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Fifty-plus years of on-site metals conservation at Sardis: Correlating treatment efficacy and implementing new approaches

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Abstract
In the last sixty-one years, the Harvard-Cornell-led excavations at Sardis, Turkey, have produced over 5,000 copper-alloy and iron finds. Since their excavation, these finds have been stored in on-site depots, which provide only minimal buffer against seasonal fluctuations in relative humidity (RH). A condition survey conducted in 2016 and 2017 detected signs of chloride-related deterioration in roughly 40% of these finds. Conservation records since the 1960s document evolving stabilization treatment methods as new conservation research was put into practice. This paper describes a computational approach informed by network analysis that was used to correlate the history of copper-alloy stabilization treatments at Sardis with deterioration phenomena encountered during our survey. Our newly implemented approach to rehousing unstable metals in low-RH and/or anoxic Escal enclosures is discussed along with our justification for maintaining certain treatment protocols in light of our findings and procedural shifts.

INTRODUCTION

Since 1957, the Harvard-Cornell-led excavations at Sardis, Turkey, have unearthed over 5,000 copper-alloy and iron finds that have been stored on-site since excavation. Environmental data from the storage depots indicate that relative humidity (RH) often climbs above 50% in the spring and fall, and reaches between 80% and 100% in damp, winter months. A condition survey carried out during the 2016 and 2017 field seasons identified chloride-related deterioration in roughly 40% of these finds. Conservation records since the 1960s document a history of stabilization treatment methods that evolved over the years as new conservation research was put into practice. In this paper, we summarize treatment history and present our recent efforts to analyze historic and contemporary data using a computational approach to understand the effectiveness of benzotriazole (BTA) treatment and aqueous soaking on the stability of copper-alloy finds. Our project to rehouse all unstable archaeological metals at Sardis in low-RH and/or anoxic micro-enclosures is explained and our current treatment protocols are discussed in light of our findings.

HISTORY OF TREATMENT AT SARDIS

The documented history of conservation treatment at Sardis dates back to 1960. From the outset, various methods were employed to clean and stabilize copper-alloy finds, including soaking in citric or acetic acid, electrochemical reduction, and coating with Krylon spray (acrylic resin). Beginning in the mid-1960s, treatments aimed specifically at inhibiting recurring bronze disease involved localized excavation and spot treatment with silver oxide slurries and/or intensive soaking with sodium carbonate/sesquicarbonate solutions. The results of these treatments were often inconsistent, with objects frequently requiring retreatment over many subsequent seasons. In 1974 and 1975, tests were conducted to determine the effectiveness of the corrosion inhibitor BTA, and by the late 1970s the standard treatment of copper-alloy finds involved aqueous mechanical cleaning, “desalination” in distilled water, passivation with BTA, and coating with Incralac and, later, Paraloid B-44 to protect the passivation layer. Beginning in the 1990s, the “desalination” step involved soaking in deionized water changed daily until conductivity measurements read below 10 μS. Since 2010, copper-alloy and iron finds have been coated primarily with 7.5% Paraloid B-48N, which appears to have slightly superior aging characteristics than Paraloid B-44.[1] It is thought that these resins—

formulated to bond with metal surfaces—provide additional protection against the corrosion of metal artifacts.

CONDITION SURVEY AND VISUAL GLOSSARY

The ongoing instability of copper-alloy and iron finds excavated in seasons past necessitated a complete survey of all catalogued and uncatalogued metal finds stored on-site at Sardis. Prior to this survey, the collection had never been systematically condition checked or stabilized en masse, due to the sheer quantity of material and limited staffing. Over two seasons, 2,348 copper-alloy and 3,261 iron objects were surveyed. Each item's storage location, excavation metadata, lab treatment record number, and a brief condition assessment were recorded. The survey found that roughly 40% of all metals (37% of copper-alloy and 43% of iron finds) exhibited some sign of ongoing deterioration.[2] A photo-illustrated glossary was created to aid in standardizing the required vocabulary throughout the survey, which was conducted by a team of conservators with varying levels of experience in identifying metal corrosion phenomena.[3]

EFFICACY OF PAST TREATMENT

The data collected in the 2016 Metals Survey—together with lab records and computational analyses—were used to examine the efficacy of historic treatments and to find correlations. Preliminary analysis on copper-alloy finds targeted two questions: (1) Is the corrosion inhibitor BTA effective in stabilizing archaeological copper alloys? (2) Does soaking in water—a common procedure in the treatment of metal objects on archaeological sites despite the insolubility of nantokite[4]—contribute meaningfully to stabilizing objects? These questions were used to test and illustrate a method for preparing and examining data from the collection of previously treated archaeological objects stored on-site after treatment and to highlight trends relating treatment to stability in such a collection.

Our computational method uses the language of *networks* but is not formal network analysis (though it does utilize a Python library in common with that approach). This approach to treatment history draws influence from graphing and visualization techniques such as sequence comparison/similarity (i.e., pattern recognition, similar to those used in DNA analysis and to predict stock market trends). The method allows examination of conservation treatments in relation to the interim (between-treatment) stability and current stability of objects. The visualization of an object's treatment history as a path leading to current stability or instability—with *nodes* of individual treatment steps and *edges* delineating chronology, colored by interim stability (Figure 1)—can be manipulated to highlight the introduction of specific treatment steps and their distribution with regard to current stability.

The catalogued information on copper-alloy finds collected in the 2016–2017 Metals Survey was used as the foundation for the dataset of 852 objects underlying this project. Before use, the data were cleaned by translating treatment information from database entries or handwritten logbooks into queriable *treatment_steps* that represented the object's treatment history. This list was checked against condition information recorded throughout the 2016–2017 Metals Survey, and these proxy data were used to augment the list as necessary, resulting in a list of individual treatment steps per treatment (the set of treatment steps performed in one season) per object. Although this process was inherently subjective, each unique step was systematically recorded from the perspective of the object, not the conservator's intention. For example, from an object's perspective, soaking in deionized water to soften burial accretions is the same as soaking in deionized water to remove chlorides. In both cases, the treatment step is listed as *aqueous_soak*. In order to preserve the treatment history chronology of each object, each step was given a unique ID number (*sardismetalproject_id*) and a column listing the ID number of the next treatment step.[5] The cleaned, structured spreadsheet was pulled into a Jupyter notebook as a dataframe.[6]

In the visualization shown in Figure 1, treatment paths are listed from top to bottom in increasing chronological order based on the year of excavation and first treatment. The left central node is stable, and the right central node is unstable. Edges are colored by the attribute of the target node: if it is unstable, it is red; if it is stable, green.[7]

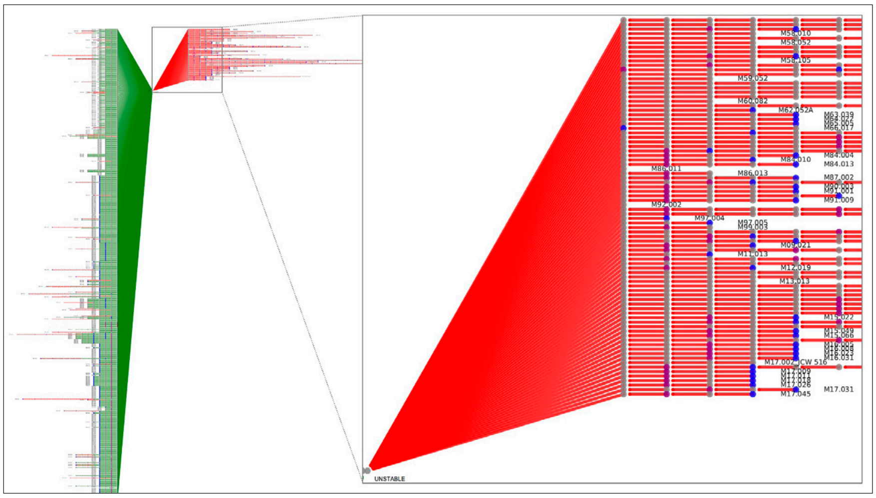

Figure 1. Overall image (left) and detail (right) of the interactive visualization, showing the treatment histories of the catalogued copper-alloy finds at Sardis. Green paths indicate interim stability, red paths interim instability, purple dots a BTA treatment step, and blue dots the use of water in a treatment step. (This image is available at https://sardis-images.s3.amazonaws.com/pdf/cu-treatment-history-visualisation.pdf as a digital file so that the zoom feature is usable, rendering the figure legible)

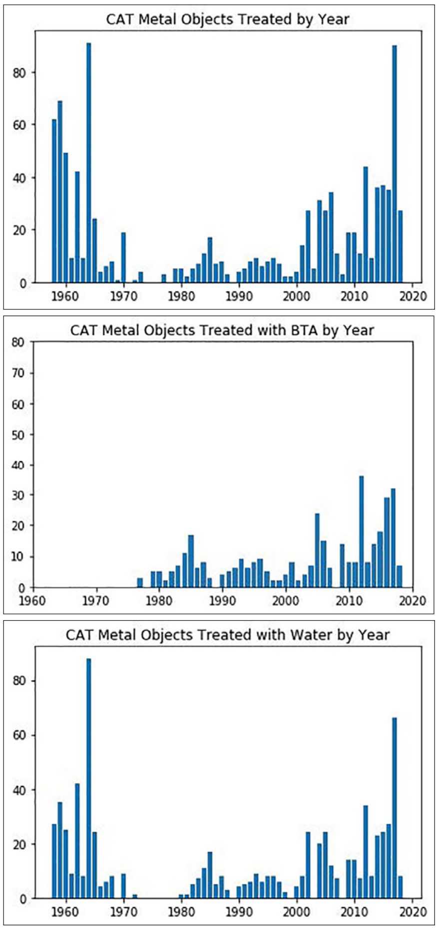

Figure 2. Histograms indicating instances per year of (a) any treatment, (b) any BTA treatment, and (c) any aqueous treatment of an object with a unique catalogue number

The network map behind Figure 1 can also be examined using principles of *set inclusion* (Figure 2) and *substring similarity* (Figure 3). Here, treatment histories are the sets whereas the substring similarity refers to ordered treatment steps. This approach allows questions such as: How many unique catalogued objects received a BTA treatment? How many of those objects have an interim stability of unstable after any BTA treatment? How many of those objects are currently stable? Furthermore, edges and nodes may be recolored accordingly to illustrate data trends in other versions of the visualization shown in Figure 1.

History and questions: BTA treatment

BTA is a corrosion inhibitor for copper alloys that is often used to treat bronze disease. Theoretically, when an object is immersed in a BTA solution, a complex between copper and BTA forms as a passive surface layer that is insoluble in aqueous and organic solutions and nonreactive with the external environment (Sease 1978, 80–81; Scott 2002, 379–80). BTA is said to be adsorbed onto the cuprite and complexed onto the nantokite, suppressing anodic and cathodic reactions and forming a physical barrier to further corrosion (Sease 1978, 76). Whether this desirable theoretical effect works in practice is unclear. BTA is applied in multiple ways, presumably with varying degrees of effectiveness. A 2016 survey of current practice in the treatment of archaeological copper alloys across more than fifty archaeological sites globally indicated that BTA was applied using a wide range of techniques, including immersion (ranging from "quick dip" to several weeks), brush or dropper application, under vacuum or without, in concentrations varying from 3% to 10%, and using ethanol, acetone, and/or water as a solvent (Serotta et al. 2016).

Figures 2a and 2b show that since BTA came into use at Sardis in the late 1970s, it has been used to treat most of the excavated copper-alloy finds. At Sardis, BTA was applied to objects in four ways: immersion under ambient pressure conditions (i.e., dipping), soaking under ambient pressure conditions (usually for 1 hour, sometimes longer), soaking under vacuum (usually for 12 hours, sometimes 24), and localized spot treatment with a brush or dropper. Figures 3a and 3b suggest that objects treated with BTA maintain a stability ratio similar to those treated by any method in general.

Our analysis found that 73.4% of objects in the dataset are currently stable, and 82.7% of these currently stable objects were treated with a BTA step. A distinct improvement in the stability of copper alloys after BTA was introduced into standard treatment, in the mid-1970s, is also visible in the combined catalogued and numbered object data graphed in Figures 4a and 4b. Given that the use of acidic and alkaline aqueous treatments began to decline in the 1980s, it is difficult to establish a direct causal link between BTA usage and improved object stability; however, these findings do lend support to that interpretation.

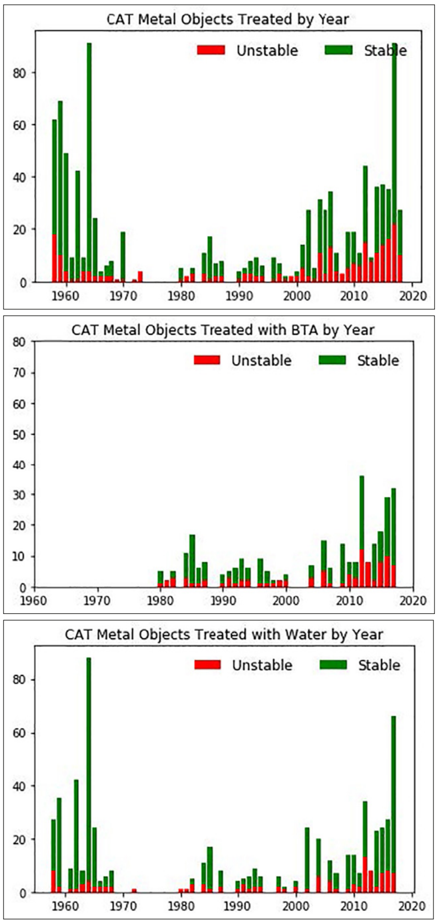

Figure 3. Histograms indicating instances per year of (a) any treatment, (b) any BTA treatment, and (c) any aqueous treatment of an object with a unique catalogue number, where green indicates those that end in a stable condition, and red those that end in an unstable condition

History and questions: Aqueous treatment

Water may come into contact with an object during a number of distinct treatment stages: mechanical cleaning, alkaline aqueous treatment (e.g., Rochelle salts and sodium carbonate/sesquicarbonate), and/or post-cleaning soaking. Figures 2a and 2c show that water has been used in treatments throughout the history of conservation at Sardis. The survey conducted by Serotta et al. (2016) indicates that the use of water in on-site treatments is declining: respondents generally avoid cleaning with water, though some use an ethanol-deionized water combination. Cleaning with acidic or alkaline solutions has also fallen out of fashion, but respondents who still do so stated that they soak metal objects in water after acidic or alkaline treatments to remove residues and neutralize the surface. Soaking in deionized water to remove chlorides and mitigate bronze disease also seems to have been more common in the past.

Given that nantokite is insoluble in water, the effectiveness of soaking objects in deionized water to mitigate bronze disease seems doubtful. Figures 2a and 2c indicate that objects treated with water maintain a stability ratio similar to that of objects treated (by any method) overall. It was also found that 90.5% of currently stable objects (648 out of 716) had been treated with an aqueous step. This percentage is higher than the 73.4% of objects that are currently stable (847 out of 1153). This is compelling though possibly misleading. Since water has been used in treatments since the beginning of conservation at Sardis, there are few objects treated with the general goal of stabilization that have not been treated with water. That said, the data do not appear to support the argument that soaking "dry" objects in water contributes to instability.

Figure 4. (a) Percentage ratio and (b) absolute ratio of currently stable (green):unstable (red) catalogued (CAT) and numbered (NUM) copper-alloy finds excavated each year at Sardis

Figure 5. Example of a low-RH Escal enclosure housing a copper-alloy find with active bronze disease

General interpretations

Based on our initial assessment of the data, a distinct improvement was observed in the stability of copper alloys after BTA was introduced into the standard treatment of metals at Sardis in the mid-1970s. Whether aqueous treatment contributed to the stability of copper alloys remains less clear, but overall it does not appear to have had a negative impact. There are, of course, many other variables at play here—including burial environment, retreatment history, storage environment, and survey subjectivity—that complicate interpretation of the data collected. Much of this information has been irretrievably lost (e.g., burial environment chemistry) and requires query by proxy (e.g., trench/year information) or has never been collected (e.g., alloy composition) and would require extensive analysis.

ESCAL REHOUSING PROJECT

Critical assessment of past treatments is important, but not at the expense of current stability and preservation efforts. Existing standard treatment protocols were clearly not enough to stabilize freshly excavated metals: soaking in deionized water is ineffective in removing nantokite from copper-alloy objects, and while BTA passivation and coating appeared to correlate with increased stability, these preventive measures are inadequate in protecting every object. For the thousands of unstable metal artifacts in varying states of deterioration, more interventive aqueous chloride extraction methods—including sodium carbonate/sesquicarbonate soaking of copper alloys and deoxygenated alkaline soaking of iron finds—are not practical on-site due to the time involved and associated material and labor costs.

Following on the research conducted by McPhail et al. (2003), Brown (2010), and Paterakis and Mariano (2013), as well as our own tests storing objects in vapor barrier film enclosures over several years, it was concluded that the most cost-effective and efficient way to halt chloride-induced deterioration across the entire collection of metal finds would be through a systematic rehousing of every unstable find in low-RH or anoxic Escal enclosures. For the vast majority of iron and copper-alloy objects, sachets of desiccated, regular-density silica gel were sufficient to create low-RH internal environments (i.e., < 10% RH) (Figure 5) capable of inhibiting chloride-induced deterioration. For metal finds with organic remains that cannot be stored at low RH (e.g., textile, wood, or bone), an oxygen scavenger system (i.e., RP System or Ageless) was included. Depending on the organic material type and its fragility, conditioned silica gel was added to ensure that the RH within the enclosure did not fluctuate with temperature fluctuation. During the 2017 and 2018 seasons, a total of 2,310 metal artifacts were rehoused in these Escal enclosures.

Most literature and anecdotal reports indicate that a properly sealed Escal enclosure can maintain a low-RH environment for at least ten years. Although a small percentage of enclosures fail due to human error in sealing, this becomes obvious through color-changing indicators within a few weeks of sealing and can be easily remedied by resealing. While these enclosures may require maintenance every decade, the benefits of this approach cannot be overemphasized.

REVISITING STANDARD TREATMENT PROTOCOLS

The implementation of our Escal Protocol marks significant progress for the conservation of metal finds at Sardis, effectively pausing the deterioration of all rehoused metal finds. It is now standard procedure that all newly excavated and newly treated metals exhibiting signs of ongoing corrosion after one year are rehoused in low-RH or anoxic enclosures. There are, nevertheless, lingering questions about how the standard treatment of metals should be optimized in light of this procedural shift. Although conservators at Kaman-Kalehöyük have abandoned traditional treatment methods in favor of housing all metal finds in individual, anoxic Escal enclosures, our standard treatment procedures for metal finds are being maintained and Escal enclosures are used only for objects known to be unstable.

BTA passivation

While our survey indicated that BTA passivation is not totally effective at inhibiting deterioration in oxygen-rich, humid storage conditions, a possible correlation was observed between its introduction at Sardis and an overall improved stability for copper alloys. It is difficult to ascertain whether objects marked stable after one year in the depot are in fact chloride-contaminated copper alloys that have been successfully passivated by BTA, or simply uncontaminated objects that would have been stable anyway. Several studies suggest that the low pH of cuprous chloride can inhibit the growth of BTA films (Scott 2002, 379). Its use on definitively unstable objects with active bronze disease may not be very effective, and alternatives, such as 2-amino-5-mercapto-1,3,4-thiadiazole (AMT), may be more effective. Research by Golfomitsou and Merkel (2004) found that immersion under vacuum for 3 hours in a lower concentration of 0.1 M BTA + 0.01 M AMT in either ethanol or deionized water performs better than the higher concentration of 3% w/v BTA in ethanol used at Sardis. Currently, the step of immersion in 3% BTA under vacuum for 12 hours is being maintained for all copper alloys; however, our use of Escal enclosures effectively obviates the immediate need for this step.

Pre- and post-cleaning soaking in deionized water

As noted above, soaking in successive changes of deionized water was part of the standard treatment protocol for copper alloys (excluding the small fraction containing remains of wood, textile, bone, or other organic or fragile, water-sensitive materials) employed since the 1990s. Given that soaking in deionized water is ineffective in solubilizing cuprous chloride, we questioned whether to continue this practice. There is a clear risk associated with keeping untreated, chloride-contaminated metals exposed to oxygen-rich, humid conditions post-excavation. In the case of freshly excavated copper-alloy and iron finds, the risk of corrosion increases exponentially with exposure to air, compared with burial or immersion in distilled or deionized water; the amount of dissolved oxygen in deionized water (~7 ppm) is negligible compared to atmospheric concentrations (~21% O_2, or 210,000 ppm).[8] Thus, at Sardis, metals are kept covered with damp sediment following excavation and brought to the lab for immediate treatment. Pre- and post-cleaning soaking in deionized water has been maintained as standard procedure (after checking for traces of organic material), but not for the purposes of chloride extraction. Soaking helps to soften compact soil and burial accretions prior to further cleaning (reducing the amount of mechanical cleaning required and hygroscopic material remaining on the surface of objects post-treatment), and it effectively serves as a temporary, low-oxygen storage environment prior to and immediately following cleaning.

CONCLUSION

This paper presents an overview of the treatment protocols for copper-alloy artifacts at Sardis implemented from the 1950s until today. Following a systematic condition survey of the collection, we explored how network-inspired computational analysis may be used to discover correlations among treatment materials and stability for a large archaeological dataset. The approach holds great potential for investigating treatment efficacy, but further research is required to develop this method as a predictive tool. We are currently investigating how such an approach might be applied to investigate the effects of coating, iron treatment methods, and other variables such as find location on object stability. This paper explains our rationale for rehousing unstable archaeological metals in low-RH and/or anoxic micro-enclosures and considers both the efficacy and the utility of maintaining traditional treatment protocols in light of our findings and the procedural shifts at Sardis.

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NOTES

[1] Both Paraloid B-44 and Paraloid B-48N are formulated to bond to and coat metals. Paraloid B-48N has greater tensile strength and is more flexible than Paraloid B-44 (Down et al. 1996, 33). Paraloid B-44 has a slightly higher glass transition temperature (60°C) than Paraloid B-48N (50°C); however, Paraloid B-48N is less prone to yellowing (i.e., cross-linking) than Paraloid B-44 (Down et al. 1996, 37) and yields a slightly thicker coating at concentrations of 7.5%.

[2] Of the 1,278 catalogued iron and copper-alloy objects surveyed, 353 (28%) were unstable; 1,924 (44%) of the 4,331 uncatalogued numbered objects surveyed were unstable.

[3] This visual glossary is available to the public at https://sardis-images.s3.amazonaws.com/pdf/visual-glossary.pdf

[4] Nantokite, the corrosion product responsible for bronze disease, is non-water-soluble; thus, it is unknown what soaking removes (Scott 2002, 123).

[5] A number of assumptions were made in constructing the dataset. It was assumed that each catalogued object was treated at least once with the standard treatment in its excavation year.

[6] The spreadsheet/dataframe and notebook can be downloaded from https://sardis-images.s3.amazonaws.com/zip/jupyter.zip

[7] Nodes are colored by an easily manipulatable dataframe. Specific treatment steps can be colored by adding RGB values into the unique treatment dataframe (unique_treatment_df) and running the "Building and Graphing Path Networks" portion of the associated Jupyter notebook. Currently, red nodes indicate a BTA treatment step and blue nodes an aqueous treatment step.

[8] Ian MacLeod succinctly articulated: "The solubility of dissolved oxygen in distilled water is around 7 mg/litre or ppm and in the moist air, as the object would be drying, you have 21 weight percent oxygen or 210,000 ppm, so it stands to reason that if you are slowly drying out the objects in the air, you are potentially doing them more harm than storing them in deionised water, if you are looking at the impact of oxidation" (MacLeod, pers. comm., 8 July 2019).

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MATERIALS LIST

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Escal™
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