7.94801E-13
Observations	6	6
Pearson Correlation	0.581875519	
Hypothesized Mean Difference	0	
df	5	
t Stat	1.078955214	
P(T<=t) one-tail	0.16494199	
t Critical one-tail	2.015048373	
P(T<=t) two-tail	0.32988398	
t Critical two-tail	2.570581836	

Table 13 – Paired T-test (Permeance)

	Control_D	Consolidated_E
Mean	1.80704E-06	1.77145E-06
Variance	3.14335E-15	9.86511E-15
Observations	6	6
Pearson Correlation	0.581875519	
Hypothesized Mean Difference	0	
df	5	
t Stat	1.078955214	
P(T<=t) one-tail	0.16494199	
t Critical one-tail	2.015048373	
P(T<=t) two-tail	0.32988398	
t Critical two-tail	2.570581836	

Table 14 – Paired T-test (Average Permeability)

	Control_D	Consolidated_E
Mean	3.28339E-08	3.21872E-08
Variance	1.03777E-18	3.25696E-18
Observations	6	6
Pearson Correlation	0.581875519	
Hypothesized Mean Difference	0	
df	5	
t Stat	1.078955214	
P(T<=t) one-tail	0.16494199	
t Critical one-tail	2.015048373	
P(T<=t) two-tail	0.32988398	
t Critical two-tail	2.570581836	

Table 15 - Color Data

Data Name	L* (D65)	a* (D65)	b* (D65)	X (D65)	Y (D65)	Z (D65)	x (D65)	y (D65)	Tint	WI	YI	B
TUMA_BULK_1	71.42	4.44	11.99	42.04	42.81	35.82	0.348	0.355	-15.67	-25.24	31.57	33.65
TUMA_BULK_2	71.63	4.45	12.58	42.34	43.12	35.65	0.350	0.356	-15.98	-28.09	32.73	33.50
TUMA_BULK_3	65.42	5.18	13.07	34.25	34.58	27.67	0.355	0.358	-19.30	-44.77	36.90	26.02
MEAN_TUMA_BULK	69.59	4.66	12.50	39.54	40.17	33.05	0.352	0.356	-16.82	-32.23	33.52	31.06
TUMA_SAND_1	52.30	4.68	13.59	20.29	20.41	15.16	0.363	0.365	-22.10	-77.55	43.93	14.29
TUMA_SAND_2	52.68	5.60	14.57	20.81	20.75	15.02	0.368	0.367	-25.38	-83.24	47.29	14.16
TUMA_SAND_3	50.27	6.25	14.22	18.86	18.64	13.43	0.370	0.366	-28.09	-86.14	48.84	12.65
MEAN_TUMA_SAND	51.77	5.49	14.12	19.99	19.94	14.54	0.367	0.366	-25.11	-82.24	46.63	13.70
D1_BEFORE	77.29	0.82	4.00	49.62	52.02	51.75	0.324	0.339	-3.45	30.46	9.74	48.42
D1_AFTER_1	75.69	1.21	3.96	47.26	49.39	49.11	0.324	0.339	-4.27	27.74	10.17	45.93
D1_AFTER_2	75.83	1.01	4.12	47.40	49.61	49.19	0.324	0.339	-3.94	27.08	10.33	46.01
D1_AFTER_3	74.73	1.33	4.83	45.83	47.84	46.73	0.326	0.341	-4.98	21.15	12.34	43.73
MEAN_D1_AFTER	75.42	1.18	4.30	46.83	48.95	48.34	0.325	0.340	-4.39	25.36	10.93	45.23
D2_BEFORE	80.65	0.90	3.53	55.20	57.85	58.21	0.322	0.338	-3.27	39.51	8.47	54.43
D2_AFTER_1	78.92	0.89	3.72	52.29	54.79	54.87	0.323	0.338	-3.40	35.11	9.03	51.32
D2_AFTER_2	80.94	0.86	3.54	55.68	58.37	58.74	0.322	0.338	-3.18	40.05	8.43	54.92
D2_AFTER_3	78.78	0.91	3.57	52.06	54.54	54.78	0.323	0.338	-3.38	35.65	8.73	51.22
MEAN_D2_AFTER	76.96	0.91	4.09	49.13	51.46	51.11	0.324	0.339	-3.68	29.40	10.04	47.81
D3_BEFORE	79.24	1.12	4.72	52.91	55.35	54.42	0.325	0.340	-4.29	30.47	11.35	50.92
D3_AFTER_1	78.73	1.16	4.77	52.07	54.46	53.47	0.326	0.340	-4.41	29.21	11.54	50.03
D3_AFTER_2	77.91	1.32	5.13	50.80	53.06	51.69	0.327	0.341	-4.94	25.68	12.57	48.38
D3_AFTER_3	78.17	1.19	4.61	51.18	53.51	52.67	0.325	0.340	-4.42	28.96	11.30	49.27
MEAN_D3_AFTER	80.07	0.97	4.57	54.23	56.80	56.04	0.325	0.340	-3.90	32.89	10.82	52.43
D4_BEFORE	83.26	0.66	3.42	59.68	62.66	63.28	0.322	0.338	-2.69	45.32	7.83	59.17
D4_AFTER_1	79.37	0.88	3.67	53.02	55.56	55.72	0.323	0.338	-3.34	36.26	8.87	52.12
D4_AFTER_2	78.03	0.99	4.12	50.87	53.26	52.90	0.324	0.339	-3.82	31.24	10.09	49.49
D4_AFTER_3	81.97	0.69	3.37	57.40	60.25	60.86	0.322	0.338	-2.77	42.97	7.84	56.91
MEAN_D4_AFTER	77.99	0.97	3.54	50.79	53.19	53.41	0.323	0.338	-3.51	34.28	8.80	49.95
D5_BEFORE	80.76	0.86	3.99	55.37	58.05	57.92	0.323	0.338	-3.39	37.32	9.41	54.17
D5_AFTER_1	77.10	1.08	4.33	49.41	51.70	51.11	0.325	0.340	-4.13	28.38	10.71	47.81
D5_AFTER_2	77.06	1.18	4.30	49.39	51.63	51.07	0.325	0.340	-4.32	28.47	10.74	47.78
D5_AFTER_3	79.72	0.83	3.71	53.59	56.18	56.31	0.323	0.338	-3.24	36.71	8.88	52.66

Data Name	L* (D65)	a* (D65)	b* (D65)	X (D65)	Y (D65)	Z (D65)	x (D65)	y (D65)	Tint	WI	YI	B
MEAN_D5_A FTER	74.37	1.27	5.06	45.27	47.28	45.95	0.327	0.341	-4.99	19.18	12.85	43.00
D6_BEFORE	79.75	0.88	4.12	53.66	56.24	55.94	0.324	0.339	-3.54	34.63	9.80	52.32
D6_AFTER_1	76.90	1.33	4.59	49.18	51.36	50.51	0.326	0.340	-4.75	26.6	11.53	47.26
D6_AFTER_2	78.51	1.73	4.94	51.93	54.08	52.91	0.327	0.340	-5.63	27.91	12.46	49.50
D6_AFTER_3	78.55	1.09	4.06	51.75	54.14	53.87	0.324	0.339	-3.95	32.62	9.97	50.38
MEAN_D6_A FTER	73.45	1.16	4.80	43.86	45.85	44.75	0.326	0.341	-4.68	18.93	12.28	41.89
E1_BEFORE	71.82	2.48	6.20	41.95	43.39	41.07	0.332	0.343	-8.30	8.11	16.99	38.44
E1_AFTER_1	77.13	1.27	3.93	49.53	51.75	51.55	0.324	0.339	-4.32	30.59	10.01	48.20
E1_AFTER_2	71.54	1.72	4.91	41.31	42.98	41.76	0.328	0.341	-6.04	14.88	13.35	39.06
E1_AFTER_3	70.54	1.17	4.60	39.74	41.52	40.56	0.326	0.341	-4.77	14.87	12.23	37.95
MEAN_E1_A FTER	73.17	1.38	4.45	43.53	45.42	44.62	0.326	0.340	-5.00	20.40	11.74	41.74
E2_BEFORE	76.87	1.25	4.67	49.10	51.31	50.38	0.326	0.340	-4.62	26.08	11.64	47.14
E2_AFTER_1	78.37	1.13	3.80	51.48	53.85	53.83	0.324	0.338	-3.93	33.66	9.47	50.32
E2_AFTER_2	76.99	1.50	4.09	49.40	51.52	51.16	0.325	0.339	-4.87	29.46	10.60	47.84
E2_AFTER_3	72.13	1.54	4.26	42.09	43.86	43.21	0.326	0.340	-5.29	19.66	11.58	40.41
MEAN_E2_A FTER	75.91	1.38	4.04	47.65	49.74	49.40	0.325	0.339	-4.65	27.74	10.48	46.19
E3_BEFORE	71.69	1.72	5.87	41.52	43.20	41.16	0.330	0.343	-6.51	9.68	15.51	38.54
E3_AFTER_1	74.64	1.85	4.13	45.87	47.70	47.23	0.326	0.339	-5.73	24.88	11.30	44.15
E3_AFTER_2	70.93	1.45	4.30	40.37	42.09	41.39	0.326	0.340	-5.21	17.30	11.76	38.71
E3_AFTER_3	75.83	1.40	3.99	47.54	49.62	49.32	0.325	0.339	-4.67	27.85	10.4	46.11
MEAN_E3_A FTER	73.85	1.57	4.13	44.59	46.47	45.98	0.325	0.339	-5.19	23.43	11.12	42.99
E4_BEFORE	77.47	1.51	4.96	50.17	52.32	51.12	0.327	0.341	-5.25	25.73	12.43	47.83
E4_AFTER_1	72.17	2.01	5.29	42.30	43.91	42.37	0.329	0.342	-6.81	13.90	14.41	39.64
E4_AFTER_2	75.99	1.33	3.99	47.75	49.86	49.56	0.324	0.339	-4.52	28.09	10.33	46.34
E4_AFTER_3	77.96	1.23	3.86	50.85	53.14	53.04	0.324	0.338	-4.18	32.53	9.74	49.60
MEAN_E4_A FTER	75.43	1.51	4.34	46.97	48.97	48.33	0.326	0.340	-5.08	25.18	11.34	45.19
E5_BEFORE	80.96	0.75	3.18	55.67	58.40	59.16	0.321	0.337	-2.82	41.94	7.56	55.32
E5_AFTER_1	80.35	0.91	3.78	54.69	57.31	57.39	0.323	0.338	-3.41	37.60	9.05	53.67
E5_AFTER_2	79.53	1.22	3.28	53.42	55.85	56.41	0.322	0.337	-3.81	38.61	8.33	52.73
E5_AFTER_3	80.68	0.90	2.54	55.25	57.89	59.33	0.320	0.336	-2.83	44.73	6.34	55.43
MEAN_E5_A FTER	80.19	1.01	3.20	54.45	57.02	57.71	0.322	0.337	-3.34	40.34	7.90	53.94
E6_BEFORE	77.38	1.16	4.61	49.88	52.16	51.31	0.325	0.340	-4.39	27.41	11.35	48.00
E6_AFTER_1	79.90	0.96	3.77	53.95	56.51	56.59	0.323	0.338	-3.52	36.79	9.10	52.91
E6_AFTER_2	80.09	1.03	4.15	54.29	56.84	56.52	0.324	0.339	-3.81	35.14	9.97	52.86
E6_AFTER_3	79.53	1.13	4.05	53.38	55.84	55.61	0.324	0.339	-3.99	34.57	9.90	52.01

Data Name	L* (D65)	a* (D65)	b* (D65)	X (D65)	Y (D65)	Z (D65)	x (D65)	y (D65)	Tint	WI	YI	B
MEAN_E6_A FTER	79.84	1.04	3.99	53.88	56.40	56.24	0.324	0.339	-3.77	35.50	9.66	52.59
F1_BEFORE	76.48	0.89	4.18	48.37	50.68	50.21	0.324	0.340	-3.69	27.96	10.28	46.98
F1_AFTFR_1	76.83	1.20	3.78	49.04	51.26	51.19	0.324	0.338	-4.13	30.83	9.66	47.87
F1_AFTFR_2	74.70	2.26	4.39	46.12	47.81	47.10	0.327	0.339	-6.70	23.64	12.25	44.04
F1_AFTFR_3	77.29	1.31	4.21	49.79	52.01	51.54	0.325	0.339	-4.52	29.40	10.64	48.20
MFAN_F1_A FTFR	76.29	1.58	4.12	48.32	50.36	49.95	0.325	0.339	-5.08	27.99	10.82	46.70
F2_BEFORE	80.22	0.99	3.42	54.49	57.07	57.52	0.322	0.338	-3.41	39.21	8.36	53.77
F2_AFTFR_1	82.09	0.81	3.41	57.65	60.46	61.04	0.322	0.338	-2.99	43.02	8.01	57.06
F2_AFTFR_2	80.16	0.86	2.95	54.34	56.96	57.92	0.321	0.337	-2.95	41.56	7.23	54.13
F2_AFTFR_3	78.33	0.81	2.60	51.28	53.77	54.97	0.321	0.336	-2.76	39.91	6.57	51.36
MFAN_F2_A FTFR	80.21	0.83	2.99	54.42	57.06	57.97	0.321	0.337	-2.91	41.43	7.30	54.18
F3_BEFORE	82.00	0.92	4.49	57.54	60.29	59.67	0.324	0.340	-3.69	37.27	10.39	55.83
F3_AFTFR_1	76.27	1.30	3.83	48.19	50.33	50.20	0.324	0.338	-4.37	29.52	9.91	46.94
F3_AFTFR_2	82.05	0.89	4.09	57.63	60.40	60.21	0.323	0.339	-3.45	39.43	9.53	56.32
F3_AFTFR_3	77.91	1.30	4.77	50.79	53.06	52.05	0.326	0.340	-4.73	27.57	11.78	48.69
MFAN_F3_A FTFR	78.81	1.15	4.23	52.20	54.60	54.15	0.324	0.339	-4.15	32.22	10.38	50.65
F4_BEFORE	72.13	1.61	5.12	42.11	43.86	42.46	0.328	0.342	-5.87	14.75	13.63	39.74
F4_AFTFR_1	76.51	1.10	4.18	48.48	50.71	50.25	0.324	0.340	-4.12	28.03	10.47	47.00
F4_AFTFR_2	72.18	1.10	3.83	42.01	43.92	43.66	0.324	0.339	-4.15	22.16	10.16	40.83
F4_AFTFR_3	72.38	1.67	4.15	42.49	44.23	43.69	0.326	0.339	-5.51	20.72	11.44	40.85
MFAN_F4_A FTFR	73.73	1.28	4.05	44.33	46.29	45.87	0.325	0.339	-4.57	23.63	10.68	42.89
F5_BEFORE	77.02	1.13	4.78	49.31	51.57	50.54	0.326	0.341	-4.44	25.79	11.75	47.29
F5_AFTFR_1	80.70	0.93	4.22	55.29	57.93	57.56	0.324	0.339	-3.63	36.00	9.97	53.83
F5_AFTFR_2	78.96	0.83	3.90	52.34	54.87	54.76	0.323	0.339	-3.36	34.21	9.37	51.21
F5_AFTFR_3	79.08	0.91	4.33	52.55	55.06	54.52	0.324	0.340	-3.71	32.17	10.35	51.00
MFAN_F5_A FTFR	79.59	0.89	4.15	53.39	55.95	55.61	0.324	0.339	-3.57	34.13	9.90	52.01
F6_BEFORE	73.81	1.55	5.51	44.53	46.41	44.67	0.328	0.342	-5.83	15.68	14.19	41.81
F6_AFTFR_1	77.77	1.05	4.14	50.47	52.82	52.43	0.324	0.339	-3.95	30.66	10.2	49.04
F6_AFTFR_2	73.01	1.64	4.74	43.38	45.18	44.13	0.327	0.341	-5.68	18.54	12.66	41.27
F6_AFTFR_3	75.54	1.27	4.08	47.04	49.13	48.74	0.325	0.339	-4.47	26.76	10.53	45.58
MFAN_F6_A FTFR	75.48	1.31	4.31	46.96	49.04	48.43	0.325	0.340	-4.65	25.44	11.06	45.30

Table 16 - Paired T-test (ΔT_{int})

	Control_D	Consolidated_E
Mean	-0.75667	0.808333
Variance	0.467987	1.876857
Observations	6	6
Pearson Correlation	0.229755	
Hypothesized Mean Difference	0	
df	5	
t Stat	-2.77075	
P(T<=t) one-tail	0.019665	
t Critical one-tail	2.015048	
P(T<=t) two-tail	0.03933	
t Critical two-tail	2.570582	

Table 17 – Paired T-test (ΔW_I)

	Control_D	Consolidated_E
Mean	-9.61167	5.601667
Variance	55.46106	44.58218
Observations	6	6
Pearson Correlation	0.745878	
Hypothesized Mean Difference	0	
df	5	
t Stat	-7.3272	
P(T<=t) one-tail	0.000371	
t Critical one-tail	2.015048	
P(T<=t) two-tail	0.000742	
t Critical two-tail	2.570582	

Table 18 – Paired T-test (ΔYI)

	<i>Control_D</i>	<i>Consolidated_E</i>
Mean	1.516667	-2.21167
Variance	1.849267	4.608057
Observations	6	6
Pearson Correlation	0.705494	
Hypothesized Mean Difference	0	
df	5	
t Stat	5.972132	
P(T<=t) one-tail	0.000942	
t Critical one-tail	2.015048	
P(T<=t) two-tail	0.001885	
t Critical two-tail	2.570582	

Table 19 – Paired T-test (ΔB)

	<i>Control_D</i>	<i>Consolidated_E</i>
Mean	-6.52	1.228333
Variance	23.97136	10.47818
Observations	6	6
Pearson Correlation	0.533556	
Hypothesized Mean Difference	0	
df	5	
t Stat	-4.53212	
P(T<=t) one-tail	0.003107	
t Critical one-tail	2.015048	
P(T<=t) two-tail	0.006213	
t Critical two-tail	2.570582	

Table 20 - T-test: Two samples assuming equal variance (Frost Resistance-Volume Retainage%)

	Control_G	Consolidated_H
Mean	32.30063	32.03855
Variance	11.84441	381.8513
Observations	3	3
Pooled Variance	196.8478	
Hypothesized Mean Difference	0	
df	4	
t Stat	0.022878	
P(T<=t) one-tail	0.491422	
t Critical one-tail	2.131847	
P(T<=t) two-tail	0.982843	
t Critical two-tail	2.776445	

Note : The value of the failed sample, G1, was replaced with the mean value of G2 and G3 for the statistical evaluation purpose. Here, the P two tail value (0.982843) is larger than the confidence level of 0.05. This indicates that volume retainage percent via consolidation is not significantly differ from the control samples.

C3. Photomicrographs

Petrographic Observation with Nikon Alphaphot-2 Microscope and Phtographs taken with a Nikon DS Fi-1 Camera with NIS Elements BR Software

a. Unconsolidated Control Sample:

Locator (PPL, mag.5x)

Surface of the sample (PPL, mag.10x)

Locator (XPL, mag.5x)

Surface of the sample (XPL, mag.10x)

Petrographic Observation with Nikon Alphaphot-2 Microscope and Phtographs taken with a Nikon DS Fi-1 Camera with NIS Elements BR Software

b. Consolidated Sample:

Locator (PPL, mag.5x)

Surface of the sample (PPL, mag.10x)

Locator (XPL, mag.5x)

Surface of the sample (XPL, mag.10x)

Note : Each arrow indicating consolidating behavior of nanolime;
1 - bridging, 2 - lining, 3 - filling pores

APPENDIX D : Photographs of All Facsimile Samples

with Color Change Graphs for (D, E, and F)

	A1	A2
a. Before
e. After
	A3	A4
a. Before
e. After
	A5	A6
a. Before
e. After

D4

a. Before consolidation

Color Comparison (a vs e)

b. After pre-consolidation
1 application of E-5

c. After consolidation(1)
1st application of E-25

d. After consolidation(2)
2nd application of E-25

e. After 28 days of curing

E2

a. Before consolidation

b. After pre-consolidation
1 application of E-5

c. After consolidation(1)
1st application of E-25

d. After consolidation(2)
2nd application of E-25

e. After 28 days of curing

Color Comparison (a vs e)

E3

a. Before consolidation

b. After pre-consolidation
1 application of E-5

c. After consolidation(1)
1st application of E-25

d. After consolidation(2)
2nd application of E-25

e. After 28 days of curing

Color Comparison (a vs e)

E4

a. Before consolidation

b. After pre-consolidation
1 application of E-5

c. After consolidation(1)
1st application of E-25

d. After consolidation(2)
2nd application of E-25

e. After 28 days of curing

Color Comparison (a vs e)

E5

a. Before consolidation

b. After pre-consolidation
1 application of E-5

c. After consolidation(1)
1st application of E-25

d. After consolidation(2)
2nd application of E-25

e. After 28 days of curing

Color Comparison (a vs e)

E6

a. Before consolidation

b. After pre-consolidation
1 application of E-5

c. After consolidation(1)
1st application of E-25

d. After consolidation(2)
2nd application of E-25

e. After 28 days of curing

Color Comparison (a vs e)

F1

a. Before consolidation

b. After pre-consolidation
1 application of E-5

c. After consolidation(1)
1st application of E-25

d. After consolidation(2)
2nd application of E-25

e. After 28 days of curing

Color Comparison (a vs e)

F3

a. Before consolidation

b. After pre-consolidation
1 application of E-5

c. After consolidation(1)
1st application of E-25

d. After consolidation(2)
2nd application of E-25

e. After 28 days of curing

Color Comparison (a vs e)

F4

a. Before consolidation

b. After pre-consolidation
1 application of E-5

c. After consolidation(1)
1st application of E-25

d. After consolidation(2)
2nd application of E-25

e. After 28 days of curing

Color Comparison (a vs e)

F5

a. Before consolidation

b. After pre-consolidation
1 application of E-5

c. After consolidation(1)
1st application of E-25

d. After consolidation(2)
2nd application of E-25

e. After 28 days of curing

Color Comparison (a vs e)

a. Before
consolidation

b. After pre-
consolidation

1 application of
E-5

c. After
consolidation(1)

1st application
of E-25

d. After
consolidation(2)

2nd application
of E-25

e. After 28 days
of curing

Color Comparison (a vs e)

	G1	G2	G3
a. Before consolidation
b. After pre-consolidation 1 application of E-5			
c. After consolidation(1) 1st application of E-25			
d. After consolidation(2) 2nd application of E-25			
e. After 28 days of curing

	I1	I2	I3
a. Before consolidation
b. After pre-consolidation 1 application of E-5
c. After consolidation(1) 1st application of E-25
d. After consolidation(2) 2nd application of E-25
e. After 28 days of curing			

Index

A

ASTM 3, 26, 27, 33, 37, 40, 41, 43, 53, 54, 56, 58,
59, 60, 64, 65

C

calcite 91
calcium carbonate 4, 7, 17, 24, 83
calcium hydroxide 2, 4, 16, 18, 19, 21, 22, 24, 31,
42
carbonation .. 7, 16, 23, 24, 33, 42, 43, 45, 49, 93,
96
consolidant ... 1, 2, 3, 9, 15, 17, 18, 19, 20, 24, 26,
29, 30, 31, 34, 40, 43, 44, 45, 47, 49, 50, 64,
66, 68, 69, 76, 81, 82, 83, 84, 91
curing..... 33, 37, 42, 43, 48, 49, 76, 83, 93, 96

F

façade 4, 8, 9, 10, 11, 14, 93, 96
flexural strength 25, 27, 52
friability 1, 35, 39, 43
frost resistance 3, 51, 66, 86, 87, 92

L

lime..... 1, 4, 7, 8, 9, 16, 34, 35, 36, 40
aged 7
dolomitic 91
quicklime..... 4
slaked 4, 5, 14, 16, 40
Type S hydrated 40
lime-based..... 18
materials 1, 7, 23, 31, 93
plaster 1, 2, 3, 18, 50, 64, 76, 83, 93, 94, 95
limewater 2, 16, 17, 18, 28, 30

N

nanolime..... 1, 2, 3, 15, 16, 19, 20, 21, 23, 24, 28,
29, 30, 31, 33, 40, 43, 45, 46, 47, 48, 49, 50,
76, 77, 81, 82, 83, 84, 88, 91, 92, 93, 94, 95,
96

CaLoSiL® ... 2, 19, 20, 21, 22, 28, 31, 47, 48, 49
Nanorestore® 2, 19, 20, 21
nanotechnology 15, 18
National Park Service..... 1, 12
I&M 12
Sonoran desert..... 12

P

paired t-test..... 3, 72, 76, 81, 92
permeability
water vapor transmission ... 50, 60, 61, 62, 79,
81, 92
porosity..... 56, 59
liquid nitrogen..... 3, 56, 58, 77
mercury intrusion..... 56
water absorption..... 56
portlandite..... 4, 42

R

RILEM..... 3, 66

S

SEM-EDS 68, 69, 70, 91
Spanish Colonial 1, 4, 40, 42
splitting tensile strength..... 3, 52, 55, 68, 76, 92
stucco 2, 3, 9, 10, 11, 93, 95

T

Tumacácori . 1, 2, 3, 4, 7, 8, 12, 13, 14, 15, 33, 34,
40, 66, 93, 94, 95, 96

W

white haze 30, 45, 64, 82, 94
white index 83, 94
whitening..... 30, 82, 84, 94

Y

yellow index..... 83