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Los Angeles

Propolis for the Sustainable Treatment
of Bronze Disease on Remote Archaeological Sites

A thesis submitted in partial satisfaction
of the requirements for the degree
Master of Arts in Conservation of Cultural Heritage

by

Kathryn Peneyra

2025

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ABSTRACT OF THE THESIS

Propolis for the Sustainable Treatment of Bronze Disease on Remote Archaeological Sites

by

Kathryn Peneyra

Master of Arts in Conservation of Cultural Heritage

University of California, Los Angeles, 2025

Thiago Sevilhano Puglieri, Chair

Treating copper and copper alloy artifacts afflicted with bronze disease remains highly important in the field of cultural heritage conservation. Doing so on remote archaeological sites poses particular challenges, especially with regard to sustainability. Existing methods of treating bronze disease using corrosion inhibitors may pose risks to the environment and to the user. The need for to develop sustainable practices is paramount across disciplines. This thesis will investigate propolis as a more sustainable option for the treatment of bronze disease on pre-corroded copper alloy coupons. Raman Spectroscopy and X-ray Diffraction Spectroscopy revealed that clinoatacamite and other copper chloride hydroxides were formed on the copper alloy coupons during pre-corrosion. Scanning Electron Microscopy was used to observe differences between the surface morphology of untreated and inhibitor treated pre-corroded coupons. Lastly, weight change experiments were conducted to assess the inhibitor efficiency of propolis on pre-corroded copper alloy coupons. The results in this study do not indicate that an 100 ppm inhibitor solution of propolis is affective at inhibiting bronze disease; however, the hypothesis that propolis may demonstrate efficacy at higher concentrations should be tested in future studies.

The thesis of Kathryn Peneyra is approved.

Caitlin O'Grady

Glenn Wharton

Thiago Sevilhano Puglieri, Committee Chair

University of California, Los Angeles

2025

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1 Introduction

1.1 What is Bronze Disease?

The inhibition of corrosion is a necessary task in the conservation of metal. This is especially true of archaeological artifacts. While buried, artifacts will reach an equilibrium with their environment, resulting in slowed deterioration. Upon excavation, however, the artifact will once again begin to corrode more rapidly due to a sudden change in environment and, in particular, sudden exposure to higher oxygen levels (Wellman, 2013). In the case of bronze artifacts which have been exposed to chloride salts in their burial environment, a cyclical corrosion process called “bronze disease” can occur, which has the potential to fully consume the original metal, leaving only corrosion product in its place. Bronze Disease, despite its name, can occur not only with copper-tin alloys but with any copper alloy as well as with pure copper (Selwyn, 2004).

The corrosion products that are important in bronze disease are the copper chlorides: nantokite, atacamite, paratacamite, clinoatacamite, and botallackite (Scott, 2000; Selwyn, 2004). Nantokite, CuCl , is not itself bronze disease, but it is often a precursor for bronze disease (Selwyn, 2004). It is a gray-green, translucent, waxy solid. Its formation is favorable when pH and oxygen content are low and chloride ions are present, such as in a burial environment (Selwyn, 2004). The other four aforementioned compounds are polymorphs of copper chloride hydroxides with the chemical formula $\text{Cu}_2\text{Cl}(\text{OH})_3$. Atacamite is an orthorhombic polymorph (Scott, 2000). It is the most common copper chloride hydroxide observed and appears as a continuous, sugar-like coating of crystals ranging from emerald to blackish green. Paratacamite is a rhombohedral polymorph and clinoatacamite is a monoclinic polymorph, and both appear as powdery, light green secondary corrosion layers on a patinaed surface or as pustules. Lastly, botallackite is the least stable polymorph. It is also a monoclinic polymorph and is similar in appearance to paratacamite and clinoatacamite (Scott, 2000). Table 1 summarizes the composition and structure of these common copper

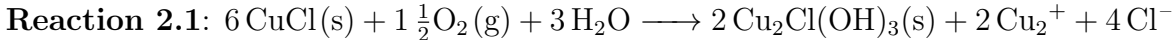
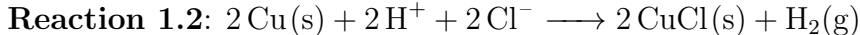
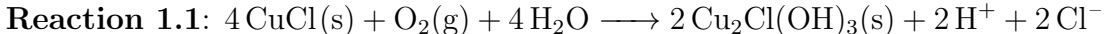
chloride hydroxides.

Common Name	Chemical Composition	Crystal Structure
Atacamite	$\text{Cu}_2\text{Cl}(\text{OH})_3$	Orthorhombic
Paratacamite		Rhombohedral
Clinoatacamite		Monoclinic
Botallackite		Monoclinic

Table 1: Summary of the composition and structure of the common copper chloride hydroxides associated with bronze disease.

Non-archaeological copper artifacts can suffer from bronze disease if the copper is exposed to chlorides through environments containing seawater or de-icing salts, or through chloride-containing solutions during intentional patination processes (Selwyn, 2004). However, bronze disease is most classically associated with excavated copper artifacts since, as previously mentioned, burial conditions are particularly conducive to nantokite production. Nantokite will typically form as a primary corrosion layer in direct contact with the metal surface. Subsequent layers of corrosion, such as cuprite or copper carbonate hydroxides, may form over the nantokite while the object is still buried. Nantokite is able to drive the production of bronze disease after the object is excavated if the surface layers of corrosion are compromised, allowing oxygen and water to react with the nantokite and the metallic surface, producing one or more of the copper chloride hydroxides described above (Selwyn, 2004).

Two possible mechanisms have been proposed for bronze disease of archaeological bronzes (Selwyn, 2004):



The intermediate reactants differ between the two proposed mechanisms, but the ultimate

results of the mechanisms are quite similar: chloride ions are gradually removed as they become bound in solid copper chloride hydroxides. Because of this, if only a small amount of nantokite is present, it is possible that the corrosion will stop once the chloride ions have been fully consumed by the reaction. If there is a significant layer of nantokite, the metal can be completely destroyed, leaving only corrosion product in place of the original metal (Selwyn, 2004).

The mechanism of various corrosion processes can be quite complicated, but the basics can be boiled down to thinking about corrosion as an electrochemical cell (Monticelli et al., 2018). Bronze disease, like most corrosion processes, is the result of the formation of an anodic and cathodic site within the metal or its corrosion products in the presence of an electrolyte (MacLeod, 1981). The electrolyte is supplied by a very thin layer of water forming on the metal surface in humid conditions. The anodic site is where the metal loses electrons. In the case of bronze disease, pits will form at the anodic site as the copper is bound by Cl^- . Since electrons can flow freely in a metal, the electrons lost at the anodic site can freely travel through the bulk metal to the cathodic site where the electron can be used in an oxidation reaction. Atmospheric oxygen as well as aqueous H^+ supplied by the layer of water that can form on the metal surface due to relative humidity in the atmosphere will facilitate the oxidation reaction at the cathodic site (MacLeod, 1981; Monticelli et al., 2018).

1.2 Treatment Methods for Bronze Disease

Three methods that have been commonly used to stop the cyclic degradation process of bronze disease are preventative conservation, coatings, and corrosion inhibition. These conservation methods are not mutually exclusive and can be done concurrently. The foremost, preventative conservation, is the protection of metal artifacts through environmental control. Whereas cellulosic and proteinaceous materials benefit from humidity that is neither too high nor too low, metals, particularly iron, copper, and their alloys, benefit from an environment with a humidity that is as low as possible (Mezzi et al., 2012; Thomson, 1986).

In the case of bronze disease, this is because humidity supplies the water necessary for the reactions detailed above to occur.

The environmental specifications outlined in Garry Thomson’s book *The Museum Environment* (1986), have been relaxed in many situations as research has progressed and as the cultural heritage community has become more aware of their ethical obligation to partake in sustainable practices. For example, the specifications for allowable relative humidity (RH) fluctuations for organic materials were broadened from the (+/-) 5% outlined by Thomson to (+/-) 8% in some institutions such as the Smithsonian as early as 2007 (Mecklenburg, 2007). Extensive research regarding the dichotomy of the necessity of interior climate control and the need for institutions to be more sustainable remains ongoing (Elkadi et al., 2021). Unfortunately, as more research has been done, the allowable RH for metals seems to be more stringent. Thomson outlined that metal collections could tolerate an RH maintained at 40-45%, while new research suggests that bronze disease can occur when metals are exposed to RH as low as 30% (Mezzi et al., 2012).

Fortunately, passive environmental control methods can greatly aid active environmental control methods in achieving appropriate conditions for metal collections, allowing environmental control of metal collections to be less costly and less energy-consumptive than active methods alone. Microclimates can be created within space-efficient housing by using humidity stabilizers such as sorbents (Tétreault & Bégin, 2018; Thomson, 1986) or by eliminating oxygen, the other component necessary to drive bronze disease, with the use of oxygen scavengers (Frank & Castriota, 2021; Paterakis & Mariano, 2013).

Sorbents buffer humidity by taking moisture out of the air in humid conditions and supplying moisture to the air in dry conditions. The efficacy of sorbents can be compared by looking at their moisture reservoir values (M), which is a measure of the amount of water in grams gained by 1 kg of the sorbent with a 1% change in RH. Higher M values indicate the need for a lower quantity of sorbent in a given enclosure. The type of sorbent chosen will depend on many factors including the M value at the RH range of interest, the price,

the frequency with which it will need to be replaced, and the amount of space available in the enclosure. Once a sorbent has been chosen, it can be conditioned to be an effective desiccant by drying it completely in an oven (Tétreault & Bégin, 2018). Oxygen scavengers such as *Ageless* or the RP-K System produced by Mitsubishi Gas Chemical (MGC) will absorb oxygen out of the air. Oxygen scavengers can be placed with artifacts in sealed *Escal* (also produced by MGC) or the aluminized nylon and polyethylene barrier film MarvelSeal 360 to create microclimates devoid of oxygen (Paterakis & Mariano, 2013).

Preventative methods, active or passive, are not always possible on excavation sites. This could be for a plethora of reasons: the systems may not be in place for year-round climate control, the costly expense of year-round climate control may not be within the usually already limited excavation budget, obtaining sorbents may be difficult, etc. While the funding capacities of most remote archaeological sites are not published, it is nonetheless a sentiment that is anecdotally expressed by many archaeological conservators. Speaking from personal experience on excavation sites, one of the largest barriers to effective passive climate control is the labor hours required to change the sorbents in storage housing or in display cases in site museums.

Coatings or inhibitors can be used to provide additional protection against corrosion. Coatings can be synthetic, such as microcrystalline wax or acrylic resin coatings, or natural, such as beeswax (Argyropoulos et al., 2007; Frank & Castriota, 2021; Molina Delgado et al., 2023; Serotta et al., 2016). Presently, the most commonly used coatings include Paraloid B48N, Paraloid B44, Paraloid B72, Incralac, and microcrystalline wax (Serotta et al., 2016). Coatings, however, can pose several problems as they age. For example, waxes can discolor, crosslink, and become embrittled due to photooxidation (Jaeger, 2008; Perera, 2003). Acrylic resins, while generally more stable overtime, can cause the surface to have an undesirable sheen (Horie, 2013). In all cases, coatings can form a thick and unsightly layer over an artifact's surface, obscuring details and the original nature of the surface (Passaretti et al., 2021). Additionally, in the event that retreatment becomes necessary, both waxes and acrylic

coatings require removal before retreatment can occur, and removal of organic coatings can be difficult, requiring solvents such as xylene that are harmful to both the user and the environment (Horie, 2013; Jaeger, 2008). Lastly, uneven application resulting in variation in coating thickness as well as localized failure of the coating through cracking, flaking, or abrasion, can cause corrosion to develop beneath the coating (Jones, 1996; Sease et al., 1997). The problems of unevenly applied coatings have been observed in industrial and cultural heritage applications alike (“Pitting Corrosion”, n.d.; Selwyn, 1993).

Inhibitors can also be synthetic, such as benzotriazol (BTA), or natural, such as cysteine or plant-derived inhibitors. A corrosion inhibitor is a “chemical substance that when present in the corrosion system at a suitable concentration decreases the corrosion rate, without significantly changing the concentration of any corrosive agent” (Monticelli et al., 2018). One advantage of inhibitors is that the thickness of the adsorbed layer formed on the surface is typically imperceptible. Adsorption processes will be elaborated on in the next section. While the exact thickness of an inhibitor film or coating is highly variable and will depend on several factors, the average thickness of BTA is on the scale of nanometers when applied to archaeological artifacts (Golfomitsou & Merkel, 2004), while coatings will tend to be on the scale of micrometers (Pouli et al., 2005).

BTA has been the most commonly used corrosion inhibitor for copper alloy artifacts for decades because it has been deemed aesthetically appropriate and acceptably effective (Argyropoulos et al., 2007; Frank & Castriota, 2021; Serotta et al., 2016); however, it poses multiple sustainability issues. Firstly, it is known to be harmful to the environment, both flora and fauna. There is evidence that BTA persists in the environment for a very long time as it has been concluded that benzotriazoles do not biodegrade, they are UV-stable, and are resistant to oxidation (Shi et al., 2019). Thus, their impact on the environment is believed to be lasting. Secondly, it is suspected that BTA may have carcinogenic effects on humans (McEnroe et al., 2025). The environmental and human health risks are of particular concern on archaeological sites where appropriate waste disposal and fume extraction may be

limited. Lastly, sourcing BTA to remote archaeological sites is costly, both from an economic perspective as well as because of the carbon footprint associated with, for example, shipping and procuring supplies (“Carbon calculator”, 2025).

1.3 The Chemistry of Corrosion Inhibitors

Faltermeier (1999) summarizes the qualities of a corrosion inhibitor suitable for use in cultural heritage fields. An inhibitor for use in cultural heritage should: be readily soluble in water or alcohol for ease of application; be affordable and accessible; be effective in conditions as low as pH 2, especially in the case of treating bronze disease in which low pH chloride pits are often observed; not significantly alter the visual appearance of the patina; not be hazardous or harmful to the user; and form a polymeric film that is not soluble in water or organic solvents so that the film is not removed when exposed to common conservation solvents (Faltermeier, 1999, pp.122-123). Consideration of an inhibitor’s environmental sustainability should be added to Faltermeier’s list in light of current best practices in conservation.

Many corrosion inhibitors have been used for the treatment of copper and copper alloy artifacts with varying degrees of success. The performance of silver oxides, zinc dust, 1H-benzotriazole (BTA) ($1,2,3\text{C}_6\text{H}_5\text{N}_3$), 2-amino-5-mercapto-1,3,4-thiadiazole (AMT) ($\text{C}_2\text{H}_3\text{N}_3\text{S}_2$) and 2-mercaptobenzothiazole (MBT) ($\text{C}_7\text{H}_5\text{NS}_2$) as corrosion inhibitors have been the most extensively studied for decades (Faltermeier, 1999; Junior et al., 2007; Mohamed et al., 2004; Sharma et al., 1995; Zucchi et al., 1996).

Monticelli (2018) describes that inhibitors can be anodic, cathodic, or mixed type inhibitors. As described in Section 1.1, corrosion processes typically involve an anodic site where electrons are donated and the metal is consumed and a cathodic site that is commonly attributed to the oxygen reduction reaction. As the name suggests, the inhibitor film formed by an anodic-type inhibitor will retard the anodic reaction, the film formed by a cathodic-type inhibitor will retard the cathodic reaction, and the film formed by a mixed-type inhibitor affects the reaction at both the anodic and cathodic sites (Monticelli et al.,

2018). BTA, for example, is reportedly a mixed-type inhibitor, which means that it retards both the anodic and cathodic sites of corrosion (Finšgar & Milošev, 2010).

Monticelli (2018) categorizes inhibitor films into three different classes: passivating films, precipitation films, and adsorption-only films. Passivating films include oxidizing inhibitors such as chromates and nitrates which form an oxide passivation layer. However, as a result of this class's toxicity, this inhibition class is primarily used only in cases where degradation caused by corrosion could pose a threat to human life, such as in the aeronautical industry. Precipitation films are inhibitors which form complexes with metal ions in solution followed by precipitation onto the substrate surface. When a copper artifact is treated with BTA, for example, one proposed mechanism of action is the formation of a precipitated copper-BTA salt layer on the substrate surface (Finšgar & Milošev, 2010; Monticelli et al., 2018). The mechanism of BTA inhibition is still under investigation, and this will be discussed further below.

Adsorption-only films are inhibitors which interact with the substrate surface through adsorption processes alone. All classes of inhibitors including the passivating films and precipitation films act by preliminary adsorption. Adsorption can either be electrostatic interactions (London-dispersion forces, dipole-dipole interactions, and hydrogen bonds) between the inhibitor and the substrate surface (physisorption) or can form a coordination bond involving an exchange of electrons (chemisorption) (Monticelli et al., 2018).

Chemically, whether or not a particular compound will be an effective corrosion inhibitor will depend on the electron density of its donor atom and its polarizability (Monticelli et al., 2018). Effective inhibitors contain heteroatoms: oxygen, nitrogen, or sulfur can have high electron density and therefore are effective as donor atoms (Rani & Basu, 2012). Additionally, inhibitors featuring non-bonded (lone pair) electrons and electrons in π -bonds will facilitate electron transfer between the inhibitor and the metal. As can be seen in Figure 1, the chemical structure of BTA features heteroatoms (nitrogen) in a conjugated ring. The efficacy will also increase when a hydrogen attached to a carbon in a conjugated ring is replaced by

a substituent group, notably -NH, -NO, -CHO, or -COOH (Rani & Basu, 2012).

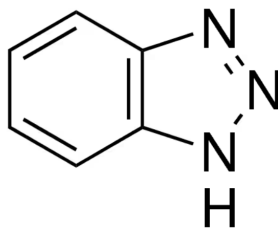


Figure 1: The chemical structure of benzotriazol.

The delocalized electrons of the triazole ring allow for the formation of a Cu-N bond. One proposal for the complex formed at the substrate surface when the substrate is pure copper is shown in Figure 2 (Finšgar & Milošev, 2010). The exact surface structure and composition of the Cu-BTA complex is still not completely understood, especially for archaeological bronzes whose surfaces are heterogeneous (Mezzi et al., 2012). Mezzi et al. (2012), for example, found that a Cu(I)-BTA complex was favored when BTA chemically interacted with cuprite grown on pure copper, while a Cu(II)-BTA complex was favored when BTA chemically interacted with copper chloride hydroxides on pure copper. A mechanism has been proposed for the latter which involves the formation of a copolymer Cu(I)-Cl-Cu(I)BTA-Cu(I) (Hashemi & Hogarth, 1988). Furthermore, a stable film which lacks consistency in copper oxidation state was observed when BTA chemically interacted with copper chloride hydroxides on a 95% Cu, 5% Sn alloy.

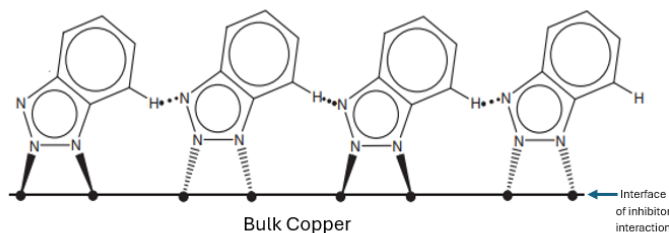


Figure 2: A diagram detailing a proposed mechanism of BTA chemisorption to pure copper.

1.4 Research into Sustainable Treatment Methods

It is clear that the mechanisms of corrosion inhibition, particularly on corroded copper alloys is complicated and difficult to elucidate. Researchers, however, have been able to pinpoint alternatives to BTA for use in cultural heritage by understanding the basics of corrosion chemistry outlined in the previous section.

Researchers have sought alternatives to BTA, natural or otherwise, for several reasons. One reason is because BTA is not particularly effective at inhibiting the pitting corrosion caused by bronze disease (Golfomitsou & Merkel, 2004). Bronze disease pits are acidic, with pH values as low as 2 having been observed, and BTA is significantly less effective in acidic environments (Gravgaard & van Lanschot, 2012, p. 14). The hazards to the user and the hazards to the environment that were discussed in Section 1.2 have also more recently driven professionals in industrial settings and conservation alike to find more sustainable alternatives. As mentioned in Section 1.2, the hazards to the user and the environment are especially of concern when used in archaeological settings where adequate fume extraction or waste disposal is less likely to be available.

Naturally occurring compounds demonstrating the same chemical motifs as described in the previous section have been identified as possible alternatives to BTA. Table 2 details several natural compounds that have been investigated and have been shown to be effective (80% or greater inhibitor efficiency) on various uncorroded metals (Conway, 2024; Conway et al., 2022; González-Parra & Di Turo, 2024; Rani & Basu, 2012; Varvara et al., 2017).

It is important to note that most of these inhibitors have been tested on uncorroded coupons immersed in corrosive solutions with and without inhibitor. Because the presence of a corrosion layer modifies the corrosion inhibitor mechanism as discussed in Section 1.3, the outcomes of and the methods developed during investigations on uncorroded metal are not directly applicable to the treatment of archaeological metals. Only cysteine, black pepper, ginger, and jatropha have been tested on pre-corroded metals (Abu-Baker et al., 2013; Conway et al., 2022; Elshahawi et al., 2022; González-Parra & Di Turo, 2024).

Inhibitor Source	Active Inhibition Compound(s)	Metals Tested	References
Aloe vera	Tannic acid	Cu, Bronze, Fe	Benzidia et al. (2019)
Banana (Musa sapientum) peels	Unspecified	Steel	Eddy et al. (2009)
Black locus (Robinia pseudoacacia) pods	arabinose, rhamnose, galactose, gluconic acid, rutin, 4 methoxygluconic	Cu, Bronze	Pourzarghan and Fazeli-Nasab (2021)
Black pepper (Piper nigrum) drupe	Piperine	Cu, Bronze, Steel	Conway (2024) Conway et al. (2022) Eid (n.d.)
Carob (Ceratonia siliqua) pods	Condensed tannins	Cu, Brass	Fouda et al. (2015)
Garlic (Allium sativum) root	Unspecified	Cu, Fe, Steel	Conway (2024)
Ginger (Zingiber officinale) root	Gingerol	Cu, Fe	Conway (2024) Conway et al. (2022) Eid (n.d.)
Henna (Lawsonia) leaf	Lawsonic acid (2-hydroxy-1, 4- naphthoquinone resin and tannin, coumarin, Gallic acid, and sterols)	Steel, Ni, Zn	Chetouani and Hammouti (2003)
Hibiscus (Hibiscus sabdariffa) leaf	Ascorbic acid, amino acids, flavonoids, pigments, carotene	Steel	Oguzie (2008)
Honey	Unspecified	Cu, Steel, Sn	Pourzarghan et al. (2017)
Nettle purges (Jatropha)	Phytol, stigmasterol, campesterol, sitosterol	Cu, Bronze	Elshahawi et al. (2022)
Natural amino acids	Cysteine, alanine, glycine, leucine	Cu, Bronze, Steel	Abu-Baker et al. (2013) González-Parra and Di Turo (2024)
Olive tree (Olea europaea) leaf	Oleuropein	Cu	Rahal et al. (2016)
Papaya (Carica papaya) leaf	Various ascorbic, amino, benzoic, succinic, carboxylic acids	Cu	Okafor and Ebenso (2007)
Passion fruit (Passiflora edulis) leaf	Various active compounds	Cu	Tan et al. (2022)
Propolis	Variable flavonoids and phenols	Cu	Varvara et al. (2017)
Sugarcane (Saccharum officinarum) leaf	Various active compounds	Cu	Gao et al. (2020)

Table 2: An overview of several investigations of natural corrosion inhibitors to date.

The efficacy of the protein cysteine as a natural inhibitor has been investigated and has been shown to have higher efficacy than BTA in bronze disease pits (Gravgaard & van Lanschot, 2012) and it has shown up to 89% IE on uncorroded 5% Sn bronze coupons (Abu-Baker et al., 2013). When tested on pre-corroded metals, however, the characteristic blue/green corrosion turned grey after treatment with cysteine (Abu-Baker et al., 2013).

The results of black pepper and ginger tests on pre-corroded coupons were presented during a presentation at the 2022 Association of North American Graduate Programs in Conservation annual conference. Their efficacy was only qualitatively investigated by visual comparison before and after a two-week aging period for coupons that were treated or not treated with inhibitor (Conway et al., 2022).

Jatropha, shown to have 86% IE when tested on uncorroded coupons, was actually tested on copper alloy artifacts; however, the IE when applied to archaeological artifacts was not investigated (Elshahawi et al., 2022).

Because so many natural inhibitors have demonstrated high IE on uncorroded copper coupons, one needs to clearly identify their goals when choosing one to investigate on pre-corroded copper coupons, otherwise the options can become overwhelming. Because accessibility is one of the important criteria to consider when choosing a corrosion inhibitor for use in cultural heritage as outlined in Section 1.3, and because accessing conservation materials on remote archaeological sites is a particular challenge, accessibility was the main criteria in selecting a natural corrosion inhibitor to investigate further in this study. Plant-derived inhibitors, especially when the plants being used are regionally grown, have the benefit of being easier to obtain than compounds like natural amino acids which might still have to be sourced from chemical distributors. Black pepper, ginger, and propolis fit the criteria of being accessible as they are easily sourced worldwide.

The chemical structures of black pepper and ginger can be seen in Figures 3 and 4, respectively. The presence of heteroatoms, nonbonded electrons, and π -bonds can be seen in both compounds.

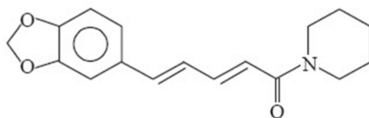


Figure 3: The chemical structure of piperine, the primary active inhibitor compound in black pepper extract.

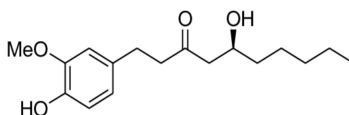


Figure 4: The chemical structure of 6-gingerol, the primary active inhibitor compound in ginger extract.

Propolis is a bee product. It is a mixture of resins that bees collect from leaf buds and tree sap with wax and bee secretions, and it is a hive’s defense against bacteria and infection (Conrad, 2016). Native bee species exist on every continent except Antarctica (United States Geological Survey, 2024), making bee products accessible worldwide. Honey, of course, is also a bee product, but honey has only demonstrated 73% IE on uncorroded copper coupons (Pourzarghan et al., 2017) while propolis has demonstrated up to 95% IE (Varvara et al., 2017). The active inhibition compound in propolis extract will vary based on the plant source of the sap the bees are collecting. The extracts of propolis have been investigated using chromatography, as was done by Varvara et al. (2017), and researchers have determined that various flavonoids and phenolic acids are responsible for the inhibitor properties observed from propolis extract. Figure 5 details the four most abundant compounds identified by Varvara et al. (2017, p. 1110) in the propolis they investigated. All four major compounds identified in propolis extract feature heteroatoms with nonbonded electrons in conjugated systems.

Natural materials such as propolis in which it is impossible to relate IE to a single compound pose a challenge for conservators. Historically, conservation as a field has been averse to uncertainty (Henderson, 2018), but having to identify the major inhibitor compounds in every source of propolis would be laborious and costly. In a materials-based mindset, it can

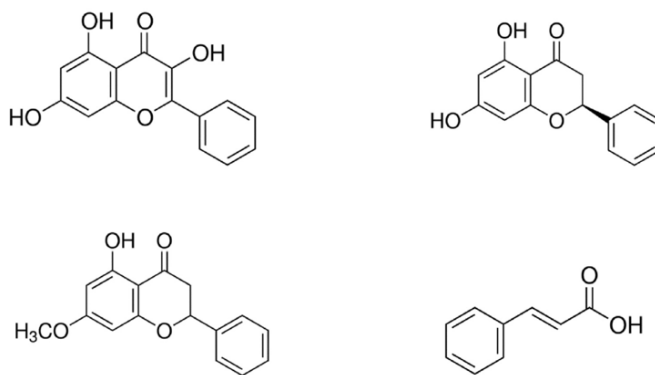


Figure 5: The chemical structure of the most abundant flavonoids and phenolic acids identified by Varvara et al. in the propolis used in their study. Top left is galangin, top right is pinocembrin, bottom left pinostrobin, and bottom right is t-cinnamic acid

be hard to accept any degree of lack of control when treating artifacts. As conservation moves more towards people-based approaches rather than exclusively materials-based approaches (Sully, 2013), and as sustainability concerns are coming to the forefront of practice across disciplines (De Silva & Henderson, 2011), perhaps some degree of uncertainty can be tolerated. If multiple sources of propolis are investigated and demonstrate high IE on pre-corroded coupons, perhaps the benefits of propolis- environmental, economic, human- in conjunction with demonstrated IE across sources would justify uncertainty.

1.5 Research Question

This goal of this thesis is to investigate natural corrosion inhibitors specifically for their efficacy of use on remote archaeological sites to treat bronze disease. The natural corrosion inhibitor selected for study would hopefully address the aforementioned inadequacies of the use of BTA on remote archaeological sites. The criteria for selection for the natural corrosion inhibitors examined in this paper were: 1) previous published studies have shown high IE on uncorroded copper alloy coupons, but these previous studies lacked quantitative information about their performance on pre-corroded surfaces and 2) that they can be easily and locally sourced on remote archaeological sites across the world. Pepper, ginger, and propolis proved

to meet both of those criteria.

Ultimately, only propolis will be investigated at length in this study. As the major compounds in propolis extract can vary between propolis sources, propolis from three different sources were used as inhibitors in this study. The surface effects and IE of all three propolis used in this study will be investigated at length on corroded copper alloy coupons. The decision was made to exclude pepper and ginger from the experiments in this study since previous studies have already identified the compounds in their extracts, and unpublished work has investigated their effect on pre-corroded copper alloy coupons. It was deemed more important to focus on the more understudied material for this research.

This study will provide more evidence for the viability of use of these natural corrosion inhibitors on remote archaeological sites through experiments and theoretical discussions.

2 Materials and Methods

2.1 Coupon Specifications

Copper alloy (95% Cu, 5% Sn) sheets (6 x 12 x 1/8 in) were purchased from McMaster-Carr. This alloy composition was chosen for three reasons. First, it was important for the coupon composition to be representative of the alloy compositions of archaeological materials since the objective of investigating propolis as an inhibitor, as stated in Section 1.5, would be to demonstrate that it is suitable to be used on archaeological artifacts. A 95% Cu, 5% Sn alloy is within the range of compositions of archaeological bronzes from various geographical regions and historical periods outlined in the literature (Abu-Baker et al., 2013; Craddock, 1977; Facsády & Verebes, 2009; Ingo et al., 2006; Selwyn, 2004; Tian et al., 1990). The second was based on availability. The variability in the composition of the copper alloys used throughout history makes it difficult to select a ‘most common’ or ‘average’ alloy to represent archaeological bronzes, so the alloy was chosen from among the alloys available to order through the University. Lastly, though archaeological bronzes can contain other

alloying metals such as Pb, an alloy containing only Cu-Sn was chosen to reduce the variables in the experimental design.

24- 2.5 x 2.5 cm square coupons were cut from the copper alloy sheet for use in the experiments outlined in this report. The copper alloy sheet was cut with a bench-top manual abrasive cutter.

2.1.1 Preparation

20 coupons were equally divided between five experimental groups (four coupons for each group). The remaining four coupons were prepared as backups in case additional coupons were needed. The experimental groups were the Control group (CG), BTA treated group (BTA-G), "Propolis 1" treated group (P1), "Propolis 2" treated group (P2), and "Propolis 3" treated group (P3). Four coupons were used for each experimental group so that one coupon from each group could be used for analytical investigation while the remaining three were used for weight change experiments. Coupon allocation is detailed in Figure 6.

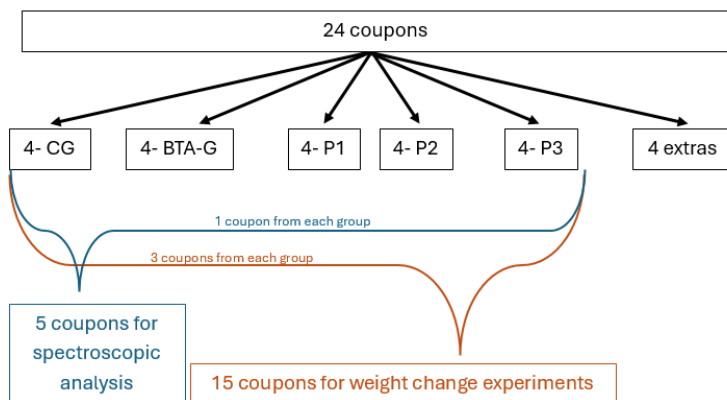


Figure 6: Allocation of coupons between experimental groups.

The specifications of the BTA and Propolis 1, 2, and 3 can be found in Section 2.2. All 24 coupons were corroded as detailed below before experiments or analyses were performed. The CG coupons were corroded and not treated with any inhibitor, the BTA-G coupons were corroded and then treated with BTA, the P1 coupons were corroded and then treated

with Propolis 1, the P2 coupons were corroded and then treated with Propolis 2, and the P3 coupons were corroded and then treated with Propolis 3. The coupons were corroded using a method that was slightly adapted from the method outlined by Faltermeier (1999). The coupons were:

1. Sanded with 600 grit sandpaper
2. Degreased in 100 mL of acetone in an ultrasonic bath for 5 minutes
3. Dried for 5 minutes at 50°C in an oven and then for 10 minutes in a box buffered to 0% RH with silica gel
4. Weighed in triplicate
5. Immersed in 1 M cupric chloride in deionized (DI) water at room temperature
6. Rinsed in DI water for 20 minutes (3x)
7. Immersed in 200 mL of ethanol
8. Dried for 5 minutes at 50°C in an oven
9. Exposed to 105°C in an oven for 60 minutes
10. Dried and cooled for 24 hours in a box buffered to 0% RH with silica gel
11. Exposed to 100% RH for 48 hours at room temperature
12. Dried for 5 minutes at 50°C in an oven and then for 10 minutes in a box buffered to 0% RH with silica gel

For Step 5, the 24 coupons were distributed between 4- 250 mL beakers. All of the coupons were immersed in 1M CuCl₂ solution by filling each of the four beakers with 100 mL of the CuCl₂ solution. As can be seen in Figure A.16 in Appendix A, the coupons were

propped against the wall of the beaker, rather than laid flat, to expose more of the surface area to the cuprous chloride solution.

For the rinsing step, the 24 coupons were distributed between 2 beakers. All of the coupons were immersed in DI water by filling each of the two beakers with 400 mL of DI water for 20 minutes. The DI water was gently agitated with a magnetic stir rod to promote movement of the water during the rinsing step. The DI water was discarded and replaced with fresh DI water between each of the three rinses. As can be seen in Figure A.17, the coupons were once again propped against the wall of the beaker, rather than laid flat, to allow water to flow over both sides of the coupon.

For all heating steps, the coupons were placed on inert supports made of archival grade Coroplast (polypropylene copolymer) and then placed in an oven set to the appropriate temperature (either 50°C or 105°C, depending on the step). The supports are detailed in Figure A.18. The supports allowed for airflow on both sides of the coupon which, again, would not have been possible if the coupons were laid flat.

As a last step, the coupons were placed in a humidification chamber on the same supports that were used during the heating steps. Due to time constraints, the coupons were placed in the chamber before 100% RH was achieved. As seen in Figure A.19, the starting RH was 59%. 100% RH was achieved after the coupons had been in the chamber for approximately 16 hours. The coupons were left in the chamber for 48 hours total. The coupons after the corroding process can be seen in Figure 7.

2.2 Inhibitor Specifications

2.2.1 Benzotriazol

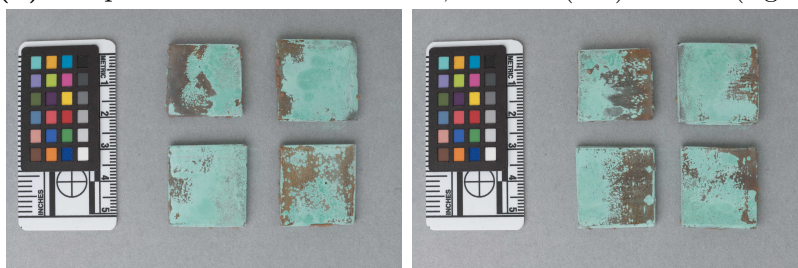
The BTA used in these experiments was sourced from Sigma-Aldrich (ReagentPlus, 99%, product number B11400).



(a) Coupons to be used in CG, obverse (left) and reverse (right)



(b) Coupons to be used in BTA-G, obverse (left) reverse (right)



(c) Coupons to be used in P1, obverse (left) and reverse (right)



(d) Coupons to be used in P2, obverse (left) and reverse (right)



(e) Coupons to be used in P3, obverse (left) and reverse (right)

Figure 7: Copper alloy coupons after corroding using the method adopted from Faltermeyer.

2.2.2 Propolis

Three different propolis were used in this experiment because, as discussed in Section 1.4, the chemical compounds that would be responsible for their ability to inhibit corrosion may vary from one propolis source to the next. A map of climate zones in the United States derived from the Köppen-Geiger climate zones presented by Beck et al. in 2018 was used to choose three propolis that were likely to be made from different plant sources.

Propolis 1 was propolis that was sourced locally from a Los Angeles bee farm, The Valley Hive. The Valley Hive is located in a temperate and dry, hot summer (CSA) climate zone. Some examples of native plants grown in and around this bee farm include California buckwheat (*Eriogonum fasciculatum*), California fuschia (*Epilobium canum*), and California sagebush (*Artemisia californica*). Carrying out the process of using a locally sourced propolis was an important proof of concept for this experiment since one of the primary justifications of choosing propolis to investigate in this study is that bees, and therefore bee products, can be readily and easily sourced worldwide (United States Geological Survey, 2024). The ability to source propolis in Los Angeles, a major metropolitan area, is, of course, not a perfect proof of concept since many archaeological sites are in much more remote areas; however, the process of obtaining and processing local propolis felt important to demonstrate nonetheless.

Propolis 2 was ordered from Mickelberry Gardens in Portland, OR. They source their products from multiple hives in the Portland area. Portland is located in a temperate and dry, warm summer (CSB) climate zone. Mickelberry Garden’s websites names Pacific blackberry (*Rubus ursinus*) and, broadly, native wildflowers as the plant sources for their bees.

Propolis 3 was ordered from Gil’s Honeybees. They have multiple farms in the Ithaca and the Finger Lakes region of New York. The Finger Lakes area of New York is a continental, no dry season, warm summer (CFB) climate zone. Gil’s Honeybees’ websites names goldenrod (*Euthamia graminifolia*), basswood (*Tilia americana*), and sumac (*Rhus typhina*) as the plant sources for their bees.

2.2.3 Preparation and Application

A solution of 3% BTA, the concentration that is standard to use in conservation (Faltermeier, 1999; Frank & Castriota, 2021) was prepared in ethanol.

The Valley Hive provided hive scrapings, a ball of waxy solids which contains propolis and which requires heating in water in order to isolate the propolis. The hive scrapings were baked at 95°C in a beaker filled with approximately 700 mL of water for three hours. This process allowed the waxy and plant material, which float in water, to separate from the propolis, which sinks in water. Images of the separation process can be found in Figure A.20 in Appendix A. Once cooled, the floating material and the water was poured off the propolis, and the propolis was allowed to dry thoroughly before being used to make an extract (Conrad, 2016). The other two propolis were sourced from propolis traps, which did not require this additional preparation step.

Due to time limitations, the concentration of the corrosion inhibitors prepared in this study was replicated from similar experiments in the literature rather than testing a range of concentrations. 1 g of each natural inhibitor was each mixed with 100 mL of ethanol to make stock solutions (Conway, 2024; Conway et al., 2022; Eid, n.d.; Fidrusli et al., 2018; Varvara et al., 2017). 1 g of each inhibitor can be seen in Figure A.21 in Appendix A. The mixture was stirred using a magnetic stir bar for 2.5 hours, at which point each mixture was filtered through pre-weighed Whatman No. 1 filter paper. The filter paper had been pre-weighed so that the weight of residual solids that did not go into solution could be weighed, and a concentration in parts per million (ppm) of each solution could be calculated.

After filtration, each filter paper along with residual solids was dried in an oven at 60°C for 1 hour, cooled in a silica gel buffered environment for 20 minutes, and then weighed again. Initial ppms are reported in Table 3. Calculated volumes of each stock solution were combined with ethanol to achieve 50 mL of solution with a final concentration of 100 ppm for propolis. Images of the inhibitor stock solutions can be seen in Figure A.22 in Appendix A.

Inhibitor	Initial Concentration (ppm)
Propolis 1	6329
Propolis 2	5063
Propolis 3	3797

Table 3: The concentration of each natural inhibitor solution prior to diluting them to 100 ppm.

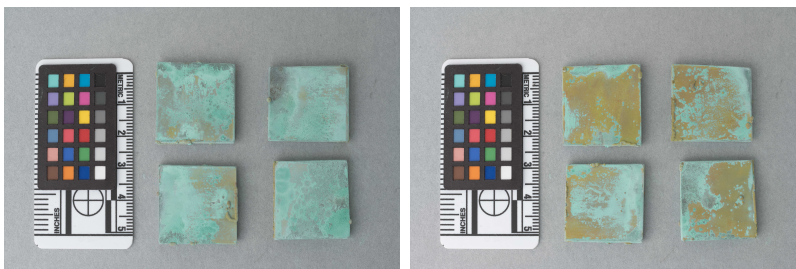
To treat the samples with the inhibitors, the 4 coupons for each experimental group were immersed in inhibitor solution detailed above (or in pure ethanol in the case of the CG) for 24 hours. Again, the coupons were propped against the wall of the beaker to allow the inhibitor solution optimal access to all sides of the coupon. Images of the immersion process can be seen in Figure A.22 in Appendix A.

After 24 hours, samples were dried in an oven at 30°C. The weight of the samples was checked after samples had been in the oven for 45 minutes and were successively checked every 10 minutes until no change in weight was observed (approximately 65 minutes in total). The samples were then cooled in a silica gel buffered environment for 20 minutes. Images of the coupons after treatment with each inhibitor can be seen in Figure 8.

One sample from each experimental group- 5 coupons total- was set aside for analysis with Raman spectroscopy, X-ray diffraction spectroscopy (XRD) and scanning electron microscopy (SEM). Justification for choosing these methods will be discussed in the remainder of this section as well as in Section 3. The remaining 15 coupons were placed on individual Coroplast stands and weighed in triplicate for use in weight change experiments.

2.3 Raman Spectroscopy

Raman spectroscopy was carried out using a Renishaw inVia Microscope system including a Leica DM2500 M microscope coupled to a Renishaw Peltier-cooled CDD array detector. The aim of the analysis was to characterize the corrosion products present on the corroded



(a) CG coupons after 24 hour immersion in ethanol



(b) BTA-G coupons after 24 hour immersion in 3% BTA solution



(c) P1 coupons after 24 hour immersion in 150 ppm Propolis 1 solution



(d) P2 coupons after 24 hour immersion in 150 ppm Propolis 2 solution



(e) P3 coupons after 24 hour immersion in 150 ppm Propolis 3 solution

Figure 8: Corroded coupons after immersion in inhibitor solution (or pure ethanol in the case of the CG).

coupons before aging for the weight change experiment. Because of time and resource limitations and, as will be discussed in Section 3.1.1, because the signal-to-noise ratio (S/N) was low, only the control coupon was analyzed with Raman. Excitation was performed with a diode laser at a wavelength of 785nm (1200 lines/mm grating). The laser power was kept below values that could degrade the sample. The laser line was focused onto the control coupon that was being analyzed with the Leica microscope's x50 objective. The spot size diameter was 1-5 μm . Multiple spots on the coupon were analyzed in order to explore the surface and account for possible inhomogeneity or inconsistencies of crystal orientation of solids in corrosion product across the surface; the results might not be representative of the entire surface if only a couple spots are tested. The wavenumber range of data collection was 100-1800 cm^{-1} . The Raman spectra were analyzed using the Renishaw WiRE 3.1 software and OriginPro 2025 software.

2.4 X-Ray Diffraction

XRD diffractograms were recorded using a Rigaku R-axis Spider. The analysis was conducted using 40 μA , 50kV, 0.3mm collimeter, and an image plate area detector. The image plate area detector allows for microgram sized samples due to higher sensitivity when compared with other types of detectors. The aim of this analysis was also to characterize the corrosion products before aging for the weight change experiment. XRD could elucidated information about the crystalline structure of the corrosion products on the surface of the corroded coupons, observing if there are changes in the chemical structure between the inhibitor treated and control groups. Analysis was carried out before aging for the weight change experiments. Samples for analysis were prepared by scraping small areas of the surface of each coupon. Sample was collected from three distinct locations on each coupon analyzed. The scrapings were not ground, resulting in low S/N and large backgrounds in the diffractograms.

2.5 Scanning Electron Microscopy

SEM was carried out using Hitachi's FlexSEM 1000. The aim of the analysis was to obtain information regarding differences in the corrosion distribution and morphology on the surface of the corroded coupons from each experimental group. Analysis was carried out before aging for the weight change experiments. Electron micrograph images were obtained for three spots on one coupon from each experimental group.

2.6 Weight Change

The aim of the weight change experiment was to track the weight gain of the coupons over time as a measure of the rate of corrosion over time. Although this method takes a long time compared to electrochemical studies of inhibitor efficiency (IE), it is still used today because it requires equipment that is often readily available in laboratories, and it is still considered more accurate than electrochemical methods (Abdel-Karim & El-Shamy, 2022; Pourzarghan et al., 2017; Varvara et al., 2017). As discussed in Section 1.1, since bronze disease is the result of reactions with moisture and oxygen in the surrounding environment, the resulting corrosion product will be heavier, and thus weight gain will be observed with continued corrosion. Comparing the rate of weight change between the control and treated groups is a simple way to measure IE with the following equation:

$$IE = 1 - \frac{\Delta \text{Weight of Treated}}{\Delta \text{Weight of Control}} \times 100 \quad (1)$$

(Pourzarghan et al., 2017)

The artificial aging methodology outlined in the 2013 study by Abu-Baker et al. was closely followed to artificially age the coupons during the weight change experiments in this study. Artificial aging of all 15 coupons was conducted in an United Scientific desiccator

glass conditioned to 92% RH with a saturated Potassium Nitrate solution in an oven set to 30°C (Abu-Baker et al., 2013). 92% RH and 30°C was chosen because those are conditions that could be feasibly achieved in uncontrolled storage on archaeological sites.

All 15 coupons that were prepared for weight change experiments were placed into the desiccator on their individual Coroplast stands. Examples of what the individual stands looked like can be seen in Figure A.23 in Appendix A. The coupons were weighed on their stands in triplicate once a week for 5 weeks.

3 Results

3.1 Identification of Corrosion Products Formed

As discussed in Section 1.1, atacamite, paratacatmite, clinoatacomite, and botallikite are the known polymorphs of chloride corrosion formed as a result of bronze disease (Scott, 2000). In Faltermeier’s 1999 corrosion inhibitor test on artificially corroded coupons, whose artificial corrosion process was modified for use in this study as outlined in Section 2.1.1, Faltermeier identified paratacamite as the primary corrosion product formed using XRD. Nantokite and cuprite were also identified in smaller amounts in Faltermeier’s study using metallographic cross-sectional analysis (Faltermeier, 1999, pp. 124-125). Raman and XRD were employed in this study as complementary techniques to investigate the corrosion products induced in the artificial aging, since the latter technique can characterize only crystalline materials and the former both crystalline and amorphous materials (Stuart, 2007).

3.1.1 Raman

As discussed in Section 2.3, the surface of one CG coupon was explored by collecting data at multiple points across the surface to account for possible inhomogeneity and differences in crystal orientation across its surface. Ultimately, nine points were investigated. Although the S/N was significantly low (see Figure 9), the spectra presented bands of similar shape and

intensity; thus, suggesting that the surface was homogeneous or that the corrosion products are very similar in terms of molecular structure across the surface.

Raman results (Figure 9) suggest that clinoatacamite was the polymorph formed in this study. This identification was made by comparison with the spectra of atacamite, paratacamite, and clinoatacamite shown in Frost’s 2003 study as well as with the RRUFF database of clinoatacamite (R061066) and all the available copper oxides, hydroxides, carbonates, and chlorides. Figure 9 shows the average Raman spectrum from three of the nine spots analyzed on one CG coupon.

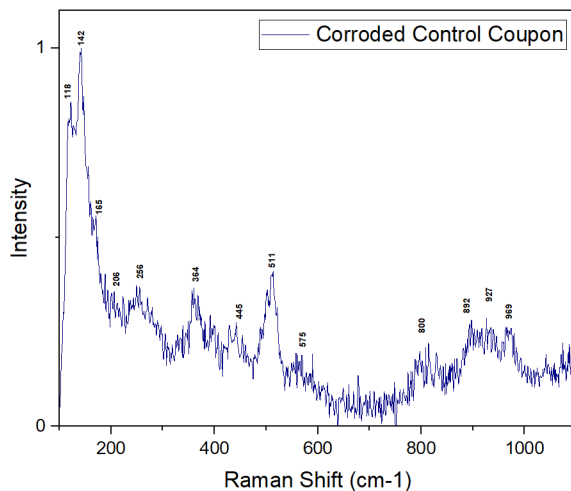


Figure 9: Average Raman spectrum (785 nm) of the corrosion product formed on the surface of one CG coupon. The spectrum shown here is a summed and normalized spectrum of data collected from three of the nine points analyzed on the surface of the coupon.

Primary bands can be noted at 118, 142, 165, 256, 364, 445, 511, 575, 800, 892, 927, and 969 cm^{-1} . Bands at 800, 892, 917, and 969 cm^{-1} can be attributed to the hydroxyl deformation modes, and bands at 364, 445, 511, and 575 cm^{-1} can be attributed to CuO stretching vibrations (Frost, 2003). It’s possible that the band at 256 cm^{-1} is related to lattice modes, and the bands in the lower wavenumber region can likely be attributed to OCuO bending (Frost et al., 2002).

Because the S/N is quite low in the Raman spectra, definitive identification of corrosion

products is quite difficult. This is especially the case with corrosion products that may be present in lesser quantity, such as the possible presence of nantokite or cuprite suggested by Faltermeier’s findings, as any signal from minor compounds is likely masked by the spectral noise. The S/N is often measured as peak-to-peak fluctuations in intensity which is expressed as the root mean square (rms) or standard deviation of the data, as is shown in Equation 2.

$$\text{rms deviation} = \left[\frac{(\sum[\text{amplitude}]^2)}{(N - 1)} \right]^{\frac{1}{2}} \quad (2)$$

(Vandenabeele & Edwards, 2018)

The low S/N can be due to many factors. The intensity of Raman signal is proportional to the number of scatters, the variation of the polarizability during the vibrational transition, and the intensity of the incident beam (Potma & Mukamel, 2016). One cannot increase the number of scatters nor the variation of the polarizability during the vibrational transition in these compounds being analyzed but can increase the intensity of the incident beam. However, when increasing the intensity, degradation of the investigated spots was observed, limiting the obtention of better S/N. Examples of degradation are shown in Figure 11. Because the S/N was so low, researchers did not proceed with Raman spectroscopy for the other experimental groups. The time and cost required to perform Raman spectroscopy were considered unjustified by the quality of the results produced.

3.1.2 XRD

XRD was used to characterize the corrosion product on coupons from each of the experimental groups as outlined in Section 2.4. Significant background and preferential orientation effects were observed because the samples could not be ground before analysis.

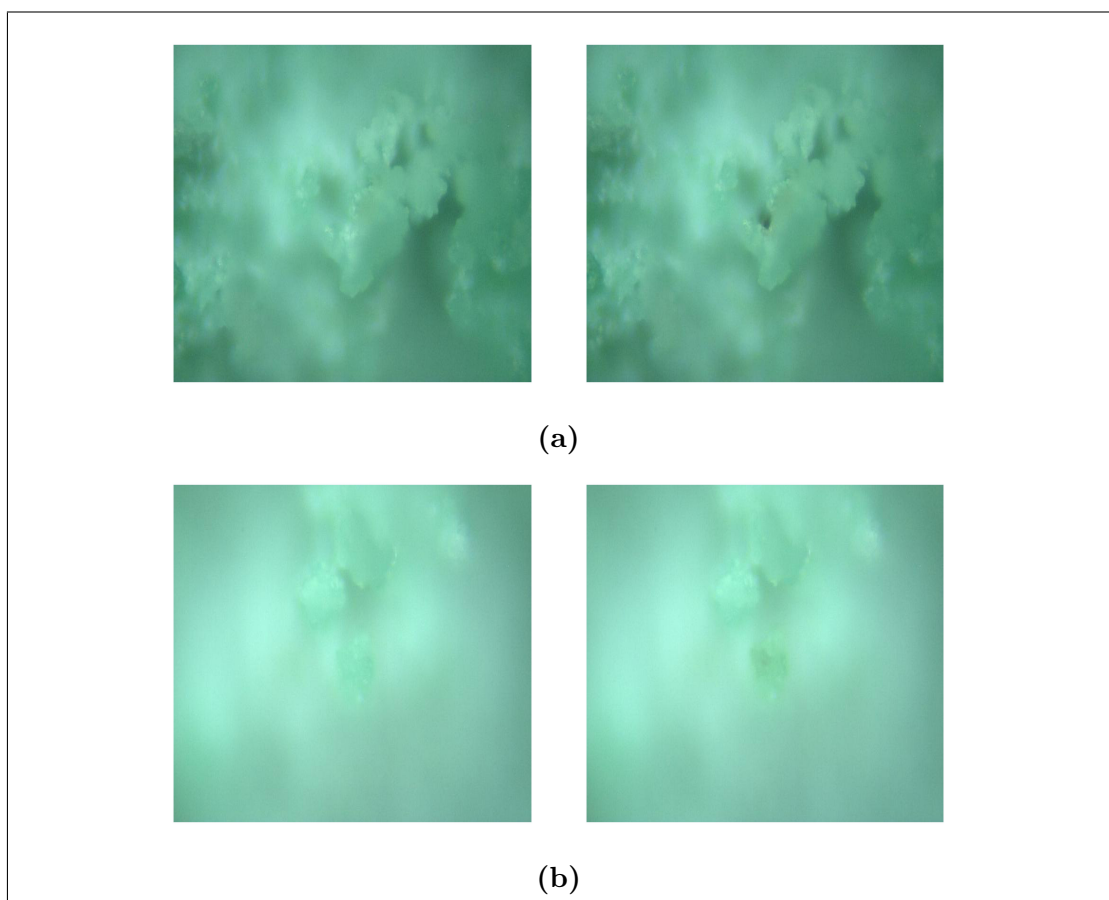


Figure 11: 50x magnification of 2 points (a and b) investigated with Raman spectroscopy, showing degradation of sample after irradiation with laser power of 1 mW. Images before the irradiation are shown on the left. Images after the irradiation are shown on the right, evidencing changes in color of the analyzed spots

Differences between the XRD diffractograms from the CG and the treated groups can be observed, which is especially evident in Figure 12. The single peak at $32\ 2\theta$ in the CG appears as a doublet for each treated group, the single peak at $39.7\ 2\theta$ in the CG appears as a doublet in P1 and P3, and the peaks at 50.2 and $53.6\ 2\theta$ in the treated coupons are not present in the CG. The absence of the peaks at 50.2 and $53.6\ 2\theta$ and splitting may be related to phase transformations during the inhibitor application. Such changes need to be investigated further, repeating these measurements with a larger amount of ground sample and using complementary techniques. A larger amount of sample would help avoid interference related to inadequate particle sizes and preferential orientation (Luzia da Silva et al., 2011).

The XRD diffractograms of all investigated coupons are shown in Figures 12 and 13. Considering the previously discussed Raman results, the XRD data were first compared with the clinoatacamite diffractograms from RRUFF (Figure 12, reference R061066) and next with the Rigaku Corporation PDXL 2 software (version 2.8.4.0, Figure 14) database. XRD results corroborate the Raman results, indicating the presence of clinoatacamite, but some of the peaks (at approximately 17.5 , 21.5 , 24 , and $28.5\ 2\theta$) cannot be attributed to clinoatacamite. All copper carbonates, oxides, chlorides, and hydroxides available in the databases were considered, but no exact match was observed.

The presence of compounds based on tin were also considered, but did not match with the missing peaks. Another possibility considered was the contamination from the aluminum foil that the samples were stored in for transportation to the instrumentation. When the samples were unwrapped, the area of foil that had been in contact with the sample looked visually different than the rest of the foil. However, no matches were found when looking for compounds based on Al.

When comparing the XRD data with references from copper chloride hydroxides, peaks in similar positions are observed, for example, in copper chloride hydroxide hydrate (Figures 13 and 12), including the presence of doublets around $16\ 2\theta$, not previously observed in the

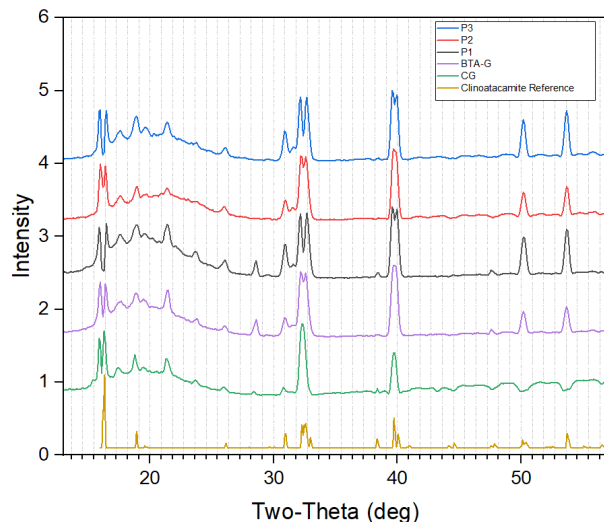


Figure 12: XRD diffractograms from each experimental group compared to the clinoatacamite reference diffractogram in the online RRUFF database.

clinoatacamite references. This observation suggests that, although no perfect match was obtained, other copper chloride hydroxides are possibly present. Note that ‘anatacamite’ shown in Figure 12 is now recognized as the same compound as clinoatacamite.

The results of Raman and XRD confirm that bronze disease was induced during the corroding process outlined in Section 2.1.1. Because of this, observations of the surface morphology and weight change experiments after treatment with inhibitors were then carried out.

Because the S/N of Raman was so low and because samples were not ground for XRD, no minor corrosion products were able to be detected. Confirming the presence of a copper chloride hydroxides does confirm that bronze disease was induced during the corroding process outlined in Section 2.1.1. Observations of the surface morphology and weight change experiments after treatment with inhibitors were carried out because bronze disease was confirmed.

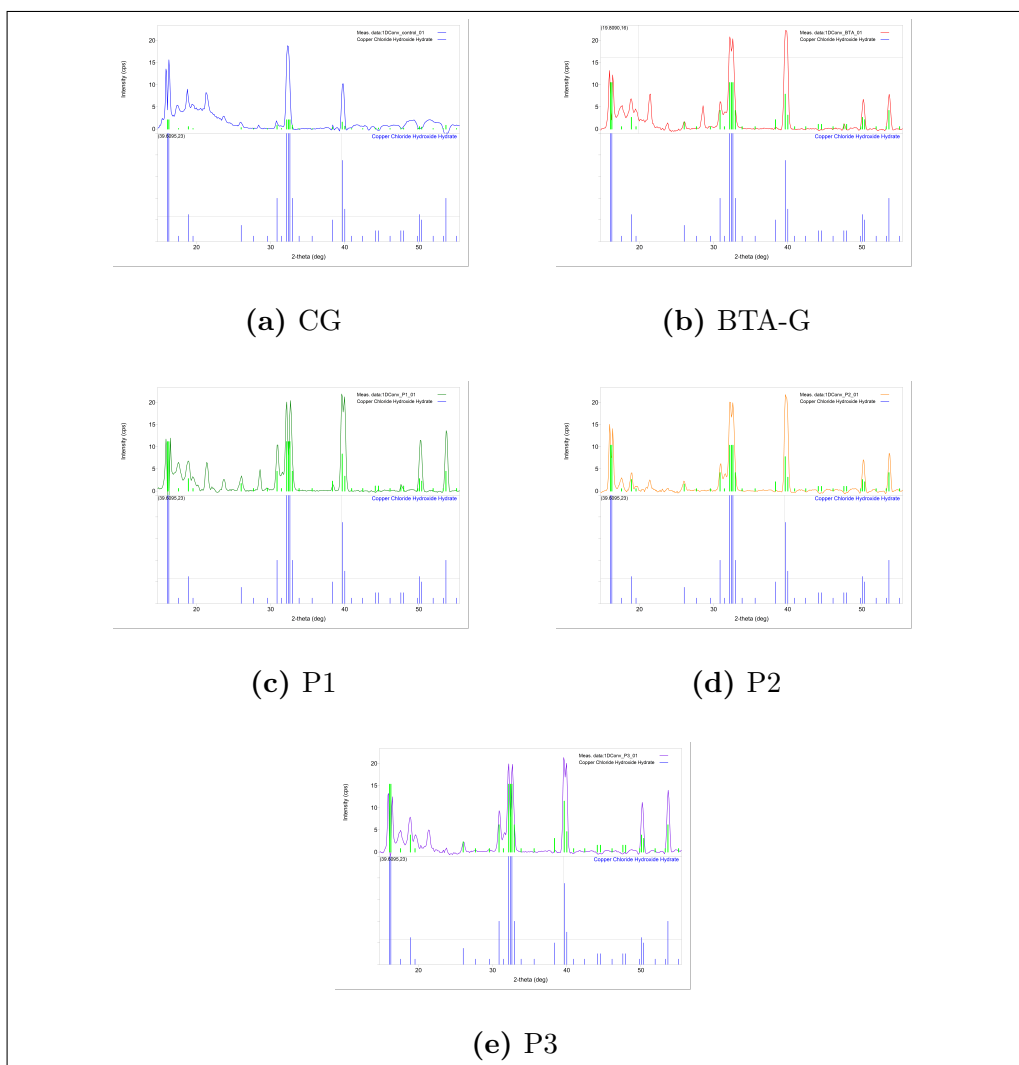


Figure 13: XRD diffractogram from each experimental group analyzed using Rigaku Corporation PDXL 2, version 2.8.4.0 software identified copper chloride hydroxide hydrate as the match from the spectral library.

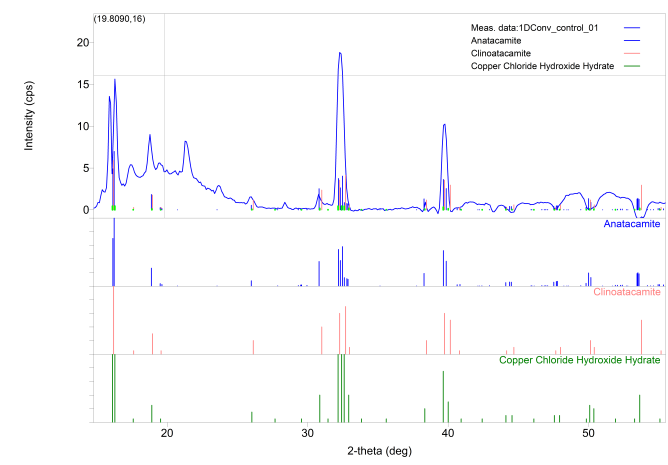


Figure 14: XRD diffractogram of CG analyzed with Rigaku Corporation PDXL 2, version 2.8.4.0 software suggests that "anatacomite" (now recognized as clinoatacamite) and clinoatacamite are possible matches in addition to the copper chloride hydroxide hydrate.

3.2 Observation of Surface Morphology

Many studies have used SEM coupled with energy dispersive X-ray spectroscopy (SEM/EDS) to investigate the capabilities of various corrosion inhibitors to adsorb to metal surfaces. Many of these studies investigated uncorroded coupons immersed in corrosive solutions with and without inhibitors, and both natural (Dahmani et al., 2021; Gao et al., 2020) and synthetic (Haruna et al., 2019; Ling et al., 1995) inhibitors have been investigated. These studies are often in the context of metal to be used for industrial purposes. Although there are studies using SEM (Abu-Baker et al., 2013) or SEM/EDS (Golfomitsou & Merkel, 2004) to investigate synthetic inhibitor adsorption onto pre-corroded surfaces, there is a lack of published research investigating the adsorption of natural inhibitors to pre-corroded surfaces.

All studies referenced above note that the surface topography of the treated coupons differs compared to untreated coupons. For example, in the case of uncorroded coupons, less pitting and unevenness of the surface was observed after exposure to corrosive solution with inhibitor than after exposure to corrosive solution without inhibitor (Dahmani et al., 2021,

p. 5; Gao et al., 2020, pp. 7-8). In the case of pre-corroded coupons, researchers observed that BTA forms a thin film that conforms to the morphology of the copper crystal structure (Golfomitsou & Merkel, 2004, p. 356). The studies that employ EDS observe decreases in the weight percent (Wt.%) of the metal and an increase in the Wt.% of oxygen and carbon (Dahmani et al., 2021, p. 6, Golfomitsou and Merkel, 2004, p. 358. The decrease in Wt.% of the metal and increase in Wt.% of O and C was attributed to the thickness of the adsorbed film, and thus, was taken as evidence that the inhibitor successfully adsorbs to the metal (uncorroded or corroded) surface.

Resource and time constraints prevented the use of EDS alongside SEM in this study. SEM was employed to qualitatively observe differences between the topography of one CG coupon with one coupon from each of the treated groups as outlined in 2.5.

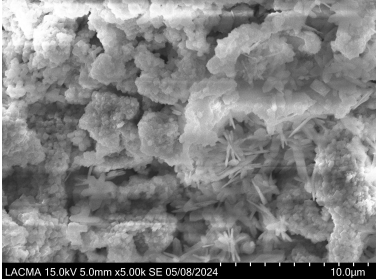
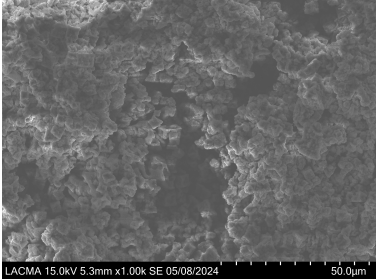
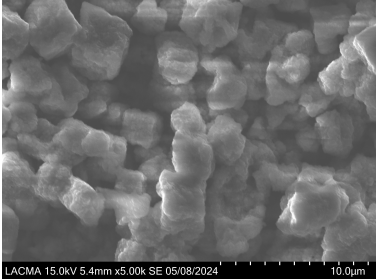
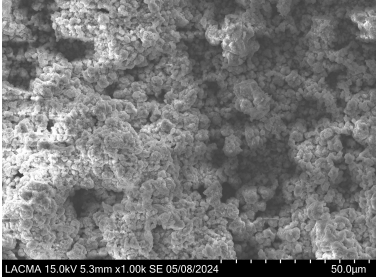
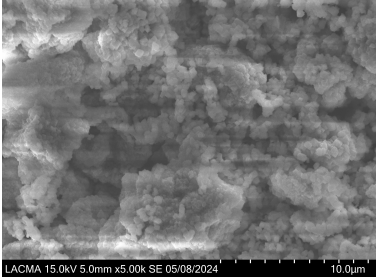
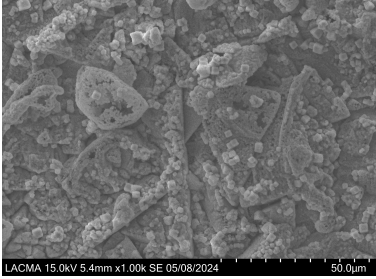
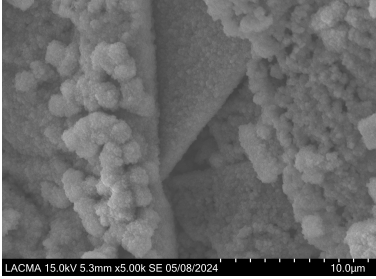
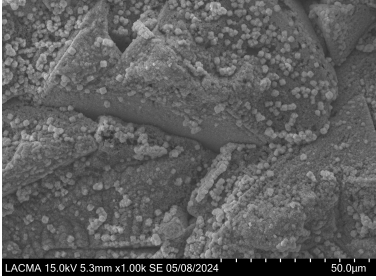
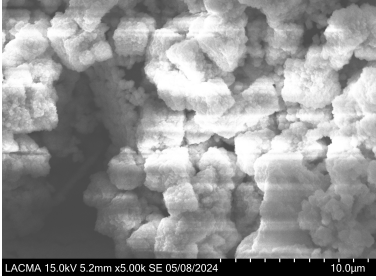
3.2.1 SEM

Two of the SEM micrograph images, one at x1000 magnification and the other at x5000, from each of the experimental groups is shown in Table 4.

As discussed in Section 1, the polymorphs of bronze disease take on orthorhombic, rhombohedral, or monoclinic crystalline structures, all of which would appear as cuboids with vertices at varying angles (Callister Jr & Rethwisch, 2020). Because of this, and because clinoatacamite and other copper chloride hydroxides were confirmed with Raman and XRD, the cuboid structures seen in all of the micrographs can likely be attributed to bronze disease. Furthermore, some of the cuboids could be attributed to cuprite if cuprite is present as a minor corrosion product that not detected by XRD and Raman (Scott, 2000).

The needle-like crystals visible in the two CG micrographs shown in Table 4 were present in all CG micrographs and were not present in any of the experimental group micrographs. Needle-like corrosion product on copper has been attributed to brochantite ($\text{Cu}_4\text{SO}_4(\text{OH})_6$) (Kwon & Cho, 2023), but brochantite was not detected, nor is a sulfur corrosion product expected, on the pre-corroded coupons prepared in this study. Although EDS would be

Table 4: x1000 and x5000 magnification SEM micrographs for each experimental group.

Experimental Group	x1000	x5000
CG		
BTA-G		
P1		
P2		
P3		

required for definitive evidence of adsorption of the corrosion inhibitors to the surface, this visual difference between the CG and the experimental groups suggests that some surface changes occurs because of the inhibitors.

3.3 Determining Inhibitor Efficacy

Varvara et al. (2017) report the efficacy of propolis as a corrosion inhibitor on uncorroded coupons immersed in a corrosive solution of Na_2SO_4 to be up to 95% using electrochemical methods. As discussed in Section 2.6, efficacy was not investigated with electrochemical methods in this study, but rather weight change experiments were conducted over a period of five weeks.

3.3.1 Weight Change

The results of the weight change experiments are shown in the graphs in Figure 15. Figure 15a shows that the relationship of weight change and time is logarithmic. The data has been manipulated by taking the logarithm of the elapsed time in Figure 15b to linearly show the relationship between weight change and time.

The weight changes reported in Figure 15 are presented as a percentage of the original coupon weight (%WC). Since the coupons were cut manually, the size of the individual coupons was variable. It was therefore important to account for this discrepancy when calculating the rate of change. As outlined in Section 2.6, there were three coupons being aged for each experimental group. The trendlines in Figure 15 were created by averaging the %WC of the three coupons, and error bars showing the minimum and maximum %WC from among the three coupons are included to show the variability.

It is visually apparent that there is no difference in the rate of change of P1, P2, or P3 compared with CG while there is a decreased rate of weight change for BTA-G when compared with CG. The inhibitor efficiency calculated using the equation presented in Section 2.6 is approximately 0% for Propolis 1, Propolis 2, and Propolis 3, and approximately 50%

for BTA.

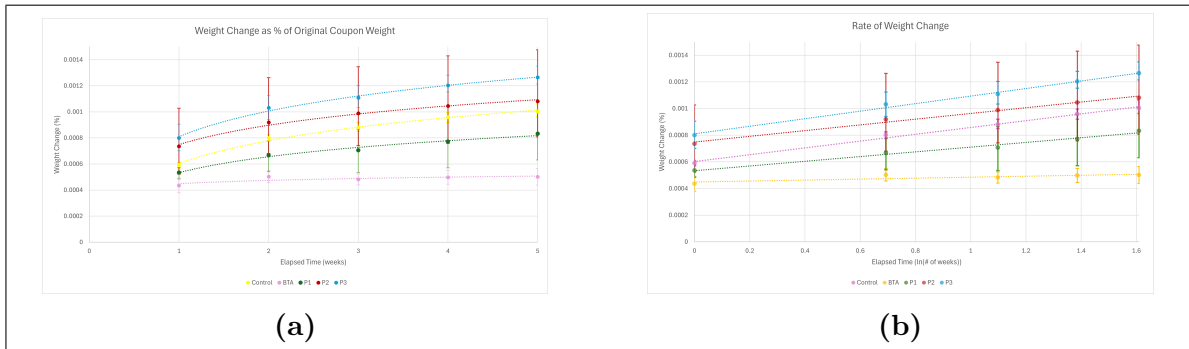


Figure 15: Graphs showing the relationship between weight change and time of exposure to the artificial aging environment, showing a) the logarithmic relationship between %WC over a 5 week period of time and b) %WC expressed linearly by reporting the y-axis as the logarithm of elapsed time such that the rate of change can be assessed.

4 Discussion

4.1 Inhibitor Efficiency

The IE of the propolis reported in Section 3.3.1 does not definitively indicate that propolis is not an effective corrosion inhibitor for corroded bronze artifacts because there is reasonable evidence within the literature to, in hindsight, hypothesize that the 100 ppm concentration used might have been too low. The concentration of the three propolis inhibitor solutions (100 ppm) was quite low compared to the concentration of BTA (3% which is equivalent to 30000 ppm). As discussed in Section 2.2.3, the decision to use 100 ppm as the concentration of propolis was based off of methods detailed in papers investigating natural corrosion inhibitors for copper. In general, the concentrations of experimental natural inhibitors have been between 20-200 ppm. For some natural inhibitors, IE was shown to increase with increasing concentration of natural inhibitors (González-Parra & Di Turo, 2024). Propolis, however, was shown by Varvara et al. (2017, p. 1104) to be less effective at 250 ppm than 100 ppm. Additionally, Elshahawi et al. (2022, p. 872) found 30 ppm to be the most effective on

uncorroded coupons and, resultingly, treated archaeological bronzes with 30 ppm. Because of this, 100 ppm was used instead of testing a range of inhibitors or matching the 3% of the BTA inhibitor solution.

In hindsight, this decision was inherently flawed. As discussed in the Introduction, most published experiments are on uncorroded coupons being immersed in corrosive solutions with and without inhibitor, and inhibitors are expected to act differently on corroded surfaces than on an uncorroded surface. Though researchers investigating jatropa used the same inhibitor concentration on archaeological artifacts as the concentration demonstrating the highest efficiency during their tests on uncorroded coupons, as discussed in Section 1.4, they ultimately did not investigate the IE on the treated archaeological bronzes (Elshahawi et al., 2022). Additionally, BTA used on uncorroded metals in industrial settings is at a lower concentration than the 3% which is standard to use on copper alloys in conservation. On uncorroded metals in industrial settings, BTA is used at a concentration of 0.1M, or approximately 1200 ppm (Bokati & Dehghanian, 2018).

Experiments in the future should first test a range of concentrations, perhaps 0.5%, 1%, 2%, and 3%, of one source of propolis. If a higher concentration demonstrates high IE, then the methodology of the weight change experiments presented in this paper could be repeated using that determined concentration. Pepper and ginger extracts could be investigated in this manner as well.

Future experiments which incorporate black pepper and ginger should note that the volume of ginger and pepper powder required to achieve these higher concentrations will be much greater than that of propolis when using ethanol as the solvent for extraction. When the inhibitor solutions were made, it was noted that the solids remaining after extraction were substantial. It is possible that water could be used for extraction of pepper and ginger in future experiments.

4.2 Proposed Future Analyses

Slight changes could be made to the methodology of analytical investigation in future studies for higher quality results. Raman and XRD could still be used as complimentary techniques to confirm the corrosion products formed in future experiments; however, the samples to be analyzed with XRD should be ground and stored in Eppendorf tubes in future experiments. A larger volume of sample could be used for XRD as well. Determination of inhibitor film adsorption could be done by coupling EDS analysis with SEM in future experiments.

Future experiments could also undertake additional analysis of the propolis. Chromatography could be used to identify the major components of each propolis source. This, however, would be a high-cost undertaking as having standards is necessary for component identification (Varvara et al., 2017).

Change in color of corrosion products before and after application of inhibitor should be assessed in future experiments, qualitatively and/or quantitatively. Color change was only nominally visually observed, if at all, with application of 100 ppm propolis for all three propolis, but more significant color change might be observed if higher concentrations of propolis are required to achieve acceptable IE. Many studies have qualitatively assessed color change when an inhibitor is applied to pre-corroded coupons through visual observation (Abu-Baker et al., 2013; Conway et al., 2022; Elshahawi et al., 2022). A colorimeter could be used to quantitatively assess the color change, using the color change observed with the application of BTA as the standard of what is an acceptable degree of color change.

Pest activity should also be considered in future experiments. It will be important to determine whether the use of natural corrosion inhibitors attracts pests. A natural inhibitor film that attracts pests would significantly limit the applications of that inhibitor in cultural heritage since pest infestations in storage facilities are of utmost concern in conservation.

Lastly, efficacy over time should be considered in future experiments. It is known that retreatment with BTA is required after about five years (Gravgaard & van Lanschot, 2012).

A methodology based on methods outlined in the existing literature should be developed to monitor natural inhibitor film adsorption over several years.

5 Conclusion

Clinoatacamite, in addition to other possible copper chloride hydroxides, was found to be the primary corrosion product formed on the pre-corroded coupons prepared for this study. Visual differences were observed between the surface morphology of the control coupons compared with all treated groups, and future experiments could utilize SEM/EDS to more definitively confirm adsorption of propolis, black pepper, and ginger inhibitor films to surfaces afflicted with bronze disease. Despite the visual differences in the surfaces between control and treated groups observed with SEM, a three propolis did not demonstrate IE. This lack of IE could be due either to inhibitor inefficiency or to the use of inhibitor concentrations that were too low, a hypothesis should be tested in future studies.

In conclusion, this study establishes a framework for future investigations of propolis, black pepper, and ginger on artificially corroded coupons. A range of higher concentrations should be tested, and then the methods outlined here can be followed to assess corrosion products formed, film adsorption, and IE on pre-corroded coupons treated with natural inhibitor. Demonstrating efficacy of natural corrosion inhibitors that are easily accessible worldwide will allow the treatment of artifacts exhibiting bronze disease on remote archaeological sites to be safer for the user, safer for the environment, and more sustainable from economic and carbon footprint perspectives.

A Coupon and Inhibitor Preparation and Treatment Images

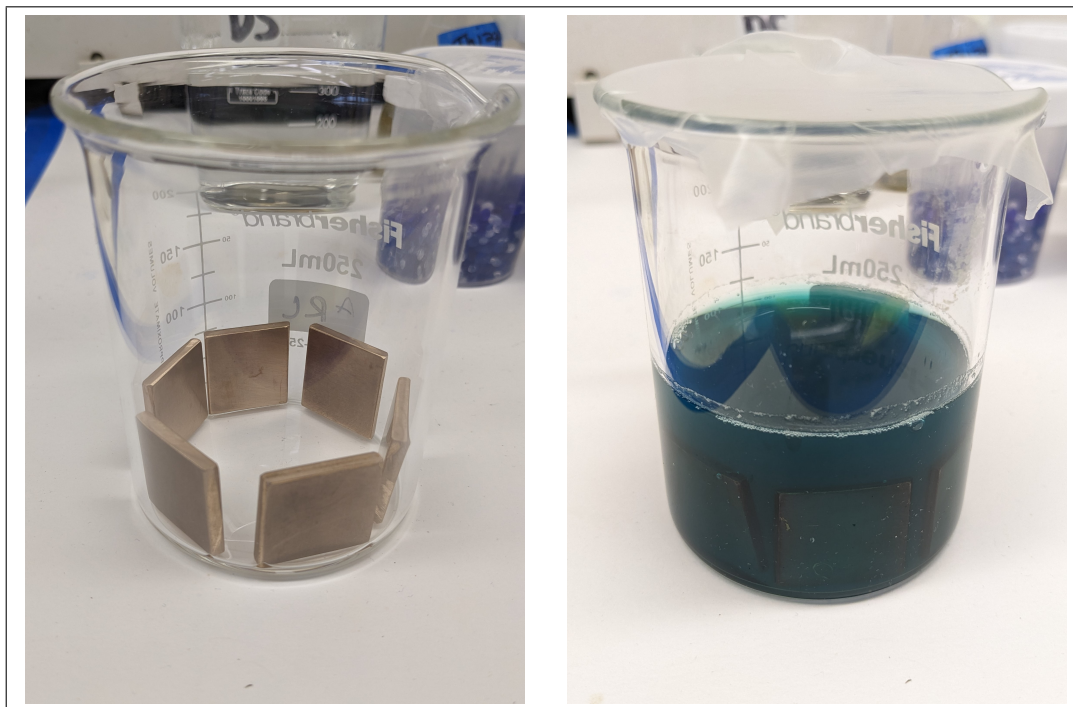


Figure A.16: Image detailing coupons propped against sidewall of beaker during immersion in CuCl_2 . The beaker was covered with Parafilm for the duration of immersion.

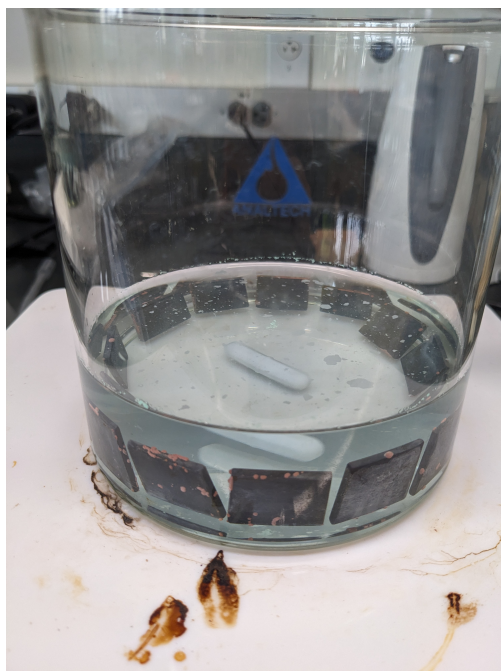


Figure A.17: Image detailing the rinsing step. Note that a stir bar was used to agitate the water and that, again, the coupons are propped against a the sidewall.

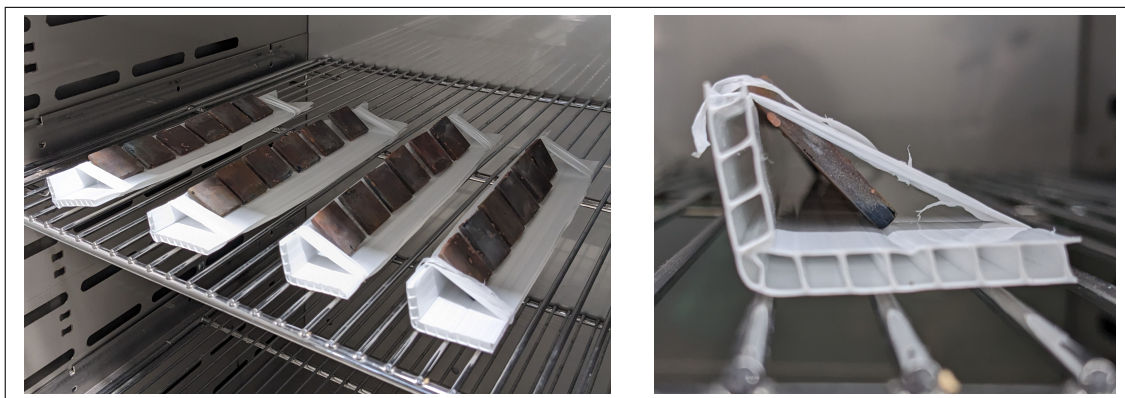


Figure A.18: Image detailing the stands the coupons were propped against during the corrosion process.

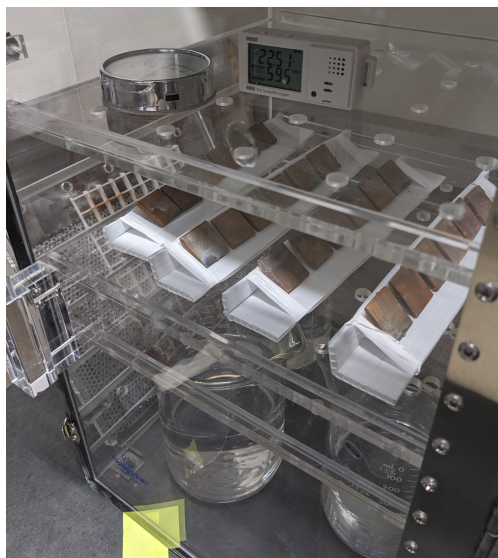


Figure A.19: Image detailing the coupons on their stands in the humidity chamber during the corrosion process.



Figure A.20: Image detailing the separation process of the hive scrapings to obtain the pure propolis used as Propolis 1.



Figure A.21: Image detailing 1 g of black pepper (top right), ginger (bottom right), P1 (top left), P2 (middle left), and P3 (bottom left).



Figure A.22: Image detailing the immersion of all the coupons in inhibitor solution. From left to right: CG coupons immersed in pure ethanol, BTA-G coupons immersed in 3% BTA, P1 coupons immersed in 100 ppm of propolis 1, P2 coupons immersed in 100 ppm of propolis 2, and P3 coupons immersed in 100 ppm of propolis 3.



Figure A.23: Image detailing the individual coupons stands used during the artificial aging during the weight change experiments.

B Table of Abbreviations

Abbreviation	Meaning
M	Moisture reservoir value
MGC	Mitsubishi Gas Chemical
BTA	Benzotriazole
IE	Inhibitor efficiency
DI	Deionized
CG	Control group
BTA-G	Benzotriazole treated group
P1	Propolis 1 treated group
P2	Propolis 2 treated group
P3	Propolis 3 treated group
S/N	Signal-to-noise ratio
XRD	X-ray diffraction spectroscopy
SEM	Scanning electron microscopy
rms	Root mean square
%WC	Percent weight change
EDS	Energy dispersive X-ray spectroscopy

Table B.5: A summary of the abbreviations used throughout this paper.

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