Formulation and Evaluation of a Biophilic Protective Surface Treatment for Stone Substrates

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Abstract
This thesis develops and preliminarily tests a biophilic adhesive filler for the fossilized tree stumps at Florissant Fossil Beds National Monument (FLFO), which are rapidly deteriorating due to the impacts of precipitation and freeze-thaw cycling. At the crown of Stump P47, lichens have been observed to have a consolidating effect, preventing further fragmentation. Recent conservation research confirms that in certain environments, with specific substrates and organisms, microflora and macroflora can act as protective and consolidating agents for stone substrates. This thesis explores these benefits by considering potential materials for the formulation of a biophilic adhesive filler, which could be used as a protective surface treatment on the FLFO stumps. The adhesive filler for open cracks and fissures could offer temporary protection, consolidation, waterproofing, and a bioreceptive and nutrient-rich surface on which lichens may continue to flourish. In order to develop the surface treatment, optimal performance characteristics were established. Materials were researched and selected based on their adherence to these characteristics, then preliminarily tested for their properties individually and in combination with other materials as composite systems. Qualitative observations determined which formulations met the outlined characteristics, and recommendations for future confirmatory testing are made. This thesis suggests an innovative direction for future research for cultural heritage protection.

Keywords
biomimetic, biogrowth, bioprotection, adhesive filler, consolidation

Disciplines
Historic Preservation and Conservation

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FORMULATION AND EVALUATION OF A BIOPHILIC PROTECTIVE SURFACE TREATMENT FOR STONE SUBSTRATES

Caitlin Siobhan Livesey

A THESIS

in

Historic Preservation

Presented to the Faculties of the University of Pennsylvania in Partial Fulfillment of the Requirements of the Degree of

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Advisor and Program Chair
Frank G. Matero
Professor
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1. Introduction

For decades, conservators have been investigating new solutions to remove biological growth from stone monuments and buildings and prevent future organism colonization. Microflora, or microscopic bacteria, algae, and fungi, and macroflora, or a plant that can be seen with the naked eye, have the potential to cause significant deterioration and damage to buildings and monuments, as well as having obvious aesthetic consequences; however, recent research has demonstrated the bioprotective qualities of both biological growth and vegetation. In certain environments, with specific substrates and organisms, biogrowth can act as a protective and consolidating agent for the substrate. This research explores these benefits by considering potential materials for a formulated biophilic adhesive filler to be used as a protective surface treatment on stone substrates and developing a preliminary testing program for performance evaluation. This research was developed specifically to address the deterioration of the fossilized tree stumps at Florissant Fossil Beds National Monument (FLFO).

FLFO, a National Park Service site in Florissant, Colorado, is home to nine above-ground fossilized *Sequoia affinis* tree stumps, preserved in a volcanic mudslide over 30 million years ago. These natural monuments are rapidly deteriorating from exposure to weathering in the harsh climate. One of those stumps, labeled “P47,” is significantly covered in organismal growth of various types, including herbaceous vegetation, algae, and lichens. It has been observed that at the top of the stump, or crown, lichens have a consolidating effect, holding splintering fragments of petrified wood together and preventing further material loss from the stump massing. As conservation
research supports the observation that biological growth, especially lichens, can serve as a protective cover for stone monuments, this thesis aims to research the formulation of adhesive fillers for open cracks and fissures that could offer temporary protection, consolidation, and waterproofing, as well as a bioreceptive, nutrient-rich surface on which lichens may continue to flourish. The goal of this treatment is to be an ephemeral preservative that will ultimately be subsumed by the lichens that it is meant to promote.

In order to formulate a protective and bioreceptive treatment as outlined above, optimal performance characteristics were established in order to determine potential material components of the treatment. These materials were researched and selected based on their adherence to these properties, then tested preliminarily for their properties.
individually and in combination with other materials as composite systems (e.g., binder and filler). Qualitative observations determined which formulations met the outlined requirements, and recommendations for future confirmatory testing were made.

A literature review of recent research on bioprotection and biodeterioration, as well as an examination of existing protective treatments for stone substrates and methods of growth promotion in other fields of study guided basic concepts and potential treatment formulations. Studies of petrified wood and past treatment attempts on the FLFO stumps were also examined. The focus of the thesis is the development of performance parameters for a biophilic adhesive filler based on the requirements for treatment of the FLFO stumps and testing protocols for selecting potential formulations. It presents the methodology and results of the preliminary testing, and it proposes further testing parameters to identify potential formulation candidates for field application and monitoring. Finally, it suggests potential applications for this type of treatment for this growing field of study.

For the purpose of this thesis, the biological growth sought includes lichens, biofilms, and algae, as they have been reported to provide protective action at FLFO. Though some macroflora has also been found to have a protective function in some circumstances, their root systems can cause harm to the already vulnerable stumps through existing cracks and fissures, as has been demonstrated in condition assessments.¹ This thesis does not detail the different conditions or nutrients necessary to foster the

growth of the many forms of microflora and macroflora observed and reported on in the literature. It also does not test the treatment’s ability to rapidly create biological growth, given the limited time period for testing. Instead, it relies upon the literature to demonstrate the bioreceptivity and nutrient content of the materials, thereby suggesting their ability to support biological growth. It does not consider the theoretical benefits and detriments of the aesthetic effects of biological growth cover on cultural heritage, nor does it study the varying effects of different forms of biological growth and the differing conditions under which they are protective. Further investigation into these topics is necessary to better understand the potential uses of a protective and bioreceptive adhesive filler for stone.

This thesis researches and tests various materials and formulations in order to create a protective and biophilic surface treatment for a stone substrate. It suggests an innovative direction for future research for cultural heritage protection that has the potential to revolutionize conservation practices.


2. Review of the Literature

2.1 Bioprotection in Conservation

Historically, biological growth on historic buildings and monuments, including rock art, has been considered detrimental, with the potential to cause material damage over time. In recent decades, there has been a significant shift in thinking concerning the effects of micro- and macroflora on cultural heritage, particularly stone monuments and buildings. This section reviews the evolution of thought on the potential of biogrowth to have positive and protective impacts on stone heritage.

The term “bioreceptivity” was defined in 1995 by Olivier Guillitte, referring to the ability or tendency of a material to be inhabited by living organisms.\(^2\) This definition was revolutionary in conservation because it provided a neutrality to the presence of organisms upon built heritage, free of negative connotations. Prior to this, only terms such as “biodeterioration” were used, clearly focusing on the potential adverse effects of biological growth on building materials.\(^3\) With his 1995 articles, Guillitte essentially began the conversation and change of mindset that would lead to theories of bioprotection.

In a 2005 synthesis of past research in bioprotection, Carter and Viles demonstrate that the concept of beneficial properties of biogrowth and vegetation on substrates has been considered since the 19th century but re-emerged in the late 20th century.

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century. They assert that there is a lack of research in this field. This pioneering review is one of the first comprehensive looks at bioprotection.

Lichen is one form of biological growth that has been the most significantly researched for its potentially protective qualities. Studies since the early 2000s have shown that lichen can act as a barrier layer from the abrasive effects of wind and salt, as well as a protection against frequent temperature changes. It can absorb moisture and prevent temperature fluctuations, particularly in damp, hot environments, as well as limit water permeability of a surface. Lichen has also been found to act as a surface consolidant by limiting detachment of asbestos-cement particles.

Sandstone and limestone have both been found to benefit from bioprotection. Entrapped lichens can help protect limestone by filling the porous surface, acting as a water and sulfate barrier, which could thereby slow deterioration. This is significant because, as a calcareous stone, limestone is particularly sensitive to acid precipitation,

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10 Concha-Lozano, “Protective effect.”
and lichens have the potential to release acidic metabolites onto a substrate.\textsuperscript{11} The fact that lichens have been found to act as a macro-preservative of this stone in some instances, rather than only as a source of slow damage from mineral decomposition, shows the potential of lichens to protect a variety of surfaces, including those that have traditionally been considered susceptible to biodeterioration.

Lichens are a form of fungi that form a symbiotic relationship with photosynthesizing organisms, such as algae or cyanobacteria. They are able to grow on almost all surface environments on Earth.\textsuperscript{12} Research that has focused on the bioprotection of masonry from lichen has primarily considered how the biogrowth layer protects the substrate from the effects of granular disaggregation, moisture infiltration, thermal fluctuations, humidity variations, and other aggressive external effects. Little research has considered the consolidative effects of organisms such as lichen and biofilms, besides Favero-Longo’s finding that lichen prevents particular detachment from the carbonatic matrix.\textsuperscript{13}

Algae are rootless, photosynthetic organisms commonly found in aquatic systems.\textsuperscript{14} They are often eukaryotic and autotrophic, and they have been utilized for

\textsuperscript{13} Favero-Longo, “Lichens on asbestos-cement roofs.”
their ability to detoxify minerals and molecules.\textsuperscript{15} Algae, too, have been found to be protective of stone in some instances. Despite aesthetic consequences and conceptions that “greening” or algal staining might have deteriorative effects on stone, research suggests that it may have the opposite effect. In a study, algal greening was not found to have a significant impact on stone deterioration. In fact, the films were thought to prevent moisture from entering the stone.\textsuperscript{16}

In addition to biological growth like lichen, bacteria, and algae, larger macroflora has been found to provide beneficial protection to masonry substrates.\textsuperscript{17} For example, field studies determined that ivy protects masonry from pollution particulates and relative humidity changes.\textsuperscript{18} Ivy can absorb atmospheric particulates, especially pollutants from vehicles in busy, high-traffic areas, though its effectiveness varies. This is beneficial for human health, and it can prevent particulate matter from reaching stone surfaces and causing deterioration. Of course, this absorptive quality is not necessarily a property of all vegetation, as ivy is valued for its evergreen quality, moistness, and its canopy growth patterns.\textsuperscript{19} Additional research has found that ivy can provide thermal buffering and limit


\textsuperscript{18} Viles, “Ivy.”

\textsuperscript{19} Sternberg, “Dust particulate absorption by ivy.”
freeze thaw cycles on limestone.\textsuperscript{20} Despite the potential for protection, researchers recognize that ivy also has the potential to cause damage through root jacking in foundations and imperfections in masonry walls.\textsuperscript{21}

Vegetation living directly atop cultural heritage, like ivy, can be preservative, but adjacent vegetation can also have bioprotective effects. For example, evergreen trees can help to decrease temperature and moisture content fluctuations of nearby buildings and monuments. These effects can lower the frequency of freeze-thaw cycling and the occurrence of efflorescence.\textsuperscript{22}

Bioprotection has not been as heavily researched as biodeterioration, but the body of literature on the subject is rapidly growing. In addition to increased interest in higher plants, as well as algal and lichen biofilms, “soft-capping” is an increasingly popular method involving the placement of soil and vegetation on top of walls, especially ruins. This layer acts as a buffer to the elements, and it is cost effective. Soft-capping is one of many methods considered to be nature-based solutions that incorporate “green elements” into conservation.\textsuperscript{23} It has been considered as a possible alternative to “hard-capping,” or layers of lime, cement, and mortar intended to protect compound walls. Hard-capping has the potential to crack and allow moisture infiltration. Soft-capping has been studied as a method to avoid the issues of hard-capping, as plants’ utilization of moisture can prevent

\begin{itemize}
\item \textsuperscript{20} Coombes, “Thermal blanketing by ivy.”
\item \textsuperscript{21} Coombes, “Thermal blanketing by ivy.”; Sternberg, “Dust particulate absorption by ivy.”; Viles, “Ivy.”
\item \textsuperscript{22} Yonghui Li, et al., “Role of the urban plant environment in the sustainable protection of an ancient city wall,” \textit{Building and Environment} 187 (2021), \url{https://doi.org/10.1016/j.buildenv.2020.107405}.
\item \textsuperscript{23} Martin A. Coombes and Heather A. Viles, “Integrating nature-based solutions and the conservation of urban built heritage: Challenges, opportunities, and prospects,” \textit{Urban Forestry & Urban Greening} 63 (2021), \url{https://doi.org/10.1016/j.ufug.2021.127192}.
\end{itemize}
moisture from reaching the wall below. It also may act as a thermal and protective barrier.

Even as the field develops, there is much that has yet to be understood about bioprotection, and many organisms and materials yet to be studied. For example, little research exists that considers biofilms as a form of protective layer over masonry substrates, but one study hypothesizes the benefits of both lichen and biofilms.\(^{25}\) While lichens serve as a protective buffer and contribute to masonry consolidation, the oxalic acid secreted by both lichen and biofilms is thought to be case hardening, thereby protecting the substrate.\(^{26}\) Biofilms themselves have rarely been studied as protective.

Conservation research has not delved into the prospect of actively promoting biological growth or vegetation on a substrate. Rather, it considers organisms that are already present for its protective or deteriorative effects. In fact, Favero-Longo et al. conclude that “no effective techniques are currently available for increasing lichen colonization on rock-like substrates,” in order to increase bioprotection.\(^{27}\) Gadd and Dyer similarly propose microbially mediated varnishes to assist in bioprotection, adding that strategies to increase lichen colonization would be necessary.\(^{28}\) Little research discusses such techniques for increasing lichen growth on stone built heritage, perhaps because the


\(^{26}\) Broxton, “Rhyolitic Tuff.”

\(^{27}\) Favero-Longo, “Lichens on asbestos-cement roofs.”

most frequent downside cited to tolerating or propagating microflora or macroflora on architectural and sculptural surfaces in aesthetic discoloration.

For the most part, those that assert the benefits of biogrowth and vegetation protection of masonry substrates admit that there is potential for deterioration from biogrowth and vegetation, as well. Some studies have found that the conclusion of bioprotection is uncertain, and that other factors could be at play that cause further deterioration in areas where lichen is absent, such as that lichen cannot form on disaggregated masonry.\textsuperscript{29} Others consider the competing protective and deteriorative factors of microflora and macroflora, determining that results could vary depending upon biogrowth species and substrate environment.\textsuperscript{30} Yet another study has found neutral effects of biogrowth, asserting that it may be neither detrimental nor beneficial.\textsuperscript{31} Clearly, the impact of biological growth on its surroundings is highly variable, with much left to be explored.

2.2 Biomimetic Treatments

Bacteria specifically has been employed for its potential to benefit stone heritage conservation, and it has been used as a cement additive for the purposes of increasing


Recent research has successfully employed biomimetic treatments in conservation using bacteria to encourage the formation of protective layers over stone, known as biomineralization, on limestone, gypsum, and brick. *Myxococcus xanthas* is a bacteria that has been used for the conservation of limestone because it causes calcium carbonate precipitation. The biomineralization forms a hard surface over the substrate that is better able to resist stress than the substrate itself. *Colletotrichum acutatum* is another organism, a fungus, that has been used for biomineralization, also for the purpose of calcium carbonate production on limestone. This fungus is considered safe for bioprotective purposes because of the ability to control the organism and therefore the risk of damage to the stone. *Escherichi coli* has been used as a bioproduct in the protection of ceramic bricks by inducing biosilicification and the formation of biofilms, which provide a barrier against water penetration for the masonry. Biomineralization has also been induced using carbanatogenic bacteria to protect gypsum plaster substrates by producing vaterite biocement, which acts as a porous consolidant. In the case of the Double Tower in Lingyin Temple, Hangzhou, China, researchers recognized natural biomineralization in the form of a translucent protective film that had formed over the

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surface. Their biomimetic work consisted of a replication of the calcium oxalate monohydrate biomineralization in order to produce a protective treatment that could be applied to stone substrates.\textsuperscript{37}

These biodeposition processes and biomimetic treatments were intended primarily to protect the surfaces of vulnerable stone masonry like limestone. Unlike this thesis, the research did not advocate any goals of encouraging biological growth; rather, bacteria was a mechanism to induce the process of biomineralization, which subsequently formed protective biomineral layers over the given substrates.

2.3 Biodeterioration in Conservation

Some argue that the detrimental effects of, algae, fungi, lichen, biofilms, and bacteria, and the resulting biodeterioration, remain of paramount concern in the evaluation of biogrowth on stone substrates, and most researchers in bioprotection acknowledge the potentially harmful effects of these same organisms. The potential for damage and deterioration caused by both microflora and macroflora cannot be ignored. Micro- and macroflora can be protective in certain circumstances and on certain substrates, but it is important to consider the potential for harm by these organisms and to acknowledge that their growth is not always protective.

Deterioration of stone has been found to be a result of lichen’s geochemical and geophysical metabolic actions.\textsuperscript{38} Biofilms often contain fungi and cyanobacteria, which can damage stone masonry by producing acid metabolites, siderophore, and osmolytes. In


\textsuperscript{38} Sohrabi, “Lichen colonization.”
addition to harmful secretions, microorganisms can penetrate stone surfaces, and they can negatively impact the appearance of the substrates.\textsuperscript{39} In contrast to reported beneficial buffering of biogrowth such as lichen, one study found that biofilms have a deteriorative effect by acting as a barrier.\textsuperscript{40} Biofilms have the potential to prevent conservation treatments from reaching a substrate, trap moisture, and create uneven heat transfer. Additionally, fungal cells, algae, and lichen can cause sheet separation, as well as nodule and grain alterations in a substrate.\textsuperscript{41}

Earlier preservation literature is especially focused on biodeterioration, detailing the damaging effects of various organisms and explaining the potential chemical and mechanical degradation that can result from algae, fungi, bacteria, lichens, and higher plants.\textsuperscript{42} However, it is important to recognize that recent research continues to explore the deleterious effects of various forms of biogrowth and the different types of damage they cause. Significantly, this varies by species and stone type.\textsuperscript{43} Researchers continue to warn against the long-term negative effects of lichens.\textsuperscript{44} Methods of biogrowth removal,


such as laser cleaning, also continue to be studied and tested, as mechanical methods and biocides can sometimes be harmful or ineffective.\textsuperscript{45} For example, biofilms on the dome of the Jefferson Memorial were removed using laser ablation and steam cleaning. In this situation, marble erosion had created grooves in which biofilms were able to grow extensively.\textsuperscript{46} and cause dark discoloration of the white stone surface. Biological growth removal is a prevalent and accepted practice in stone conservation, and will likely continue to be, as bioprotection is dependent upon specific circumstances.

Some research studying biodeterioration briefly raises the prospect of protective effects of biogrowth, as well. For example, Scheerer mentions that biofilms, while destructive in some ways, might also act as a consolidant.\textsuperscript{47} Sohrabi, too, mentions the concept of bioprotection, only to argue that research on the subject is limited to specific aggressive environmental conditions in which biogrowth acts as a protectant.\textsuperscript{48}

2.4 Biological Growth Promotion

In industries other than conservation, there have been countless efforts to promote the growth of microflora and macroflora for various reasons. Those methods investigated for this research focused primarily on the agriculture industry. Often, such methods

\textsuperscript{47} Scheerer, “Microbial Deterioration of Stone Monuments.”
\textsuperscript{48} Sohrabi, “Lichen colonization.”
involve the retention and absorbance of water, and the provision of nutrients to allow for nitrification processes.

Biogenic soils are one such method. Research has found that biogenic amorphous silica in soils increases the soil’s capacity to hold water, thereby increasing the water available to plants and potentially mitigating the impacts of drought.\(^49\) It has also been found that the biogenic structures of earthworms enhance the fertility of soil, increasing nutrient availability, as well as carbon and nitrogen transfer.\(^50\) Similar effects were found for manure.\(^51\) Research by Garcia-Pichel on biological soil crusts studies the abilities of cyanobacteria that are activated with moisture exposure and can survive with little moisture for long periods of time within a formed crust. This is because cyanobacteria move to the surface during wetting periods. Such crusts may also be colonized by other forms of microflora and macroflora due to their increased stability.\(^52\)

Plant growth promoting rhizobacteria have been found to promote growth, as they release hormones into the soil and have been seen to increase the stress tolerance of crops to various factors.\(^53\) They may also improve uptake of nutrients like nitrogen, potassium,

\(^{49}\) J. Schaller, et al., “Biogenic amorphous silica as main driver for plant available water in soils,” *Scientific Reports* 10, no. 2424 (2020), [https://doi.org/10.1038/s41598-020-59437-x](https://doi.org/10.1038/s41598-020-59437-x).


\(^{52}\) Ferran Garcia-Pichel and Olivier Pringault, “Cyanobacteria track water in desert soils,” *Nature* 413 (2001): 380-381, [https://doi.org/10.1038/35096640](https://doi.org/10.1038/35096640).

phosphorus and iron.\textsuperscript{54} Plant growth promoting rhizobacteria are just one form of biofertilizer employed in the effort to stimulate crop growth. Others include arbuscular mycorrhizal fungi and nitrogen-fixing rhizobia. All of these biofertilizers are comprised of microorganisms that enhance nutrient availability through various mechanisms.\textsuperscript{55}

2.5 Stone Protection

Many forms of stone protection include stopping or preventing biological growth on stone surfaces. Masonry coatings have been researched extensively, and products exist to serve as consolidants, and to provide waterproofing penetrants or water-resistant films; however, no research has examined or attempted to create protective treatments that simultaneously encourage biogrowth on masonry. On the contrary, they have generally been valued for their ability to prevent organismal growth. Some of these protective methods, such as masonry coatings, can ultimately be detrimental to the substrate. For example, hydrophobic coatings may also be vapor impermeable, preventing the escape of water vapor from the substrate, thereby allowing damage to the masonry, as well as the coating. Such coatings can also alter substrate appearances.\textsuperscript{56}

In addition to waterproofing, masonry protectants may be water repellant, in that they prevent liquid water infiltration but allow for vapor permeability. Common water


repellants include silicones and silanes, metal compounds such as aluminum stearate, and organics, such as acrylics.\textsuperscript{57} Acrylic resins are widely used as a conservation surface protection treatment and consolidant, valued for their stability.\textsuperscript{58} The effectiveness of silicon-based compounds varies by specific product and can pose a risk of increased damage. If any water repellant product is applied improperly, it may harm the substrate or fail as a protectant.\textsuperscript{59}

Recent research has also explored the possibilities of nanotechnology as a protective treatment for stone. Nanocomposite coatings have been tested for their ability to consolidate and protect stone masonry as well as prevent biological activity.\textsuperscript{60} While nanoparticles may have chromatic effects on the applied surface, they are considered an effective alternative to previous chemical treatments, with promising biocidal qualities.\textsuperscript{61} Nanoparticle treatments also aim to develop treatments that impact hydrophobicity to surfaces, as well as self-cleaning abilities.\textsuperscript{62}

Historically, masonry coatings have been used as a surface treatment to limit water absorption, provide surface consolidation, and address aesthetic aspects such as

\textsuperscript{59} Charola, “Water-Repellent Treatments.”
soiling, sometimes with biocidal additives, but they can have detrimental effects. 63

Treatment success depends on their evaluation for permeability, transport of moisture in liquid or vapor form, hygroscopicity, appearance, penetration and uniform absorption into the substrate, low thermal expansion, durability, biological inertness, and retreatability. 64 Existing masonry coatings and films are generally intended to prevent biogrowth from forming on the masonry substrate rather than encourage it. In some cases, research has been devoted to improving the biocidal qualities of masonry coatings that serve as consolidants and water protectants. 65 Organic polymer matrices have also been studied for their ability to resist soiling. 66 Koestler reports on various commonly used coatings in masonry conservation and the extent to which they successfully discourage fungal growth, suggesting the additions of biocides or the use of products that better resist biogrowth. 67 This conclusion further shows the tendency toward organism-resistant treatments, as opposed to those that actively encourage such growth.

3. Site Overview

3.1 Brief History of Florissant Fossil Beds National Monument

Approximately 34 million years ago, when Mount Guffey erupted in Florissant, Colorado, a 5-meter layer of lahar, or volcanic deposit, settled into the surrounding valley. A forest of *Sequoia affinis*, a relative of the modern California Redwood, was buried beneath that lahar, resulting in a lack of oxygen to the roots and the death of the sequoia trees. This also caused the stumps of those trees, entrapped in lahar, to become fossilized. This transformation occurred in countless organisms in the Florissant valley, including insects, fish and other plant forms.

Native Americans, living on or near the Florissant land for thousands of years, knew of the area’s fossil resources and were forced off the land by federal policy in the late 19th century. European settlers rediscovered the Florissant’s fossils in the 1860s, after which followed scores of scientists, and later, tourists, who excavated the fossils from the soil and lahar that had covered them for millions of years.\(^68\) One apparent method of excavation of the stumps was dynamite.

In 1969, after a public court battle, the National Park Service acquired the fossil park from private landowners, establishing Florissant Fossil Beds National Monument (FLFO), to preserve the fossil park, and the petrified stumps, in perpetuity. Today, nine out of approximately 21 recorded stumps are visible for viewing on the grounds of the 6,000 acre park.

FLFO is not the only fossil park in the United States. Fossil parks can be found across the country, and four of the country’s forty-five National Natural Landmarks,
designated for their paleontological resources, are located in Colorado alone.\textsuperscript{69} Additionally, other petrified forests are located around the world. The fossilized stumps at FLFO are, however, some of the largest-in-diameter petrified stumps known.\textsuperscript{70} FLFO is home to the only extant petrified stump trio. The setting at FLFO also provides an ideal study, due to the extensive research that has already been performed there, and the lahar deposit’s defined stratigraphy and geology.\textsuperscript{71} It is therefore imperative that these petrified stumps be preserved to allow the opportunity for further paleontological research, education, and the appreciation of some of the earth’s wonders.

\textit{Figure 3.2 – The Big Stump today (Source: “Big Stump,” Florissant Fossil Beds National Monument, National Park Service, https://www.nps.gov/places/big-stump.htm)}


3.2 Climate of Florissant, Colorado

The climate at FLFO is a harsh environment of extremes that causes significant stress to the fossilized stumps. The park, is located in Climate Zone 5B, “Cool Dry,” as defined by the IECC, and adjacent to Climate Zone 7, “Very Cold.”72 Florissant, CO receives an average of 16.88 inches of precipitation every year. On average, the hottest month in Florissant is August, with an average high of 75 degrees Fahrenheit and an average low of 40 degrees Fahrenheit. This is also the wettest month in Florissant, with an average precipitation of 3.38 inches. The coldest months are December and January, with average highs of 38 and 39 degrees Fahrenheit and average lows of 4 and 3 degrees Fahrenheit, respectively. Every month has an average high above 32 degrees Fahrenheit, or freezing, and every month has an average low temperature below freezing, except for June, July, and August.73 As a result, there is potential for freeze-thaw cycling throughout the year.

The stumps are particularly vulnerable to freeze-thaw cycling in the spring and fall months, and sunlight presence or absence plays a significant role in causing rapid or delayed heating and therefore thawing. According to Young, Meyer, & Mustoe, freeze-thaw cycling can happen quickly, and multiple cycles can take place within hours. Within the stumps, water presence within the pores and microcracks and its freezing can create hydrostatic pressure and cause mechanical damage.

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Temperature data was recorded from the surface of several stumps from 2004 to 2005. The study found that 119 freeze-thaw cycles occurred at the surface of stump P47 over 289 days. The data was collected for every month except for June, July, and August, and freeze-thaw cycling took place over all of the months during which the stumps were studied. This data also indicated that freeze-thaw cycling occurs in the outer regions of the stumps, causing surface damage. There were wide ranges in relative humidity values, as well, with data from March 2005 showing a range of 16.25% to 96.75%. As the presence of moisture is necessary to cause freeze-thaw cycling, this data shows that even low levels of moisture during dry months can cause cycling and therefore damage to the stumps.\footnote{Young, “Conservation of an Eocene petrified forest.”}

3.3 Technical Description of Petrified Wood and Its Physical Properties

The stumps at FLFO are identified using a letter-number system, with each stump denoted by the letter “P” for “paleontology” and a number, corresponding to the order in which the sites were inventoried. This naming system comes from an inventory and monitoring project of paleontological sites at FLFO. As part of this project, which began in 1992, the sites are periodically monitored for visible physical changes. These sites include the fossilized stumps, as well as shale fossil beds.\footnote{Documentation information provided by Dr. Herbert Meyer.} The nine above-ground stumps have been labeled as P16, P20, P31, P42, P43, P46, P47, P54, and P55.
This study focuses on Stump P47, located adjacent to the FLFO Visitor Center and measuring 6 feet in diameter and 10 feet 3 inches in height. P47 was previously identified as an ideal subject of study for the representative variety of deteriorative conditions present on the stump, as well as its proximity to the site visitor center. The following findings of material properties of petrified wood are focused primarily on P47 specifically.

The petrified stumps at FLFO are primarily composed of silica, resulting from the siliceous volcanic minerals that caused fossilization. Silica is found in the form of opal and quartz in varying proportions in different stumps and fragments of petrified wood.
Stump P47 is composed mostly of Opal-CT, which occurs in shades of brown and gray, and quartz, which occurs as tan or cream colors in the fragments.  

The accepted theory as to the petrification permineralization process, as hypothesized by R.F. Leo and E.S. Barghoorn and confirmed by later studies, states that organic material like wood is drawn to silicic acid, resulting in the formation of a silica film over the organic cell walls. As the silica mineral forms, the organic material deteriorates, resulting in a “templating” or “replacement” of the original wood.

Despite fossilization, the petrified stumps retain properties of wood, including the cellular structure and “open intercellular spaces.” This composition can lead to splitting.

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76 Mustoe, “Mineralogy and geochemistry of late Eocene silicified wood.”
77 Ibid.
along both radial and tangential planes. Additionally, the tracheids, the long, thin cells found in trees, become more fragile with fossilization, leading to the possibility of cross-grain splitting.78 Petrified wood also behaves similarly to some stone materials. As a silica-based material, petrified wood is comprised of minerals and can have robust strength properties; however, its anatomical structure creates an unstable microstructure.

In 2017, Oxland tested the properties of FLFO petrified wood, identifying compressive strength values, modulus of rupture, the thermal coefficient of expansion, and rates of absorption. His findings from mechanical strength testing concluded that FLFO petrified wood has a higher threshold for modulus of rupture than common stones such as Indiana Limestone and Ohio Sandstone. Absorption testing revealed that water absorption occurs through microcracking in the wood samples, whereas surfaces free of cracking are not absorptive at all, perhaps due to the material’s density.79

3.4 Water Absorption Test

A water absorption test was completed according to the standard ASTM C97. Seven samples of petrified wood that had been previous collected were chosen for testing. The samples selected varied in dimension and mass. The samples were dried in an oven at 60 degrees Celsius for approximately 67 hours, or until all samples displayed the same consecutive weights. A bath was filled with cold water, and the cooled samples were fully submerged. They soaked for approximately 48 hours, were individually removed from the bath, surface dried with a damp paper towel, and weighed to obtain the

78 Young, “Conservation of an Eocene petrified forest.”
79 Oxland, “Conservation assessment.”
wet weight. Small surface loss of fragments required that the samples become
dimensionally stable before the final test was executed. The saturated samples were
placed in the oven as before and weighed periodically until, after 287 hours, it was
determined that all samples no longer showed a significant change in consecutive
weighings, indicating absolute dry weight.

The water absorption test indicated an average water absorption of 6.97%, with a
standard deviation of 3.95% and maximum and minimum measurements of 3.30% and
12.67%. It is clear from the micromorphology of the samples that water uptake was due
to microcracking and microfissures within the samples. Dry mass 1 (mean: 355.84g,
standard deviation: 161.39g) was compared with the wet mass (mean: 381.67g, standard
deviation: 177.09g), through an f-test and a t-test. The f-value of 0.83 and t-value of 0.39
indicate that the difference in variances and means of the first dry mass and the wet mass
is not statistically significant.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Dry mass 1 (g)</th>
<th>Wet mass (g)</th>
<th>Dry mass 2 (g)</th>
<th>Dimensions</th>
<th>Water Absorption (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>452.94</td>
<td>467.88</td>
<td>452.68</td>
<td>Variable</td>
<td>3.30</td>
</tr>
<tr>
<td>2</td>
<td>391.11</td>
<td>418.87</td>
<td>390.71</td>
<td>Variable</td>
<td>7.10</td>
</tr>
<tr>
<td>3</td>
<td>238.65</td>
<td>268.03</td>
<td>238.09</td>
<td>Variable</td>
<td>12.31</td>
</tr>
<tr>
<td>4</td>
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<td>643.72</td>
<td>570.56</td>
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</tr>
<tr>
<td>5</td>
<td>489.96</td>
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<td>4.19</td>
</tr>
<tr>
<td>6</td>
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<td>202.82</td>
<td>194.49</td>
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<td>4.19</td>
</tr>
<tr>
<td>7</td>
<td>152.22</td>
<td>159.88</td>
<td>152.08</td>
<td>Variable</td>
<td>5.03</td>
</tr>
</tbody>
</table>

*Figure 3.5 – Table of results from water absorption test (Source: Author, 2022)*
3.5 Brief Overview of Deteriorative Conditions and Treatment History

Though burial by lahar was necessary for the permineralization process of the stumps, it also protected them from cyclical weathering and mechanically supported their fragile state underground. Since their discovery, many stumps have been exposed. As a result, they have experienced more deterioration in the past two centuries than in the previous 34 million years since their formation. Before the establishment of FLFO, visitors had greater access to the stumps, and tourists were allowed to touch, sit on, and even remove fragments for souvenirs. In addition, anecdotal evidence has indicated that dynamite may have been used to excavate some of the stumps from the lahar, including P47.
With exposure to weathering elements, the stumps have been heavily affected by moisture from precipitation and ground water, as well as snow and daily thermal fluctuations with extreme differentials within a single stump. These temperature cycles, in combination with moisture infiltration, and the inherent wood anatomy of the stumps, have resulted in severe freeze-thaw damage, causing the stumps to fragment and splinter.

In 2016, the Center for Architectural Conservation (CAC) at the University of Pennsylvania began a partnership with FLFO to identify deteriorative conditions on the stumps and formulate a treatment plan to slow or prevent that deterioration. During Phase 1 of this project, researchers identified the following conditions on the stumps: horizontal cracking, tabular cross checking, exfoliation, soil deposits and lahar deposits, fibrous disintegration, microcracks, splintering, fractures, and the presence of lichens, algae, and herbaceous vegetation. Many of these conditions were recorded for Stump P47, with the most severe conditions being splintering, fracture, exfoliation, loss of section, and soil deposit. In addition, the landscape of P47 has very poor drainage, as it sits in a bowl-like depression as a result of excavation. Of the eight stumps surveyed, six of them were determined to be in poor condition, including P47.80

Phase 2 of the project sought to establish an appropriate treatment method for the rapidly deteriorating stumps, which would involve the securing of loose and detached fragments to P47. Research by Oxland determined that mechanical pinning was not an appropriate method of reattachment for the stump fragments, as it resulted in splitting of

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the fragments due to resulting hoop stresses.\textsuperscript{81} A continuation of the research laboratory testing of the fragments and the identification of an epoxy adhesive treatment methodology using Araldite 2015 in order to reattach the fragments.\textsuperscript{82} In 2019, the methodology was tested on site at FLFO using P47 sample fragments that remained in situ for monitoring.\textsuperscript{83}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fragmentation_of_p47}
\caption{Fragmentation of P47, marked to show loose and detached areas (Source: Author, 2021)}
\end{figure}

\textsuperscript{81} Oxland, “Conservation assessment.”
\textsuperscript{82} Joseph Bacci, “Florissant Fossil Beds National Monument (FLFO), CO Proposed In Situ Stabilization Testing for Petrified Wood Stumps (Phase 2).”

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During Phase 3 of the project, researchers applied this tested methodology on site. This involved the thorough identification of loose or detached fragments on P47 and the reattachment of as many of those fragments as possible over the course of one month of field work in the summer of 2021. The reattachments were performed using Araldite 2015 epoxy as concentrated “spot welds” on the interior adherend surfaces. The epoxy reattachments are currently being monitored, and the success of this treatment may affect whether the other stumps at FLFO are treated in a similar method to address large scale spalling and fragmentation. During this phase, it became evident that lichen growth on the stump crown and individual fragments showed the positive effects of preservation of the fragile surfaces through surface consolidation and protection.

In addition to addressing past and current mechanical damage to the stumps, the research team is exploring the design of transparent protective shelters that would limit and possibly remove the threat of freeze-thaw cycling, thereby significantly reducing the cause of much of the physical deterioration on the stumps.

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84 Oskierko-Jeznaki, “Trip Summary Report.”
4. Optimal Properties and Materials Considered

4.1 Optimal Properties

Optimal properties of the proposed treatment were established to fulfill two performance requirements: protection and stabilization of open fissures and cracks to water ingress, and bioreceptivity, the latter to encourage, or at least not restrict, the continued growth of flora, such as lichen. This treatment is intended to act as an alternative to adhesive fillers that are often hydrophobic and biologically toxic. Additionally, the color of the formulation should be compatible with the substrate so as not to draw attention and maintain the appearance of the stumps, for integrity and visitor purposes, and it should be removable, or at least allow for retreatment.

The protective qualities were established based on the environmental conditions at FLFO and the conditions of the stumps. The primary environmental causes of deterioration are precipitation and freeze-thaw cycling, so an adhesive filler must act as a barrier against these aggressors. The type of deterioration, mainly splintering, spalling, fracture, and loss of section, requires a treatment with variable viscosity for different gap filling sizes that will successfully fill those gaps without causing added stress from high shrinkage.

**Water Insensitivity**

Precipitation events are causing water infiltration into the stump due to both falling and rising damp. Though rising damp cannot be easily mitigated due to the surrounding grade and potential for excavation damage to the fossilized roots at the stump base, prevention of falling damp is possible by slowing water infiltration at the
crown. As a result, water insensitivity and the ability to act as a water resistant fill to the petrified wood is essential for the treatment. Hydrophobicity was not a desirable property, however, as the fill must be waster absorbent (and desorbent) to support biological growth.

**Durability Against Freeze-Thaw Cycling**

Along with water infiltration, subsequent freeze-thaw cycling is causing significant damage to the stumps. The frequency of these cycles and the presence of moisture when the cycles take place cause the repeated formation of ice within the stump, exerting pressure upon the substrate. This causes cracking and detachment on the stump, as well as further water penetration. Therefore, the adhesive fills need to limit water ingress and should be able to withstand freeze-thaw cycling, while acting as a thermal barrier to reduce the frequency of freezing and thawing.

**Low Shrinkage**

Shrinkage of the adhesive filler upon drying should be minimized in order to fill the cracks and fissures and to not add undue stress to the substrate by contraction. Subsequent swelling and shrinkage could exert pressure upon the substrate in a similar way to freeze-thaw cycling. Therefore, the filler must be dimensionally stable to moisture.

**Adhesive and Cohesive Strength**

The formulation must display adequate adhesive and cohesive properties in order to remain in place, as well as fill voids, cracks, and fissures that are open to the weather.
Because of the existing fragmentation of the stump, especially at the crown, “consolidation” of the surface is necessary to prevent further deterioration and loss of material.

**Variable Viscosity**

The formulation should have variable viscosity to allow for application to cracks and fissures of varying width and depth on the stump crown. When viscosity is altered based on proportions of binder and filler, as well as diluent (water), the variation will allow the formulation to reach and fill various gaps within the stump surface.

**Nontoxicity and Bioreceptivity**

The formulation must also be nontoxic to organismal growth, in order to allow for subsequent colonization and development of biological growth. Ideally, the treatment is also bioreceptive and nutrient-rich, in order to provide nutrients to the biological organisms and promote rapid growth. Lichens require light, water, and nitrogen to flourish. The protective formulation should serve as food for the organisms and eventually support that biological growth, which then itself will serve as a protective barrier to the substrate.

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4.2 Glossary of Materials

Materials that are currently used in various fields, including conservation, agriculture, medicine, biology, and chemistry were explored for their potential to meet the properties described above, and included both binders and fillers. The following materials were researched and evaluated from the literature for their ability to contribute to an adequate protective surface treatment while also promoting biological growth.

Organic Binders:

Agar

Extracted from the cell walls of a variety of species of red algae, especially of the genus *Gracilaria*, agar is a gelatinous polysaccharide comprised of agarose and agaropectin. Though insoluble in cold water, agar can dissolve easily in boiling water. It has high gel strength, and its gelation is reversible, depending upon temperature. As a natural, plant-based material, it is inert and non-toxic, though it also will also not degrade from bacteria inhabitation, as it does not act as a microorganismal food source. Agar also has variable viscosity and high porosity of 100 to 300nm for an agar concentration of 207%. Agar has had several uses in conservation, valued for its ease of clearing with water. It has been utilized as a cleaning material for porous objects, as well as for artwork. In addition to conservation, agar has found use in electrochemistry,

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microbiology, especially as a growth medium, and the food industry,\textsuperscript{88} valued for its thickening properties.\textsuperscript{89}

**Cornstarch**

Cornstarch, a carbohydrate polymer composed of the polysaccharides amylose and amylopectin, is made from corn through a wet milling process and comes in the form of a white powder.\textsuperscript{90} Cornstarch is cold water-insoluble, yet hydrophilic.\textsuperscript{91} It is able to swell to 30 times its volume, though it is not nearly as absorbent as potato starch, which can swell to 100 times its volume.\textsuperscript{92} It has also been found to have poor mechanical properties,\textsuperscript{93} and it is biodegradable. Because of these properties, plasticizers have been utilized as reinforcement of cornstarch films.\textsuperscript{94}

**Guar Gum**

Guar gum is extracted from the endosperm of the seeds of *Cyamopsis tetragonoloba*, or Guar. It is commonly used as a thickener in cooking, as it is cold-water


\textsuperscript{89} Lee, “Factors affecting yield and gelling properties of agar.”


\textsuperscript{93} Guohua, “Methylated-cornstarch/poly(vinyl alcohol).”

soluble and absorbent, and viscous in water.\textsuperscript{95} Guar is considered a tackifier, which is used in soil stabilization and hydroseeding. In a study of various tackifiers and their ability to promote biocrust formation, guar was found to have a negative impact on moss growth, as mosses treated with guar experienced less growth than moss treated with water alone.\textsuperscript{96}

\textbf{Methylcellulose}

Methylcellulose is a derivative of cellulose, a natural polysaccharide.\textsuperscript{97} The nontoxic white powder is commonly used in food, medicinal products, paper products, paints and detergents, and other common products and industries.\textsuperscript{98} Methylcellulose is water-soluble, as well as highly viscous, and it dries to a clear film.\textsuperscript{99} It has been used in conservation as an adhesive, a sizing agent, and a cleaning lubricant. It is particularly commonly used in paper conservation, including as a filler for areas of loss.\textsuperscript{100}

\textbf{Potato Starch}

As an organic material and food ingredient, potato starch is nontoxic to plants and humans. Potato starch is water-binding, water soluble, and high-swelling, with a low temperature of gelatinization.\textsuperscript{101} Potato starch is valued, especially in the food industry,

\textsuperscript{99} Nasatto, “Methylcellulose.”
\textsuperscript{100} Baker, “Methylcellulose & Sodium Carboxymethylcellulose.”
for its ability to form clear, visco-elastic gels when heated and cooled.\textsuperscript{102} When compared to other plant-based starches, potato starch is more soluble than corn, rice, and wheat starches, with a solubility of 82\%, when compared to cornstarch’s 22\% solubility. Additionally, it has vastly greater swelling power than other starches, with 1159 g/g compared to 22 g/g for cornstarch. This greater solubility may be credited to its greater phosphate group content on amylopectin, and its swelling capacity attributed to its fewer lipids than other starches.\textsuperscript{103} It is a stable material, and it has the capacity to create more highly viscous pastes than other starches.\textsuperscript{104}

\textbf{Psyllium}

Psyllium husk powder is derived from \textit{Plantago ovata}. It is widely employed for its health benefits, valued for its high fiber content.\textsuperscript{105} Psyllium is used in soil stabilization and has been found to increase soil stability, therefore allowing biological soil crusts to grow.\textsuperscript{106} Psyllium is water-soluble and has swelling properties\textsuperscript{107}, and with its high water absorption rates, it is also water-binding. When psyllium dries, it forms a stiff crust that softens when wet, allowing it to foster growth.\textsuperscript{108} Additionally, when


\textsuperscript{103} Singh, “Morphological, thermal and rheological properties of starches.”

\textsuperscript{104} Zaidul, “Correlation between the compositional and pasting properties.”


studied for its effects on moss growth, psyllium was found to have the ability to increase growth, demonstrating its role as a nutrient to microflora and macroflora.\(^{109}\)

**Xanthan Gum**

Made from the bacteria *Xanthomonas campestris*, xanthan gum is a polysaccharide used in a wide variety of industries. It is water soluble, and like other soil stabilizers, it is water-binding and becomes highly viscous when combined with water. It is also thermally stable and stable in a range of pH levels. Among its many uses, it is applied agriculturally as a stabilizer to reduce movement of fertilizer suspensions. In conservation-adjacent fields, it is used in paints, adhesives, and glazes for its suspension abilities.\(^{110}\) It is also employed in the food industry, ready-mixed concrete, and drilling, valued for its thickening properties. Though xanthan gum retains its properties of soil stabilization in sun and heat conditions, it was found to fail when exposed to 105° F heat for one week.\(^{111}\)

\(^{109}\) Blankenship, “Hydroseeding tackifiers.”


Animal-Based Binders

Gelatin

Gelatin is composed of protein from collagen, extracted from animal tissue. Gelatin has a polypeptide structure, containing 18 complex amino acids. Gelatin is used extensively in a variety of industries, including food as a thickener, pharmaceuticals, engineering, and forensics. It has also been used repeatedly in the conservation field, especially for objects and painting conservation, for its consolidative and adhesive properties. Gelatin has also been found to act as a pH buffer in paper.

As a natural material, gelatin is nontoxic and edible, as well as tasteless. It forms a colorless, flexible film that is UV resistant and cold-water insoluble. It can also be quite brittle, depending on its concentration, but can be rendered more flexible with the addition of glycerin. When examined for its properties, 10% gelatin demonstrated shrinkage, good at adhesion at high levels of relative humidity, easy removability with water, and the ability to develop mold growth at high relative humidity.

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114 Ibid.
116 Mosleh, “Structure-Property Correlations.”
Chitosan

Chitosan is obtained from chitin in crustaceous shells, often discarded from the food industry.\textsuperscript{119} It is a biopolymer with applications in the biomedical engineering industry, and chitosan-based nanoparticles have been impactful in pharmaceuticals.\textsuperscript{120} It has also been used in agriculture and water treatment.\textsuperscript{121} Chitosan is considered biocompatible and non-toxic; however, it also has antimicrobial applications for certain microorganisms, including a variety of bacteria, and depending upon pH and structural properties of the chitosan. While this is advantageous in the biomedical world, it poses a threat to chitosan’s ability to act as a bioreceptive medium. Research has also demonstrated potential toxicity of chitosan to marine life.\textsuperscript{122} Chitosan has also been utilized in soil stabilization, as it can prevent soil erosion and may contribute to the cohesion of soil in wet environments, though it has been found less effective in dry environments.\textsuperscript{123}

\textsuperscript{119} Kavazanjian, “Biopolymer soil stabilization.”
\textsuperscript{121} Kavazanjian, “Biopolymer soil stabilization.”
\textsuperscript{122} Rizeq, “Synthesis, Bioapplications, and Toxicity.”
Mineral Binders

Bitumen

Bitumen is a dark cementitious material, comprised of high-molecular weight hydrocarbons.\textsuperscript{124} Once it cures, bitumen is water-insoluble.\textsuperscript{125} It is also crack-resistant, due to its flexibility.\textsuperscript{126} It has been utilized in soil stabilization, as it mechanically strengthens soil and decreases porosity.\textsuperscript{127} In addition to potentially noxious fumes that can impact human health, bitumen production has been found to be potentially toxic, with the capacity to adversely affect the environment and ecology, as well.\textsuperscript{128}

Nanoclay

Nanoclay is the smallest division of clay particles that can occur naturally.\textsuperscript{129} It is commonly used in agriculture, for its superabsorbent water-storing capacity.\textsuperscript{130} For this reason, it is ideal for water conservation and beneficial to soil health.\textsuperscript{131} Nanoclay has thereby been used to decrease soil loss and sediment concentration. It is also water-
soluble.\textsuperscript{132} Nanoclay has found use in the conservation field, as well, as it has been used as a protective coating, for consolidation, and its surface-cleaning abilities. In fact, polymer nanocomposites have been used as protective coatings on porous stones.\textsuperscript{133} Despite these properties, nanoclay’s significant swelling capacity disqualify it from use for the purposes of this study.

Synthetic Binders

**Aquazol\textsuperscript{®} 50 (Manufactured by Polymer Chemistry Innovations, Inc.)**

Aquazol, also known as poly(2-ethyl-2-oxazoline), is a synthetic thermoplastic polymer that comes in a variety of weights. transparent film has been found to have a stable color and pH over time.\textsuperscript{134} Aquazol is soluble in water as well as a variety of solvents, and it is easily removable using acetone. As a film, it is flexible, with comparable adhesion to that of gelatin and lower shrinkage levels; however, it is also moisture absorbent at high relative humidity levels, and it shows poor adherence at a relative humidity over 84%.\textsuperscript{135} Aquazol can adhere to a variety of surfaces, owing to its polar and non-polar regions.\textsuperscript{136} It has been used widely in conservation, as a consolidant,

\textsuperscript{132} Ibid.


\textsuperscript{135} Arslanoglu, “Evaluation of the Use of Aquazol.”

\textsuperscript{136} Breidenstein, “The Use of Aquazol 500.”
an inpainting medium, an adhesive, as well as a binder for retouching paintings, and an infill.\textsuperscript{137}

**Sodium polyacrylate**

Sodium polyacrylate was researched for its use in the agricultural industry. As a highly absorbent material, it swells significantly with water. In fact, sodium polyacrylate is considered a superabsorbent, with the capacity to hold 700 times its weight in water.\textsuperscript{138} Its ability to retain water is beneficial to its role in agricultural settings, and it has been found to increase water retention and capacity in soils.\textsuperscript{139} Sodium polyacrylate has also been used in the construction industry as an additive to concrete in order to improve material performance.\textsuperscript{140}

**Fillers**

**Hemp Fiber**

Found in the stems of the hemp plant, hemp fiber is composed of cellulose, hemicellulose, lignin, and pectin, and it is highly valued for its strong and stuff properties. As it is a water absorbent material, it is also subject to potential decay. Additionally, as an


organic one, its composition and therefore its mechanical properties can vary. Recently, production of hemp fiber has vastly increased. It is widely used in composite reinforcement,\textsuperscript{141} especially to increase tensile and flexural strengths.\textsuperscript{142} Hemp fiber has also been used as an additive to sacrificial mud layers on earthen sites.\textsuperscript{143}

\textbf{Jute Fiber}

Made from cellulose and lignin, jute fiber is the second-most-produced textile fiber in the world, and it is abundantly available in India.\textsuperscript{144} Jute fiber has high tensile strength, and as an organic material, it is biodegradable. Small amounts of jute fiber have been found to have positive effects on concrete hardness, and it is considered to have a higher strength and stiffness than animal fibers.\textsuperscript{145} Recently, jute fiber has been used as a natural fiber reinforcement, and it has found success in epoxy composites, specifically. In this case, jute fiber improves tensile and impact strengths, it improves hardness, and it decreases the void content of the composite, thereby improving flexural and shear strength.\textsuperscript{146}

\textsuperscript{145} Islam, “Influence of jute fiber.”
\textsuperscript{146} Mishra, “Jute Fiber epoxy Composites.”
Silica Flour

Also called micro silica and silica sand, silica flour (SiO₂) is a fine crystalline silica in the form of an insoluble white powder that can commonly be found in rocks and soils.¹⁴⁷ In construction, silica flour has been found to improve the compressive strength of concrete.¹⁴⁸ It is also commonly used as an abrasive in common household materials like soap and cleaning products, as well as in the pharmaceutical industry, in the production of materials like clay, ceramics, and glass, and as a reinforcing filler. Silica flour has the potential to cause adverse health effects to humans when inhaled; however, it has not been found to be hazardous to the environment, including animals, microorganisms, and plants.¹⁴⁹

Fumed Silica

Fumed silica is an amorphous silicon dioxide made from the reaction of silicon tetrachloride with an oxyhydrogen flame.¹⁵⁰ This lightweight material is hydrophilic and translucent, and it is commonly used as a fill material, such as in repair of marble. It has also been found to cause problems with shrinkage when utilized in this way. Fumed silica

frequently contains little contamination from external materials and so is considered quite pure.\textsuperscript{151}

5. Preliminary Testing

5.1 Methodology

Preliminary qualitative testing was first performed to better understand what materials might be suitable for subsequent quantitative performance testing. After a wide selection of potentially suitable materials were studied for their reported properties and past uses based on a technical-literature review and product specifications, samples were ordered of those products that showed the most promise of meeting the performance requirements identified. Only aqueous binders were tested individually in various concentrations and observed for their individual qualities, including varying viscosity at different concentrations. Based upon initial observations, formulations were then created combining binders and fillers in various ratios, the latter to change viscosity, control shrinkage and deformation, and improve strength. Results from these tests informed further preliminary testing, specifically based on which binders and fillers showed success, as well as what concentrations and ratios should be modified based on testing failure.

Formulations were observed for:

- Viscosity and flowability when wet
- Breakability after drying
- Shrinkage after drying
- Color after drying
- Water sensitivity after drying
- Adhesive and cohesive strength in a facsimile coupon
Viscosity was observed by examining binders in varying concentrations in water in order to gauge whether variation in viscosity was possible, as well as which concentration yielded variation and what effects the variation had on the material’s other properties. Flexural strength and breakability were examined qualitatively, observing whether a formulation could be bent or split by hand. Shrinkage was observed qualitatively, as well. Most samples were created to fill the base of a small weighing boat, and shrinkage was clear when a formulation no longer filled the base of the boat, or when deformation and curling had occurred. Color was noted for its neutrality and similarity to the substrate in question, the FLFO stump. Water sensitivity was observed last, as it was in some cases destructive. This was tested using either a water drop test or immersion of a sample in a cold-water bath. It was noted whether samples were unaffected by the water, became softer and more easily breakable, swelled, disintegrated, or dissolved completely in the bath.

As a second phase of preliminary testing, analog facsimiles composed of glass beads to create an unconsolidated porous and permeable body were made. The facsimiles consisted of a 2” diameter PVC ring filled with 1:1 mixed glass beads of 2mm and 6mm diameter. The facsimile body was then filled with different formulations that, when tested, met the general requirements of the optimal properties set forth. This method of facsimile creation was established as a simulation of the silica-based petrified wood. The non-consolidated porous body created by the non-porous glass beads simulates the cracks, microfissures, and spaces found in FLFO petrified wood samples. This method also allowed for physical and mechanical testing of the formulations to fully infiltrate the voids and mechanically adhere to a siliceous surface.
After drying of the facsimiles, the formulations were removed from the PVC rings and observed for penetration and cohesion. This was determined by whether the facsimile held together after removal from the mold, as well as its strength against breaking by hand. It was also observed whether the facsimiles showed any signs of shrinkage or deformation within the molds. Following preliminary tests, facsimile coupons of glass beads will be mechanically tested again for strength using a Universal testing machine.

5.2 Observations and Recommended Formulations

Observations from Initial Testing

Each binder was tested individually for properties of viscosity when wet and shrinkage, water sensitivity, and hardness when dried, as well as examined for color neutrality. Binders tested included, Aquazol, 3% methylcellulose solution, xanthan gum, guar gum, cornstarch, agar in varying concentrations, gelatin in varying concentrations, and psyllium in varying concentrations.

Aquazol and methylcellulose were quickly eliminated as viable options for this surface treatment, due to their sensitivity to water. When exposed to water after drying, Aquazol became sticky, and methylcellulose degraded. Xanthan gum and guar gum dried into hard, unbreakable materials of neutral brown color. Both only exhibited slight shrinkage levels, but when placed in a water bath, both materials experienced some loss or degradation, thereby eliminating them as viable binders, as well. Xanthan gum and guar gum were tested in high concentrations at very high viscosity but were not tested in other concentrations due to these other suboptimal properties. Cornstarch of moderate
viscosity was found to be easily breakable after drying and disintegrated when exposed to water.

Agar was tested in both 5% and 10% concentrations, which showed moderate and high viscosity, demonstrating the variability of agar viscosity by concentration. Both samples dried to a neutral brown color and were found to be unbreakable and water insensitive. They also both demonstrated shrinkage upon drying. Like agar, gelatin was examined in 5% and 10% concentrations, with low and moderate viscosity, demonstrating variability. When dried, the colorless, transparent material was bendable and able to be broken with extreme bending. It was found to soften with water exposure but not considered water sensitive as it did not disintegrate, and it showed slight deformation but little shrinkage.

Psyllium was first tested in a highly viscous, 17% concentration, which exhibited some shrinkage, formed an unbreakable brown crust, developed mold growth, and was found to gelatinize and swell but retain its shape without loss when placed in a water bath. Because of these properties, psyllium was tested further in lower concentrations. These other concentrations demonstrated a variable viscosity, they experienced less shrinkage, were found to be bendable and not easily breakable, and were found to similarly hold their shape without disintegrating in water. Due to the wet and dry properties demonstrated by these binders, agar, gelatin, and psyllium were tested with fillers.
The fillers used in combination with the binders above were fumed silica and silica flour. Formulations were made and tested in varying ratios of binders and fillers. Gelatin with silica flour formed a very hard, unbreakable white material. It showed little to no shrinkage, and though it was found to become softer in a water bath, it did not readily break down. Of the concentrations and ratios examined, the 10% gelatin and silica flour in a 1:2 ratio was selected for further testing, due to its moderate viscosity and lack of shrinkage. Gelatin was also tested with fumed silica in varying concentrations and ratios. These formulations all showed significant shrinkage and deformation, due to the absorptivity of fumed silica. The formulations were observed to be hard and unbreakable, mostly water insensitive, and of a neutral yellow-beige color, plus several demonstrated mold growth after several days.
5% agar solution was tested with fumed silica, due to its lower viscosity than 10% agar solution. Though formulations were largely found to be water insensitive and unbreakable, they all showed significant shrinkage. The shrinkage may be attributed to the fumed silica or the agar itself. When formulations were made with agar and filler, the high shrinkage levels of the binder were not yet clear. Once this property was discovered, no further formulations were made using agar, and silica flour was not tested as a filler with agar.

When psyllium was examined in combination with a filler, fumed silica had been determined to be the source of shrinkage in other formulations, so only silica flour was tested. Psyllium was tested in varying ratios with filler in 2.5%, 5%, and 7.5% concentrations, to achieve lower viscosity and higher flowability. These formulations exhibited no shrinkage, they dried to a neutral white-beige color, and they were found to gelatinize but hold their shape in water. They demonstrated some elasticity but were
breakable, but this was attributed to the thin size of the formulation tested. Psyllium and silica flour was selected for subsequent facsimile testing, in a 4:1 ratio of 5% psyllium solution and silica flour.

**Facsimile Testing**

The formulations that performed successfully in initial testing were subsequently tested using the glass bead facsimiles. For the purposes of this test, the formulations chosen needed to be of a viscosity to allow it to flow between the glass bead discs and adequately fill the voids between the beads, though varying viscosities may be utilized in reality to meet field conditions. These formulations included gelatin and silica flour and psyllium and silica flour.

![PVC ring filled with mixture of 2mm and 6mm glass beads used for facsimile coupon creation](Source: Author, 2022)
Gelatin with silica flour tested successfully in the facsimile. It continued to demonstrate little-to-no shrinkage, and it displayed good cohesion, for its ability to remain intact after drying and testing for breakage by hand. Psyllium with silica flour also performed well, as it demonstrated no shrinkage and good cohesion. It demonstrated lower penetration ability, as shaking of the facsimile was necessary to encourage better penetration. As a result, an additional facsimile was created of psyllium and silica flour in an 8:1 ratio, which demonstrated slightly improved flowability, as well as good cohesion and no shrinkage.

Figure 5.4 – Facsimile coupons of gelatin and silica flour (left) and psyllium and silica flour (right) (Source: Author, 2022)
6. Confirmatory Testing

The next stage in performance testing will be to quantitatively measure the performance of selected formulations, using standardized tests to measure the identified critical properties required of the treatment. The formulations selected demonstrated low shrinkage, variable viscosity, water insensitivity, and color compatibility. They suggest good adhesive and cohesive strength through preliminary facsimile testing. Formulations include:

- 5% and 10% gelatin solution and silica flour, 1:2
- 5% and 10% psyllium and silica flour, 8:1

For each formulation to be tested, five 3” diameter PVC rings will be filled with a 1:1 mixture of 2mm and 6mm glass beads. Each formulation will then be poured into the glass bead-filled ring and allowed to dry completely before removal from the mold. The following tests will be performed to assess the consolidated mass. The density of unconsolidated and consolidated discs will be determined to compare the penetration ability of each test formulation. Weights after cure will also be taken in the event accelerated weathering is performed. Facsimile coupons will be mechanically tested for tensile strength.
<table>
<thead>
<tr>
<th>Property</th>
<th>Test</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vapor Permeability</td>
<td>ASTM E96/E96M-21: Gravimetric Determination of Water Vapor Transmission Rate of Materials</td>
</tr>
<tr>
<td>Durability</td>
<td>ASTM D7149-05: Standard Practice for Determining the Freeze Thaw Stability of Adhesives</td>
</tr>
</tbody>
</table>

Results from this testing will confirm or dismiss the above formulations as potential treatments at FLFO. Successful results should demonstrate that a formulation experiences minimal shrinkage and should be dimensionally stable to wetting and drying. It should be water insensitive in that it does not disintegrate in the presence of cold water. It should be durable against wet-dry and freeze-thaw cycling, it should not crack with thermal fluctuations, and it must be adequately strong to remain an intact protective filler against water penetration.
7. Conclusion

This thesis examined formulation of a protective biophilic adhesive filler for the fossilized stumps at Florissant Fossil Beds National. This formulation is intended to support biological growth and eventually biodegrade and be replaced by those organisms. Preliminary testing was conducted to focus on potentially appropriate materials and formulations to fulfill the optimal properties established for this bioreceptive adhesive filler.

The report synthesized past research on bioprotection and biomimetic treatments to gather literature support for the potential of a protective and bioreceptive treatment for stone. It examined the state of research in this area of conservation to identify the gap in existing literature that this thesis will fill. It examined the characteristics and conditions of the petrified stumps at FLFO in order to establish ideal properties in a protective treatment for the substrate, and it examined properties of various materials from a wide range of sources to consider as components of the protective formulation. It then tested the materials individually and in combinations of binder and filler in order to preliminarily and qualitatively determine which formulations met the established optimal properties. The formulations considered for future testing are gelatin with silica flour and psyllium with silica flour. The thesis then proposed a plan for confirmatory testing utilizing ASTM standards to quantitatively study the protective qualities of these formulations.

Biological growth has been found to be beneficial in certain circumstances, and more research is needed to determine what substrates, environmental conditions, and organisms yield beneficial rather than detrimental results. Therefore, the formulations
tested in this study may not be an appropriate treatment for all stone substrates. Additionally, the compatibility in appearance of the formulation and the substrate should be taken into account, and aesthetics may disqualify a bioreceptive treatment from some substrates and contexts.

More research is needed to identify what forms of biological growth, especially lichens, provide the properties that serve as surface protection. One must also consider the potential for a nutrient-rich surface treatment as is formulated in this study to attract both desired and undesired organisms. While surface-level microflora and macroflora such as lichens, algae, biofilms, and bioslimes are the objective, the nutrients may also support larger macroflora that have the potential to damage the substrate. As many forms of biological growth feed upon the same nutrients, these organisms were not distinguished between in this study.

Further testing should be conducted to fulfill the confirmatory testing laid out in this thesis. The recommended formulations should be examined for their fulfillment of the optimal properties quantitatively. Following this phase in testing, the formulations that perform adequately should be tested in situ. This may involve the application of the adhesive filler to a like material, such as silica Foamglas, or to a detached fragment of petrified wood, and the placement of this test substrate on site at FLFO. The success or failure of the treatment on site will determine whether it will withstand the environmental conditions and adequately protect the stump. If the treatment is successful, it may then be applied to a fossilized stump for testing on the substrate.

This preliminary testing program is the first step toward a protective and biophilic surface treatment that requires significantly more testing before its effectiveness can be
confirmed. It follows and relies upon innovative research in biomimetic treatments as a conservation action on structural heritage. It also relies upon a growing body of research in bioprotection of the built environment and the possible benefits of biological growth and vegetation. Prior research primarily explores behavior of pre-existing biological growth, and biomimetic treatments using bacteria for the formation of calcium carbonate. This is the first research to the author’s knowledge that works towards the formulation of a novel surface treatment with the express purpose of promoting biological growth as well as protecting a stone substrate. This thesis contributes to research in the promising area of learning from nature to protect the world’s built heritage.
Glossary

**Biodeterioration**: Physical and biochemical deterioration of a stone surface due to the presence of living biological organisms, resulting from penetration and metabolite excretion\(^\text{152}\)

**Biological growth (biogrowth)**: Plants and microorganisms, such as bacteria, fungi, and lichen, that may be found colonizing on stone surfaces\(^\text{153}\)

**Biomimetic**: Synthesizing artificial materials and processes through the study of biological mechanisms, mimicking the processes found in nature\(^\text{154}\)

**Bioprotection**: Physical inhibition of deterioration and stabilization of stone surfaces by biological organisms such as lichen, fungi, and biofilms\(^\text{155}\)

**Bioreceptivity**: The ability of an object to be colonized by living organisms without experiencing deterioration, requiring apt conditions for the development and multiplication of those organisms on the object in a more than transient manner\(^\text{156}\)

**Macroflora**: Plants that can be seen with the naked eye\(^\text{157}\)

**Microflora**: Microorganisms that are not visible to the naked eye, including bacteria, fungi, and viruses\(^\text{158}\)

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\(^\text{152}\) Gadd, “Bioprotection.”


\(^\text{155}\) Gadd, “Bioprotection.”

\(^\text{156}\) Guillitte, “Bioreceptivity.”


**Vegetation**: Living vegetative organism with stem, roots, and leaves, which may colonize structures, leading to root infiltration of gaps and cracks\(^{159}\)

\(^{159}\) Anson Cartwright, “ICOMOS Illustrated glossary.”
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## Appendix A: Table of Material Properties

<table>
<thead>
<tr>
<th>Material</th>
<th>Source</th>
<th>Form</th>
<th>Color</th>
<th>Water Sensitivity</th>
<th>Toxicity</th>
<th>Shrinkage/Swelling</th>
<th>UV Sensitivity</th>
<th>Strength</th>
</tr>
</thead>
<tbody>
<tr>
<td>Agar</td>
<td>Red seaweed</td>
<td>Powder</td>
<td>Light yellow-beige</td>
<td>Cold water-insoluble; hot water-soluble</td>
<td>Nontoxic growth medium often containing nutrients</td>
<td>Yes</td>
<td>Not sensitive</td>
<td>Not found</td>
</tr>
<tr>
<td>Cornstarch</td>
<td>Maize</td>
<td>Powder</td>
<td>White</td>
<td>Insoluble</td>
<td>Nontoxic</td>
<td>Yes</td>
<td>Not found</td>
<td>Not found</td>
</tr>
<tr>
<td>Guar Gum</td>
<td>Cyamopsis tetragonoloba seeds</td>
<td>Powder</td>
<td>Beige</td>
<td>Soluble</td>
<td>Nontoxic</td>
<td>Yes</td>
<td>Not found</td>
<td>Not found</td>
</tr>
<tr>
<td>Methylcellulose</td>
<td>Derivative of cellulose, a polysaccharide from plant cell walls</td>
<td>Liquid or powder</td>
<td>Colorless or white</td>
<td>Soluble in cold water</td>
<td>Nontoxic</td>
<td>Yes, low shrinkage</td>
<td>Sensitive</td>
<td>Not found</td>
</tr>
<tr>
<td>Potato Starch</td>
<td>Potato tubers</td>
<td>Powder</td>
<td>White</td>
<td>Soluble</td>
<td>Nontoxic</td>
<td>Yes</td>
<td>Not found</td>
<td>Not found</td>
</tr>
<tr>
<td>Psyllium</td>
<td>Plantago ovata seeds</td>
<td>Powder</td>
<td>Brown</td>
<td>Soluble</td>
<td>Nontoxic</td>
<td>Yes</td>
<td>Not found</td>
<td>Not found</td>
</tr>
<tr>
<td>Xanthan Gum</td>
<td>Xanthomonas campestris bacteria</td>
<td>Powder</td>
<td>Beige</td>
<td>Cold water-insoluble; hot water-soluble</td>
<td>Nontoxic growth medium in dissolved form</td>
<td>Yes, with humidity changes</td>
<td>Not sensitive; gel strength and thermal stability may increase</td>
<td>Variable; Gel strength ranges 30-300 bloom</td>
</tr>
<tr>
<td>Gelatin</td>
<td>Animal collagen</td>
<td>Powder</td>
<td>Light yellow-beige</td>
<td>Variable, sometimes soluble</td>
<td>Antibacterial</td>
<td>Not found</td>
<td>Not found</td>
<td>Not found</td>
</tr>
<tr>
<td>Chitosan</td>
<td>Polysaccharide from crustacean exoskeletons, algae, fungi, and insects</td>
<td>Powder</td>
<td>Beige</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bitumen</td>
<td>Mineral deposits</td>
<td>Liquid</td>
<td>Black</td>
<td>Variable</td>
<td>Possible environmental toxicity</td>
<td>Not found</td>
<td>Not found</td>
<td>Not found</td>
</tr>
<tr>
<td>Nanoclay</td>
<td>Natural clays or synthetic</td>
<td>Granules</td>
<td>Beige-gray</td>
<td>Swells with water</td>
<td>Nontoxic</td>
<td>Yes</td>
<td>Not found</td>
<td>Not found</td>
</tr>
<tr>
<td>Aquazol</td>
<td>Polymer</td>
<td>Granules</td>
<td>Light yellow</td>
<td>Soluble in cold water; impacted by high relative humidity</td>
<td>Nontoxic</td>
<td>No</td>
<td>Sensitive</td>
<td>Not found</td>
</tr>
<tr>
<td>Sodium Polyacrylate</td>
<td>Polymer hydrogels</td>
<td>Powder</td>
<td>White</td>
<td></td>
<td>Nontoxic</td>
<td>Yes</td>
<td>Not found</td>
<td>Not found</td>
</tr>
<tr>
<td>Hemp Fiber</td>
<td>Hemp plant</td>
<td>Fiber</td>
<td>Light brown</td>
<td></td>
<td>Nontoxic</td>
<td>Not found</td>
<td>Not found</td>
<td>High</td>
</tr>
<tr>
<td>Jute Fiber</td>
<td>Jute plant</td>
<td>Fibrous solid</td>
<td>Brown</td>
<td></td>
<td>Nontoxic</td>
<td>Not found</td>
<td>Not found</td>
<td>High</td>
</tr>
<tr>
<td>Silica Flour</td>
<td>Ground crystalline silica rock</td>
<td>Powder</td>
<td>White</td>
<td>Insoluble</td>
<td>Environmentally nontoxic</td>
<td>No</td>
<td>Not found</td>
<td>Not found</td>
</tr>
<tr>
<td>Fumed Silica</td>
<td>Amorphous silica from reaction of silicon tetrachloride with oxygen</td>
<td>Amorphous particles</td>
<td>White</td>
<td></td>
<td>Environmentally nontoxic</td>
<td>Yes</td>
<td>Not found</td>
<td>Not found</td>
</tr>
</tbody>
</table>
## Appendix B: Formulation Testing Matrix

<table>
<thead>
<tr>
<th>Sample #</th>
<th>Components</th>
<th>Ratio of Components</th>
<th>Test surface</th>
<th>Water sensitivity</th>
<th>Shrinkage</th>
<th>Color</th>
<th>Hardness/Breakability</th>
<th>Cohesion</th>
<th>Viscosity</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>10% Aquazol Solution</td>
<td>large weighing boat</td>
<td>Yes, became sticky</td>
<td>No</td>
<td>Clear</td>
<td>N/A</td>
<td>N/A</td>
<td>Variable by percentage</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>Methylcellulose</td>
<td>small weighing boat</td>
<td>No, broke easily and deteriorated</td>
<td>Some deformation</td>
<td>Clear</td>
<td>Bendable and breakable</td>
<td>N/A</td>
<td>Not variable</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>5% Gelatin Solution</td>
<td>large weighing boat</td>
<td>No, only breaks with force</td>
<td>Some deformation</td>
<td>Clear</td>
<td>Bendable and breakable</td>
<td>N/A</td>
<td>Low (Variable by percentage)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>10% Gelatin Solution</td>
<td>large weighing boat</td>
<td>No, becomes soft but does not break</td>
<td>Some deformation</td>
<td>Clear</td>
<td>Breakable and brittle</td>
<td>N/A</td>
<td>Moderate (Variable by percentage)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>10% Gelatin Solution, Silica Flour</td>
<td>1:1</td>
<td>Smaller but didn't disintegrate</td>
<td>Slight</td>
<td>White</td>
<td>Not breakable</td>
<td>N/A</td>
<td>Low</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>10% Gelatin Solution, Silica Flour</td>
<td>1:2</td>
<td>Smaller and somewhat breakable</td>
<td>Not evident</td>
<td>White</td>
<td>Not breakable</td>
<td>N/A</td>
<td>Moderate (Pourable with body)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>5% Gelatin Solution, Silica Flour</td>
<td>1:2</td>
<td>Soft and breakable</td>
<td>No</td>
<td>White</td>
<td>Not breakable</td>
<td>N/A</td>
<td>Moderate (Pourable with body)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>5% Gelatin Solution, Silica Flour</td>
<td>30:1</td>
<td>Soft but didn't break</td>
<td>Yes</td>
<td>Yellow-Beige</td>
<td>Not breakable</td>
<td>N/A</td>
<td>Low</td>
<td></td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>5% Gelatin Solution, Silica Flour</td>
<td>15:1</td>
<td>Soft but didn't break</td>
<td>Yes</td>
<td>Yellow-Beige</td>
<td>Not breakable</td>
<td>N/A</td>
<td>Low</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>10% Gelatin Solution, Silica Flour</td>
<td>30:1</td>
<td>Soft but didn't break</td>
<td>Yes</td>
<td>Yellow-Beige</td>
<td>Not breakable</td>
<td>N/A</td>
<td>Low</td>
<td></td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>10% Gelatin Solution, Silica Flour</td>
<td>15:1</td>
<td>Soft but didn't break</td>
<td>Yes</td>
<td>Yellow-Beige</td>
<td>Not breakable</td>
<td>N/A</td>
<td>Low</td>
<td></td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>5% Gelatin Solution, Silica Flour</td>
<td>10:1</td>
<td>Soft but didn't break</td>
<td>Yes</td>
<td>Yellow-Beige</td>
<td>Not breakable</td>
<td>N/A</td>
<td>Solid (mashed potatoes)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>5% Psyllium Solution</td>
<td>small weighing boat</td>
<td>Gelatinizes and visibly swells but does not lose mass and remains stiff at the core, rehardens with crust</td>
<td>Slight</td>
<td>Brown</td>
<td>Not breakable</td>
<td>N/A</td>
<td>Solid (Clumpy)</td>
<td>Mold growth</td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>5% Psyllium Solution</td>
<td>small weighing boat</td>
<td>Gelatinizes but does not disintegrate, some breakage</td>
<td>Slight</td>
<td>Brown</td>
<td>Not breakable</td>
<td>N/A</td>
<td>Solid (Clumpy)</td>
<td>Mold growth</td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>9% Psyllium Solution</td>
<td>small weighing boat</td>
<td>Gelatinizes but does not disintegrate or break</td>
<td>Not evident</td>
<td>Brown with transparency</td>
<td>Bendable but not easily breakable</td>
<td>N/A</td>
<td>High (apple sauce)</td>
<td>Mold growth</td>
<td></td>
</tr>
<tr>
<td>16</td>
<td>7% Psyllium Solution</td>
<td>small weighing boat</td>
<td>Gelatinizes and visibly swells, some</td>
<td>Slight</td>
<td>Light Brown-Beige</td>
<td>Not breakable</td>
<td>N/A</td>
<td>Solid (Clumpy but spreadable)</td>
<td>Mold growth</td>
<td></td>
</tr>
<tr>
<td>17</td>
<td>17% Psyllium Solution</td>
<td>small weighing boat</td>
<td>Gelatinizes and visibly swells but does not lose mass and remains stiff at the core, rehardens with crust</td>
<td>Slight</td>
<td>Brown</td>
<td>Not breakable</td>
<td>N/A</td>
<td>Solid (Clumpy)</td>
<td>Mold growth</td>
<td></td>
</tr>
<tr>
<td>18</td>
<td>5% Gelatin Solution, Psyllium</td>
<td>4:1</td>
<td>Soft but didn't break</td>
<td>Yes</td>
<td>Slight</td>
<td>Brown</td>
<td>Not breakable</td>
<td>N/A</td>
<td>Solid (Clumpy)</td>
<td>Mold growth</td>
</tr>
<tr>
<td>19</td>
<td>12.5% Guar Gum Solution</td>
<td>1:7</td>
<td>Gelatinizes and visibly swells, some</td>
<td>Slight</td>
<td>Light Brown-Beige</td>
<td>Not breakable</td>
<td>N/A</td>
<td>Solid (Clumpy but spreadable)</td>
<td>Mold growth</td>
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<tr>
<td>#</td>
<td>Solution</td>
<td>Ratio</td>
<td>Boat Type</td>
<td>Loss and hardens</td>
<td>Appearance</td>
<td>Breakability</td>
<td>Notes</td>
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<tr>
<td>19</td>
<td>5% Gelatin, Guaran Gum</td>
<td>4:1</td>
<td>Small weighing</td>
<td>Yes, slight</td>
<td>Light Brown-Beige</td>
<td>Not breakable</td>
<td>N/A</td>
<td></td>
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<td>20</td>
<td>5% Gelatin, Guaran Gum</td>
<td>2:1</td>
<td>Small weighing</td>
<td>Yes, slight</td>
<td>Light Brown-Beige</td>
<td>Not breakable</td>
<td>N/A, Solid (Clumpy)</td>
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<td>21</td>
<td>5% Gelatin, Cornstarch</td>
<td>1:1</td>
<td>Small weighing</td>
<td>Yes, slight</td>
<td>Light Brown-Beige</td>
<td>Not breakable</td>
<td>N/A, Moderate (Elmer's glue)</td>
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<td>22</td>
<td>5% Gelatin, Bioact</td>
<td>1:1</td>
<td>Small weighing</td>
<td>No, slight</td>
<td>Dark Brown-Black</td>
<td>Easily breakable</td>
<td>Poor Cohesion, Solid (Clumpy)</td>
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<tr>
<td>23</td>
<td>10% Agar, Fumed Silica</td>
<td>60:1</td>
<td>Small weighing</td>
<td>No, became softer</td>
<td>White-Beige</td>
<td>Not breakable</td>
<td>N/A, Moderate (Variable by percentage)</td>
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<tr>
<td>24</td>
<td>10% Agar, Fumed Silica</td>
<td>30:1</td>
<td>Small weighing</td>
<td>No, soft but did not break</td>
<td>White-Beige</td>
<td>Not breakable</td>
<td>N/A, Moderate</td>
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<tr>
<td>25</td>
<td>10% Agar, Fumed Silica</td>
<td>15:1</td>
<td>Small weighing</td>
<td>No, soft but did not break</td>
<td>White-Beige</td>
<td>Not breakable</td>
<td>N/A, High (Thick, chunky, gelatinous)</td>
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<td>26</td>
<td>10% Agar, Fumed Silica</td>
<td>10:1</td>
<td>Small weighing</td>
<td>No, broke</td>
<td>White-Beige</td>
<td>Not breakable</td>
<td>N/A, Solid (Thick; mashed potatoes)</td>
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<td>27</td>
<td>5% Psyllium, Silica Flour</td>
<td>1:1</td>
<td>Small weighing</td>
<td>No, does not break apart</td>
<td>White-beige</td>
<td>Stiff, breakable</td>
<td>N/A, High (Pasty, thick)</td>
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<tr>
<td>28</td>
<td>5% Psyllium, Silica Flour</td>
<td>2:1</td>
<td>Small weighing</td>
<td>No, does not break apart</td>
<td>White-beige</td>
<td>Some elasticity, easily breakable but stiff</td>
<td>N/A, High (Pasty)</td>
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<tr>
<td>29</td>
<td>5% Psyllium, Silica Flour</td>
<td>4:1</td>
<td>Small weighing</td>
<td>No, holds shape</td>
<td>White-beige</td>
<td>Some elasticity, easily breakable, stiff</td>
<td>N/A, Low-Moderate</td>
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<td>30</td>
<td>7.5% Psyllium, Silica Flour</td>
<td>4:1</td>
<td>Small weighing</td>
<td>No, holds shape</td>
<td>White-beige</td>
<td>Some elasticity, easily breakable, stiff</td>
<td>N/A, High (Pasty)</td>
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<td>31</td>
<td>7.5% Psyllium, Silica Flour</td>
<td>8:1</td>
<td>Small weighing</td>
<td>No, holds shape</td>
<td>White-beige</td>
<td>Some elasticity, easily breakable, stiff</td>
<td>N/A, High (Pasty)</td>
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<tr>
<td>32</td>
<td>5% Psyllium, Silica Flour</td>
<td>4:1</td>
<td>Small weighing</td>
<td>No, holds shape</td>
<td>White-beige</td>
<td>Some elasticity, easily breakable, stiff</td>
<td>N/A, Low</td>
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<tr>
<td>33</td>
<td>2.5% Psyllium, Silica Flour</td>
<td>4:1</td>
<td>Small weighing</td>
<td>No, holds shape</td>
<td>White-beige</td>
<td>Some elasticity, easily breakable, stiff</td>
<td>N/A, Low</td>
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<td></td>
<td>Composition</td>
<td>Ratio</td>
<td>Equipment</td>
<td>Deformation</td>
<td>Cohesion</td>
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<td>14</td>
<td>10% Gelatin, Fumed silica</td>
<td>15:1</td>
<td>PVC ring</td>
<td>Significant deformation</td>
<td>Moderate Cohesion - Separates into thin sheets</td>
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<td>15</td>
<td>10% Gelatin, Fumed silica</td>
<td>15:1</td>
<td>PVC ring</td>
<td>Significant deformation</td>
<td>Moderate Cohesion - Separates into thin sheets</td>
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<td>16</td>
<td>10% Gelatin, Fumed silica</td>
<td>15:1</td>
<td>PVC ring</td>
<td>Significant deformation</td>
<td>Moderate Cohesion - Separates into thin sheets</td>
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<td>17</td>
<td>5% Gelatin, Silica flour</td>
<td>1:2</td>
<td>PVC ring</td>
<td>No</td>
<td>Excellent Cohesion Moderate</td>
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<tr>
<td>27</td>
<td>Corn starch, Gelatin</td>
<td>1:1</td>
<td>PVC ring</td>
<td>No</td>
<td>Poor Cohesion - Falls apart Moderate</td>
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<tr>
<td>28</td>
<td>5% Gelatin</td>
<td>N/A</td>
<td>PVC ring</td>
<td>No</td>
<td>Good Cohesion Low</td>
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<tr>
<td>37</td>
<td>5% Psyllium, Silica Flour</td>
<td>4:1 (40ml, 2g, 10.5g)</td>
<td>PVC ring</td>
<td>No</td>
<td>Good Cohesion Low-Moderate, though fails to flow easily through beads</td>
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<tr>
<td>38</td>
<td>5% Psyllium, Silica Flour</td>
<td>8:1</td>
<td>PVC ring</td>
<td>No</td>
<td>Excellent Cohesion Low, though fails to flow easily through beads</td>
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</table>
Appendix C: Testing Images

Figure C.1: Binders after drying, clockwise from the top left, Aquazol, 10% gelatin, 5% gelatin, methylcellulose (Source: Author, 2022)

Figure C.2: 10% agar and 5% agar, after drying (Source: Author, 2022)
Figure C.3: Psyllium of varying concentrations, re-hardened following water sensitivity testing (Source: Author, 2022)

Figure C.4: Psyllium, gelatinous and wet after water sensitivity test (Source: Author, 2022)
Figure C.5: Guar gum (left) and xanthan gum (right), re-hardened after water sensitivity testing (Source: Author, 2022)

Figure C.6: Gelatin and fumed silica in varying concentrations (Source: Author, 2022)
Figure C.7: Gelatin and silica flour in varying concentrations and ratios (Source: Author, 2022)

Figure C.8: 5% Agar and fumed silica in varying ratios (Source: Author, 2022)
Figure C.9: Cornstarch with gelatin (left) and cornstarch (right), showing breakability (Source: Author, 2022)

Figure C.10: Facsimile coupons of gelatin and silica flour (left) and psyllium and silica flour (right), demonstrating flowability and depth of penetration (Source: Author, 2022)
Appendix D: FLFO Site Images

Figure D.1: Stump P47 and surrounding landscape, courtesy of Isabel Schneider (2021)

Figure D.2: Stump P47, marked to indicate loose and detached fragments (Source: Author, 2021)
Figure D.3: Fragmentation at crown of P47 (Source: Author, 2021)

Figure D.4: Cracking at base of P47 (Source: Author, 2021)
Figure D.5: Cracking and lichen growth at base of P47 (Source: Author, 2021)

Figure D.6: Lichen at crown of P47, courtesy of Isabel Schneider (2021)
Figure D.7: Crown of P47, courtesy of Isabel Schneider (2021)

Figure D.8: Lichen on crown of P47, courtesy of Isabel Schneider (2021)
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