

CORROSION STUDY OF COPPER-BASED MUSEUM OBJECTS FOR LONG TERM PRESERVATION

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Abstract

The proper characterization and diagnosis of corrosion behaviour is key for devising effective conservation measures for their long term stabilization. In this study the nature and causes of corrosion of a collection of copper based objects that are exhibited at the Museum of Jordanian Heritage was performed. The objects were excavated from two archaeological sites in Jordan: Queen Alia International Airport (QAIA) and Tell- es-Sa'idiyeh (TS). An integrated approach that combines the use of OM, SEM-EDX, XRD, and AAS was used to determine the nature and extent of corrosion, chemical composition of the objects and their manufacturing techniques. The physico-chemical parameters of the burial soils were also determined. The results revealed the complex multi-layered structure of the alteration layers and show the presence of different types of copper chlorides and their role in active corrosion of some of the objects. The results prove the strong correlation between the corrosivity of the burial environments and the post excavation corrosion behaviour of the objects. Objects excavated from burial environments of high chloride content suffer from severe active corrosion while objects excavated from soils of low chloride content are relatively stable. The study proposes the conservation measures that need to be implemented in order to ensure the long term stabilization of the objects.

Keywords: *Copper based objects; Corrosion, Bronze disease, Burial environment, Long term preservation.*

Introduction

Archaeological objects exhibited in museums are affected by two different environments: long-term burial and display [1-3]. Identification of environmental conditions and their influence on these objects allow museums to make appropriate decisions for their long-term stabilization and protection [4].

A major role in the history of metals has been occupied by copper and its alloys. Copper-based objects are exhibited in almost every archaeological museum due to their aesthetic, historical, technological, and scientific values. Museums should provide the appropriate environmental conditions to ensure long term stability of these objects.

There are many factors that control the nature and extent of the corrosion of copper-based artefacts. Some factors are related to the metallurgy of the artefacts such as their composition and manufacture. Other factors are related to the duration and physical and

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chemical characteristics of their burial and exhibition environments. The corrosion includes numerous conversions, including the modification of the alloy chemical composition and the alteration of the form and appearance of the artefacts [5-11].

Many research studies [9-17] conducted on copper-based objects have shown that the long-term corrosion behaviour of these objects are strongly influenced by the nature of their burial environments. Soil properties have the most significant role in the development of corrosion on copper-based artefacts. The different parameters of soil like chemical composition, soil type, pH and electrical resistivity and hydrological factors, significantly influence the corrosion process.

The Museum of Jordanian Heritage exhibits a large number of copper-based objects that were excavated from different archaeological sites in Jordan. The Museum monitoring report indicates variation in the corrosion behaviour of a collection of copper-based objects that are exhibited in one of the show cases of the museum. The same showcase exhibits copper-based objects that were excavated from two different sites in Jordan; *Queen Alia International Airport (QAIA)* and *Tell- ES-SA'idiyeh (TS)*. Although all the objects are displayed in the same showcase under similar environmental conditions, it has been noticed that the TS artefacts suffer badly from severe active corrosion while the objects that came from QAIA are fairly stable and have developed uniform patina.

The aim of this research is to investigate the notable difference in the corrosion behaviour of a collection of copper-based objects in order to identify the factors that govern their corrosion behaviour. All possible factors that may cause this difference in corrosion behaviour will be investigated including composition, fabrication processes and burial environments. The results of these investigations will be used to devise the proper conservation measures that can ensure the long-term stability of these artefacts.

Experimental

Materials

A representative sample of six copper-based objects that came from QAIA and two that came from TS were selected for the purpose of this study. All the selected objects are exhibited in the same showcase at the Museum of Jordanian Heritage. Figure 1 presents a brief description of the objects.

Archaeological Sites

The selected objects were excavated from two archaeological sites in Jordan: *Queen Alia International Airport (QAIA)* and *Tell-ES-SA'idiyeh (TS)* (Fig. 2). QAIA lies some 25km south of Amman, 22km east of Madaba, in a broad level plain. The site is on the edge of Jordan's eastern desert, an area of pastoral grazing. Objects 1-6 were excavated from a 3rd Century AD Cemetery [18].

The (TS) site, lies at the heart of the central Jordan Valley 15km to the north of the Dead Sea. Excavations have revealed that the site was populated from the Early Bronze Age up to the Early Islamic period of the 7th Century AD. TS were a large and prosperous city, with well-constructed architecture and evidence for highly developed municipal planning. Objects 7 and 8 were excavated from the Early Bronze age industrial area of the site [19].



Fig. 1. A brief description of the characteristics of the bronze artifacts studied



Fig. 2. The location of the T.S and QAIA sites (STEPMAP)

Methods

The characterization of the developed corrosion requires integrated analytical methods at different observation scales. A combination of analytical techniques were employed to study the nature and composition of the corrosion products formed on the objects.

The microstructural identification and classification of the corrosion layers on objects were done by Optical Microscopy (OM), Scanning Electron Microscopy (SEM) coupled with energy dispersive X-ray (EDS) and X-ray diffraction (XRD). To study the morphology, nature and extent of corrosion of the selected copper objects, cross-sections of corrosion fragments and samples of the metal core were prepared after embedding in epoxy resin for 24 hours; then sectioned using a diamond saw [20]. The cross-sections were polished with silicon carbide papers till 1200 grit, and the final polishing step was performed with diamond pastes up to 1/4 μ m to produce mirror-like surfaces. The morphology and the stratigraphy of the sectioned corrosions were acquired by a multi-focus (OM) Leica MZ FLIII microscope. The structural documentation of the corrosion products of the crystalline phases were defined by a Siemens 5000 X-ray powder diffractometer using a Ni-filtered Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$). Angular values in the range between 5° and 60° in an additive mode, a step size of 0.05° and a sampling time of 2s were used as experimental parameters.

The morphology of the surface and the elemental composition were examined by a Cambridge 360 SEM, equipped with a LaB6 filament, a four-sector back scattered electron detector and an Energy-Dispersive Spectrometer (EDS Link Analytical).

The chemical composition of the objects were determined by Atomic absorption spectrometry (AAS). Samples preparation were performed after *M.J. Hughes et al* [21]. About 10-25mg of the metal samples were carefully taken by a mini drill and then dissolved in 25mL of aqua regia (1 Vol. of HNO₃ and 3Vol. of conc. HCl). The solutions were heated to 60°C to assure complete dissolving. Finally, the dissolved samples were transferred to a 25mL Erlenmeyer flask and distilled water was added. The AAS analysis was carried out using Perkin-Elmer Atomic Absorption Spectrometer model SP9. The elemental concentrations were measured in parts per million (ppm) and then converted into weight percentages.

To assess the corrosivity of burial environments four soil samples from the archaeological context of the objects of Tell-ES-SA'idiyeh [19] and two samples from the archaeological context of the objects of Queen Alia International Airport were taken [22]. Soil particle size distribution was measured by the sieve and hydrometer method based on the standard method ASTM D422-63 [23]. Characterization of physico-chemical factors influencing soil corrosivity including pH, electrical conductivity, organic carbon content, and the content of the soluble anions ; HCO₃⁻, Cl⁻, SO₄²⁻ were determined using standard procedures [22-28].

Results and discussion

The three main factors that govern the corrosion behaviour of archaeological copper based objects, chemical composition, manufacturing techniques and burial environments, are discussed to assess their contribution and association with the corrosion behaviour of the objects.

Chemical Composition

Chemical analysis results of the objects are presented in table 1 and depicted in figure 3. These results show that the objects were made of copper alloyed with different proportions of tin, zinc and lead. Examination of the results suggests that the objects may be all classified into one general group.

They are all composed of a ternary alloy of Cu, Sn and Zn. However, there are some variations in the percentages of these elements which enable the subdivision of these objects into three compositional subclasses as follows:

A. Relatively high zinc subgroup includes three samples (number 1, 2 and 5). The objects of this subgroup are characterized of having high percentages of zinc (average = wt.13%) and a small amount of tin and lead. This zinc content suggests that the cementation

process was used to produce the alloy. This can be inferred based on the percentage of zinc which does not exceed 28 wt.% [29];

B. The high tin subgroup includes two samples (numbers 3, and 8). The samples of this subgroup contain a relatively high amount of tin. **C.** The low zinc low tin subgroup includes three samples (numbers 4, 6, and 7). A ternary alloy of cu with under 5% percentage of tin and zinc and over 2% of lead was used for the manufacturing of the objects of this group. The low zinc content could be explained based on the presence of high lead; the presence of high lead lowers the melting point of the metal and consequently reduces the amount of zinc that could be absorbed [30].

Table 1. Elemental Composition by ASS of the copper based objects

Sample No.	Cu%	Sn%	Zn%	Pb%	As%	Co%	Fe%	Ni%	Ag %
1	81.93	2.997	13.11	0.8741	0.0620	0.0153	0.3539	0.0909	0.1276
2	82.42	2.736	13.48	0.7219	0.000	0.0652	1.328	0.0991	0.0583
3	82.53	7.412	1.499	2.880	0.000	0.0682	0.0544	0.0221	0.0360
4	81.48	3.8106	4.667	2.437	0.1173	0.000	0.0110	0.0170	0.7380
5	81.79	3.459	13.64	1.618	0.000	0.0251	0.9697	0.0603	0.1068
6	81.53	4.234	5.322	2.154	0.000	0.0301	0.3219	0.0437	0.0708
7	88.65	2.208	3.982	2.150	0.5847	0.000	0.9112	0.4721	0.0386
8	82.35	10.01	4.989	0.1400	0.000	0.0003	0.3812	0.0696	0.0103

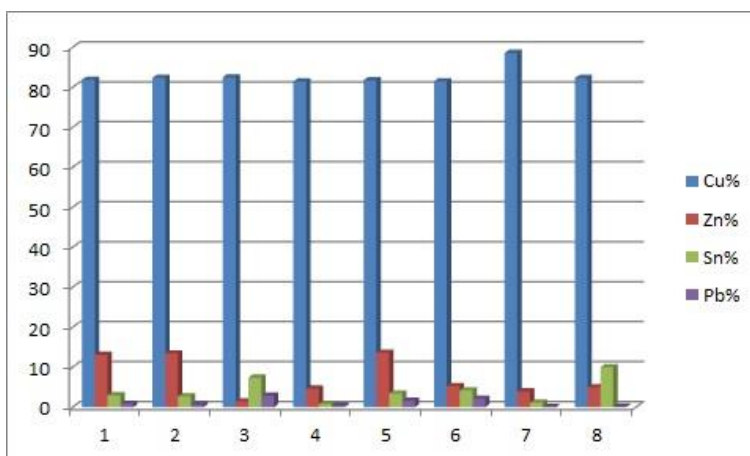


Fig. 3. Elemental wt.% concentration of the objects

As the objects can be classified under one general compositional group, the slight variation in their zinc, tin and lead content has no significant effect on their corrosion resistance [31]. Therefore, chemical composition is not responsible for the clear difference in the corrosion behaviour of the two groups of copper objects.

Manufacturing Techniques

Reflected optical microscopy revealed the microstructures of the objects which carry evidences on their manufacturing and fabrication processes. Figure 4 shows the microstructures of objects 1 and 8 as examples.

The microstructures indicate that the objects were all manufactured by adopting the traditional cycles of thermo mechanical processes used to shape the bronze objects. The microstructures are characterized by the presence of twin lines and slip lines. Some of the twin lines are quite straight, while others seem curved, indicating either hot-working or some cold-working after the final stage of recrystallization. The objects were properly annealed to relieve

the stress build-up in the internal structure resulted from the hammering. This enhances the stability and the corrosion resistance of the objects which may explain the relative stability of these objects.

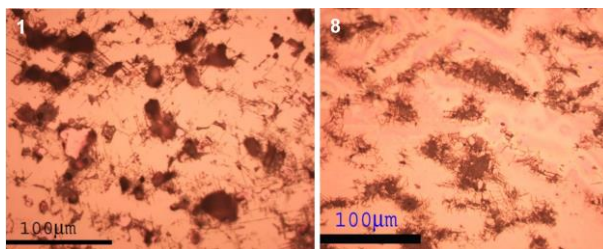


Fig. 4. Photomicrographs of thin sections of objects 1 and 8

Based on these results it can be safely assumed that manufacturing techniques of the objects cannot explain the significant difference of their corrosion behaviour.

Corrosion Analysis

A number of complementary analytical techniques were employed in this study to identify nature and structure of the corrosion products grown during the long-term burial in the soil and in exhibition. Some selected OM and SEM-EDS results are shown in figures 5 and 6.

Optical microscopy investigation allowed the classification of the corrosion layers with respect to their colours, stratigraphic sequence, and regularity. This is important for the rough identification of the nature and degree of deterioration. Microscopic investigations show that the corrosion patterns are of heterogeneous structures as illustrated in the photomicrographs shown in figure 5.

The Main constituents of the surface layer of the patina are green coloured copper (II) compounds covering a red cuprous oxide layer in contact with the metal core of the objects. Object No. 1-6 all appear to develop a compact stable patina of Malachite/Azurite covered with a white carbonate layer overlaying a red cuprous oxide layer in contact with the metal core. Bright blue/green powdery patches erupted through the overlying patina are observed in objects No. 7 and 8 indicating an active "bronze disease" corrosion.

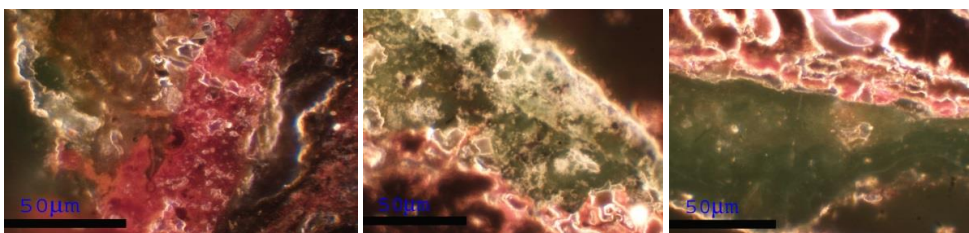


Fig. 5. Photomicrographs of corrosion layers detected on the examined objects showing their distinct colors, morphology and stratigraphy

The main purpose behind using SEM-EDS is to obtain farther information regarding the elemental composition of the different layers. The results of SEM-EDS show the elemental composition of each corrosion layers as shown for objects no. 3 and no.9 (Fig. 6). The results show that the outer corrosion layer contains the elements: Al, Si, Cl, Ca, K, Fe, Cu, Zn and Pb. Some of these elements such as Si, Al and Ca, and Cl came from the soil during burial. In the second layer elements such as Cu, Sn, Cl, and Zn are present.

Analysis of cross sections of the objects as shown in figure 6 can provide useful information on the content and distribution of chlorides within the corrosion layers.

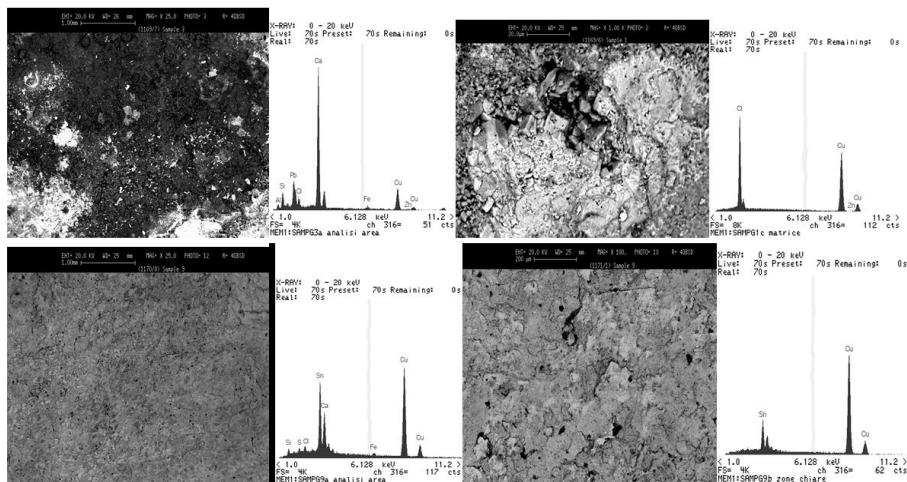


Fig. 5. Morphological details and chemical composition of corrosion layers of object no. 3 and no 9

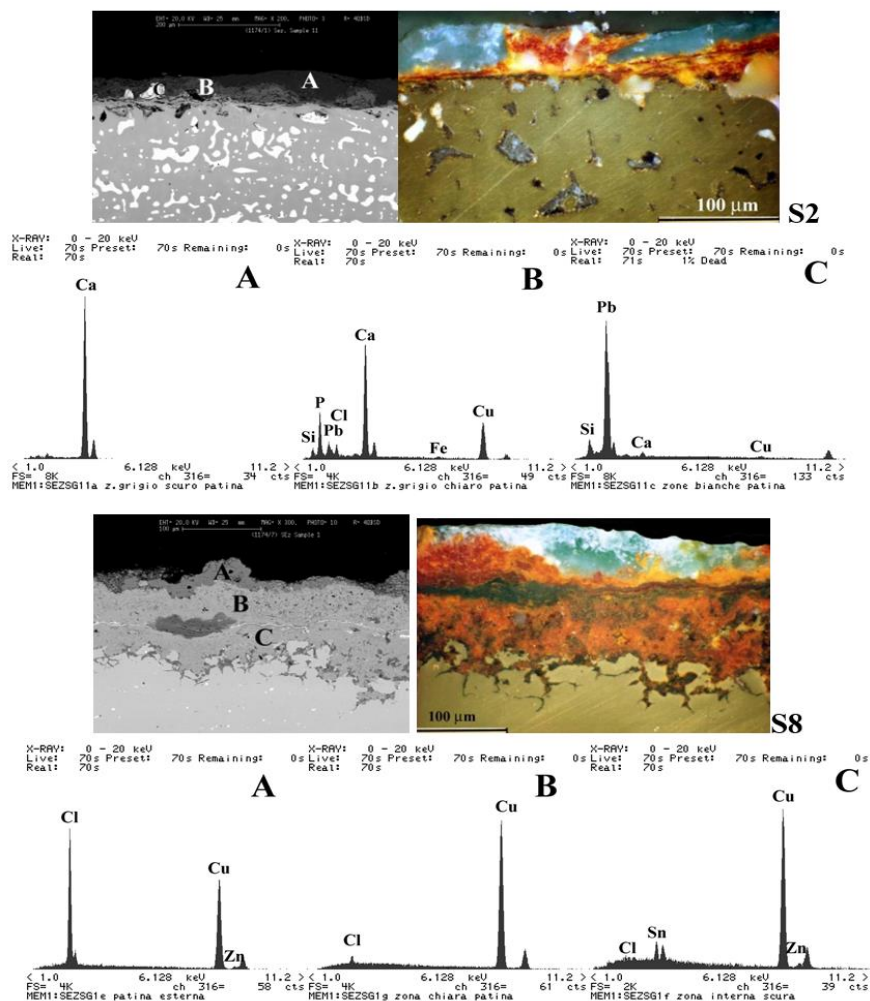


Fig. 6. Cross-section and SEM-EDS analysis of corrosion layers of 2 and 8

Objects 1-6 show detectable amounts of chlorides in layer B, the layer which is in contact with the metal core. Objects 7 and 8 show appreciable amounts of chlorides in all corrosion layers with higher contents in layer A.

OM and SEM images show the complexity of the stratified corrosion layers. The corrosion products identified based on their morphology, colour and composition are: reddish-brown layered aggregates of *Cuprite* (Cu_2O) presents in all objects, (ii) yellow-orange cuprous chloride (*Nantokite*, CuCl) at the interface between external corrosion products and metal alloy relics and along the grain boundaries, presents in object 7 and 8 (iii) green Cu (II) compounds (carbonates and/or copper-oxychlorides) presents in all objects.

SEM-EDX results are confirmed by XRD results that are shown in table 2.

Table 2. Results of XRD analysis of corrosion

Object No	Cuprite	Malachite	Azurite	Atacamite	Paratacamite	Nantokite	Cassiterite	Calcite
1	+	+	+	+	+	-	+	+
2	+	+	+	+	+	-	+	+
3	+	+	+	+	+	-	+	+
4	+	+	+	+	+	-	+	+
5	+	+	+	+	+	-	+	+
6	+	+	+	+	+	-	+	+
7	+	+	+	+	+	+	+	+
8	+	+	+	+	+	+	+	+

The XRD results show that objects 1-6 have corrosion products composed mainly of cuprite - Cu_2O , malachite - $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})$ and azurite - $\text{Cu}_3(\text{CO}_3)_2(\text{OH})_2$. *Cuprite* and *Malachite* are commonly reported corrosion products on archaeological copper alloys [32-34], Weak signals of *Paratacamite* - $\text{Cu}_2(\text{OH})_3\text{Cl}$, *Atacamite* - $\text{Cu}_2\text{Cl}(\text{OH})_3$ and *Cassiterite* - SnO_2 indicating the presence of these compounds in low content. *Calcite* - CaCO_3 also presents as outer surface deposits from the burial environment.

Objects 7 and 8 have similar corrosion products with one important difference. A strong peak of *Nantokite* (CuCl) has been identified indicating the presence of this compound in high content figure 7.

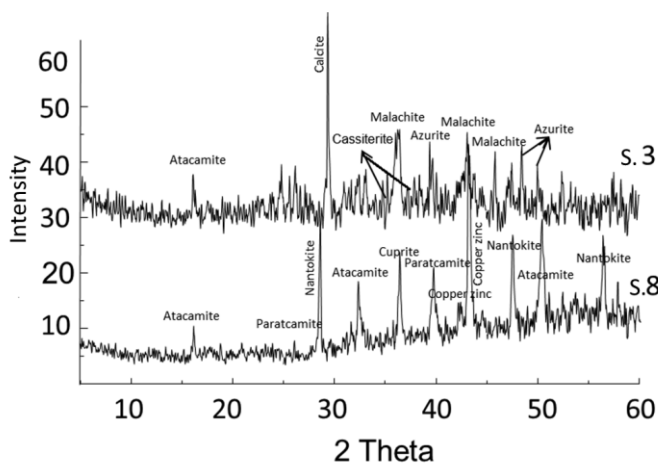


Fig. 7. XRD diffractograms of objects no. 3 and no. 8

The presence of Nantokite in addition to the presence of dangerous chlorine-base (*Atacamite* and *Paratacamite*) is an indicator of bronze disease active corrosion. It is well established that the presence of cuprous chloride (CuCl) induces the continuous cyclic copper

corrosion, defined as the “bronze disease” that progressively transforms the bronze artefact into a light green powder [35, 36]. Cuprous chlorides are very unstable mineral compounds. Once cupreous objects are recovered and exposed to air, they inevitably continue to corrode chemically by a process commonly referred to as bronze disease. In this, cuprous chloride in the presence of moisture and oxygen are hydrolyzed to form hydrochloric acid and basic cupric chloride:



The hydrochloric acid in turn attacks the uncorroded metal to form more cuprous chloride.

Soil Analysis

The chemical and physical characteristics of the soils strongly affect the corrosion behaviour of copper alloy objects [7, 37]. The results of the chemical analysis results are presented in tables 3, 4 and 5.

Table 3. Soil grain size distribution

Sample ID	< 2.0mm wt.(%)	2.0 – 1.0mm wt.(%)	1 – 0.2mm wt.(%)	<0.2mmwt.(%)
TS.1	0	0	47,40	56,88
QAIA. 1	0	0	45,59	53,96
TS.2	0	0	51,31	52,84
QAIA.2	0	0	36,98	62,87
TS.3	0	0	58,87	41,10
TS.4	0	0	61,82	41,92

Table 4. Different parameters of the Soil samples

Sample ID	PH	CE ms/cm	Density	CO ₃ ²⁻ (mg/g)	HCO ₃ ⁻ (mg/g)	Cl ⁻ (mg/g)	SO ₄ ²⁻ (mg/g)
TS.1	7.14	11.41	1.70	0	2	195.25	308.31
QAIA. 1	8.13	0.1806	2.19	0	8	3.55	329.71
TS.2	7.04	13.68	9.67	0	2	436.65	344.53
QAIA.2	8.17	0.214	3.67	0	11	3.55	329.71
TS.3	7.15	11.88	4.14	0	3	372.75	323.24
TS.4	7.20	15.13	2.28	0	2	550.25	324.77

Table 5. Soil organic carbon content

Sample ID	Organic Carbon wt.(%)	N-KT wt.(%)
TS.1	1.53	0.20
QAIA. 1	3.65	0.18
TS.2	1.99	0.12
QAIA.2	2.12	0.18
TS.3	0.43	0.13
TS.4	2,55	0.38

The soil of QAIA has a slightly basic pH = 8.14. This high pH is partly due to the relatively high levels of carbonates. In this range, pH is generally not considered to be the dominant variable affecting corrosion rates. More acidic soils obviously represent a serious corrosion risk. The higher the concentration of calcium carbonate in the soil, the lower the corrosion rate will be [38, 39]. The low chloride level makes the soil of this burial environment less corrosive. Chloride ions are generally harmful, as they participate directly in anodic dissolution reactions of copper-based alloys and their presence tends to decrease the soil resistivity. The sulphate concentration in the soil is considered to be relatively high (329mg/g). Compared to the corrosive effect of chloride ion levels, sulphates are generally considered to be more benign in their corrosive action towards copper-based alloys. The presence of sulphates does pose a major risk in the sense that sulphates can be converted to highly corrosive sulphides by anaerobic sulphate-reducing bacteria.

The chemical analysis of the soil from TS shows very high chloride level (as high as 436mg/g). This is mainly because of the closeness of the site to the huge salt reservoir of the Dead Sea which is only few kilometres away. The presence of increasing concentrations of chloride ions lowers the resistivity of soil and water and will cause an increase in the corrosion rate. Chlorides present in amounts as little of 0.3% with sulphates present can produce severe corrosion.

The high concentration of chlorides significantly lowers the soil resistivity which makes it ideal for electrolytic corrosion. This soil is very effective electrolyte. The lower the resistivity of a soil, the better it will behave as an electrolyte and the more likely it is to promote corrosion.

The close proximity of the Dead Sea combined with the very low resistivity of the soil makes this site a very corrosive burial environment. The lower level of carbonates (2mg/g) lead to the decrease in the pH of the soil (pH = 7.10).

Soil of this site is characterized by having a high moisture content, high electrical conductivity, and high dissolved salts which make this soil very corrosive toward copper based objects. This explains the high level of deterioration of the objects excavated from this site. Most of the copper objects unearthed from this site have lustrous spots indicating active bronze disease. The selected copper objects from this site have thick corrosion layers that are composed of cuprite (Cuprous oxide), the green rust of carbonate (Basic copper carbonate: malachite) and basic copper chloride probably Paratacmitite or Atacamite, crystals of metallic copper that had been re-deposited.

Assessment of the State of Conservation of the Objects

The results of the various analytical techniques employed in this study show that the selected copper based objects can be classified into two groups based on their burial environment and state of corrosion: group 1 includes objects excavated from TS. These objects have suffered from severe bronze disease due to the presence of high chloride content from their burial soil and due to their exhibition in inappropriate environmental conditions in the museum. Group 2 includes objects excavated from QAIA. These objects are in better conservation conditions with no signs of bronze disease observed in them. They were excavated from a soil with low chloride content. However, the cross section analyses prove that these objects contain within their corrosion layers some chloride containing compounds such as Atacamite and Paratacmitite. Both groups of objects are exhibited at the Museum of Jordanian Heritage under inappropriate environmental conditions. Recent measurements show that the seasonal variation in RH is ranging from 35 to 70% during the period between June to December. Furthermore, the data show that the daily fluctuation in the RH level is quite significant and is increased at certain times to over 20% in 24 hours. It is quite evident from the obtained data that variation in the outside environment is directly reflected by a variation inside the museum.

This is due to nature of the building materials in addition to the lack of any sort of environmental control in the museum both at the macro and micro levels.

Temperature monitoring in the same period shows a significant seasonal variation. The range of temperature variation during the measurement period is 13-33°C. Based on the analysis of the temperature variations in the museum, it is evident the temperature inside the museum is directly affected by the outside temperature. Any rise in outside temperature is being reflected by a rise in the temperature inside the museum and the show cases albeit to varying extents. This is due to the lack of any sort of temperature control in the museum. Temperature variation causes relative humidity variation as both values are interrelated.

It is clear that both groups of objects are at high risk. Group 1 are at risk of being soon completely destroyed by the action of cycles of bronze disease while group 2 objects can develop active corrosion due to the presence of chloride containing compounds within their corrosion and due to the high and fluctuated levels of relative humidity in their show case. It has

been found that RH over 45% is sufficient to activate bronze disease in copper based objects even if they contain low levels of chloride ions [40].

Long term stabilization of the objects

The long term stabilization of the objects requires immediate actions from the museum if the objects are to be saved from complete destruction. TS objects suffer from active bronze disease corrosion induced by oxygen and humidity exposure of the reactive cuprous chloride (CuCl) located at the interface between external corrosion products and the surviving core metal matrix. These objects need to be immediately isolated from oxygen and humidity to stop the cyclic destructive corrosion. The most viable option is the treatment of these objects Benzotriazole (BTA) alcoholic solution. BTA is a corrosion inhibitor capable of forming a protective barrier between the artefact and the surrounding environment, a condition necessary to halt bronze disease [41]. Unfortunately Benzotriazole is, toxic and a suspected carcinogen and therefore it should be only applied by a professional conservator with extreme care. Alternatively, L-cysteine may represent a safer option. Encouraging results were obtained by using this corrosion inhibitor to stabilize chloride contaminated copper based objects [42]. Treated objects should then be kept under strictly controlled environment of constant RH below 40%.

QAIA objects have no active corrosion yet but contain low levels of chlorides within their corrosion layers. This represents a future risk especially if the objects will continue to be displayed under incorrect environmental conditions.. Therefore, the long term stability of these objects can be guaranteed by implementing preventive conservation measures without the need for Benzotriazole treatment. The objects should be kept in a show case that has constant RH levels below 40%.

Conclusions

The results show that nature and level of corrosion the copper based objects are mainly governed by their burial environments. The chloride content of the soil and post excavation exposure to humidity determined to large extent the conservation condition of copper based objects. The multi-analytical techniques employed in this study demonstrated that TS objects suffer from severe active bronze disease corrosion while the QAIA objects are relatively more stable but contain within their corrosion layers some chloride compounds that represent a future stability risk. All the objects have been exposed to real risk by exhibiting them under incorrect relative humidity levels and temperatures that have induced further cycles of destructive corrosion in the case of TS objects and may initiate active corrosion in QAIA objects. The correct diagnosis of the corrosion conditions of copper based museum object is quite essential for devising effective long term stabilization of these objects. Objects suffering from active bronze disease like the TS objects should be sealed from humidity and oxygen by treatment with corrosion inhibitors that can surround the object with a protective film like Benzotriazole. In the case of relatively stable objects like those excavated from QAIA can be stabilized by preventive measures through the strict control of their environmental conditions particularly relative humidity which should be constantly maintained below 40%.

References

- [1] M.C. Bernard, S. Joiret, *Understanding corrosion of ancient metals for the conservation of cultural heritage*, **Electrochimica Acta**, **54**(22), 2009, pp. 5199–5205.
- [2] I. Sandu, N. Ursulescu, I.G. Sandu, O. Bounegru, I.C.A. Sandu, A. Alexandru, *Pedological stratification effect of corrosion and contamination products on Byzantine bronze artefacts*, **Corrosion Engineering Science And Technology**, **43**(3), 2008, pp. 256-266. DOI: 10.1179/174327807X234688.

- [3] I.G. Sandu, S. Stoleriu, I. Sandu, M. Brebu, A.V. Sandu, *Authentication of ancient bronze coins by the study of the archeological patina - I. Composition and structure*, **Revista de Chimie**, **56**(10), 2005, pp. 981-994.
- [4] O. Oudbashi, *Corrosion Risk Assessment Approach in Archaeological Bronze Collections: From Burial to Long-term Preservation Environments*, **Proceedings of the Interim Meeting of the ICOM-CC Metals Working Group**, September 26-30, 2016, New Delhi India.
- [5] H. Hassairi, L. Bousselmi, E. Triki, *Bronze degradation processes simulating archaeological soil media*, **Journal of Solid State Electrochemistry**, **14**(3), 2010, pp. 393-401.
- [6] E.F. Angelini, Rosalbino, S. Grassini, G.M. Ingo, T. De Caro, *Simulation of Corrosion Processes of Buried Archaeological Bronze Artefacts*, **Corrosion of Metallic Heritage Artefacts: Investigation, Conservation and Prediction for Long-Term Behaviour** (Editor: P. Dillmann, G. Béranger, P. Piccardo and H. Matthiesen), European Federation of Corrosion Publication 48, = Woodhead Publishing, Cambridge, 2007, pp. 203-218.
- [7] L. Robbiola, J.M. Blengino, C. Fiaud, *Morphology and Mechanisms of Formation of Natural Patinas on Archaeological Cu-Sn alloys*, **Corrosion Science**, **40**, 1998, pp. 2083-2111.
- [8] F. Ospitali, C. Chiavari, C. Martini, E. Bernardi, F. Passarini, L. Robbiola, *The characterization of Sn-based corrosion products in ancient bronzes: A Raman approach*, **Journal of Raman Spectroscopy**, **43**(11), Special Issue: SI, 2012, pp. 1596-1603.
- [9] I. Sandu, O. Mircea, A.V. Sandu, V. Vasilache, I.G. Sandu, *Study of the Liesegang Chemical Effects in Antique Bronze Artefacts During Their Stay Within an Archaeological Site*, **Revista de Chimie**, **65**(3), 2014, pp. 311-319.
- [10] O. Mircea, I. Sandu, V. Vasilache, A.V. Sandu, *Study of the atypical formations in the corrosion bulks of an ancient bronze shield, by optical and electron microscopy*, **Microscopy Research and Technique**, **75**(11), 2012, pp. 1467-1474, DOI: 10.1002/jemt.22090
- [11] O. Mircea, I. Sandu, V. Vasilache, A.V. Sandu, *Research on Atypical Formations from Corrosion Bulks of an Ancient Bronze*, **Revista de Chimie**, **63**(9), 2012, pp. 893-899.
- [12] O. Oudbashi, *A methodological approach to estimate soil corrosivity for archaeological copper alloy artefacts*, **Heritage Science**, **6**, 2018, Article Number: 2.
- [13] A.G. Nord, E. Mattsson, K. Tronner, *Factors influencing the long-term corrosion of bronze artefacts in soil*, **Protection of Metals**, **41**(4), 2005; pp. 309-316.
- [14] A.G. Nord, K. Tronner, E. Mattsson, G.C. Borg, I. Ullén, *Environmental threats to buried archaeological remains*, **Ambio**, **34**(3), 2005 pp. 256-262.
- [15] W. Gerwin, R. Baumhauer, *Effect of soil parameters on the corrosion of archaeological metal finds*, **Geoderma**, **96**(1-2), 2000, pp. 63-80.
- [16] G.M. Ingo, E. Angelini, T. de Caro, G. Bultrini, I. Calliari, *Combined use of GDOES, SEM+ EDS, XRD and OM for the microchemical study of the corrosion products on archaeological bronzes* **Applied Physics A-Materials Science & Processing**, **79**(2), 2004, pp. 199-203.
- [17] G.M., Ingo, I. Calliari, M. Dabala, G. Bultrini, T. de Caro, G. Chiozzini, *Microchemical study of the corrosion products on ancient bronzes by means of glow discharge optical emission spectrometry*, **Surface and Interface Analysis**, **30**(1), 2000, pp. 264-268.
- [18] M.I. Moawiyah, R.L. Gordon, **A Cemetery at Queen Alia International Airport, with contributions by Wolfgang Roellig et al**, Published by O. Harrassowitz, Wiesbaden, Germany, 1987.
- [19] J.N. Tubb, *Tell ES-SA 'idiyeh: Preliminary report on the first threeseasons of renewed excavations*, **Levant**, **20**(1), 1988, pp. 23-88.

- [20] I. Sandu, D. Aparaschivei, V. Vasilache, I.G. Sandu, O. Mircea, *The Archaeometric Characteristics of Some Ancient Medical Instruments from the Moesia Inferior Roman Province, Revealed by SEM/EDX and mu-FTIR*, **Revista de Chimie**, **63**(5), 2012, pp. 495-500.
- [21] M.J. Hughes, M.R. Cowell, P.T. Craddock, *Atomic absorption techniques in archaeology*, **Archaeometry**, **18**(1), 1976, pp. 19–37.
- [22] V.S. Shrivastava, *X-ray diffraction and mineralogical study of soil: A review*, **Journal of Applied Chemical Research**, **9**, 2009, pp. 41–51.
- [23] * * *, *Standard test method for particle-size analysis of soils*, **ASTM D422-63**, West Conshohocken: ASTM International, 2002. <https://doi.org/10.1520/d0422-63r02>.
- [24] M. Pansu, J. Gautheryou, **Handbook of Soil Analysis: Mineralogical, Organic and Inorganic Methods**, Springer, Berlin, 2006.
- [25] P.J.A. Howard, D.M. Howard, *Use of organic carbon and loss-on-ignition to estimate soil organic matter in different soil types and horizons*, **Biology and Fertility of Soils**, **9**(4), 1990, pp. 306–310.
- [26] * * *, *Standard test method for pH of soils*, **ASTM D4972-01**, West Conshohocken: ASTM International; 2007, <https://doi.org/10.1520/d4972-01r07>.
- [27] Y. Shirokova, I. Forkutsa, N. Sharafutdinova, *Use of electrical conductivity instead of soluble salts for soil salinity monitoring in Central Asia*, **Irrigation and Drainage Systems**, **14**, 2000, pp. 199–205.
- [28] J.J. Miller, D. Curtin, *Electrical conductivity and soluble ions*, **Soil Sampling and Methods of Analysis** (Editor: M.R. Carter and E.G. Gregorich), 2nd ed., Taylor & Francis, Abingdon, 2008.
- [29] J. Kharakwal, L. Gurjar, *Zinc and brass in archaeological perspective*, **Ancient Asia**, **1**, 2006, pp. 139-159.
- [30] A.R. Giumliamair, *The composition of copper-based small finds from a west Phoenician settlement site and from Nimrud compared with that of contemporary Mediterranean small finds*, **Archaeometry**, **34**(1), 1992, pp. 107–119.
- [31] A.B. Johnson, Jr. B. Francis, **Durability of Metals From Archaeological Objects, Metal Meteorites, and Native Metals**, Pacific Northwest Laboratory Richland, Washington 99352, 1980.
- [32] V. Vasilache, I. Sandu, C.C. Lazanu, I.G. Sandu, *Archaeometallurgical Evaluation of Two Spearheads from the Bronze Age*, **International Journal of Conservation Science**, **6**(4), 2015, pp. 633-642.
- [33] I.G. Sandu, F.A. Tencariu, D.M. Vornicu, A.V. Sandu, A. Vornicu, V. Vasilache, I. Sandu, *Establishing the Archaeo-Metallurgic Ornamentation Process of an Axe From the Bronze Age by OM, SEM-EDX, and Micro-FTIR*, **Microscopy Research and Technique**, **77**(11), 2014, pp. 918-927, DOI: 10.1002/jemt.22416
- [34] V. Vasilache, D. Boghian, A.I. Chirculescu, S.C. Enea, I. Sandu, *Conservation State Assessment and Determination of Certain Archaeometric Characteristics for Two Bronze Items from the Early Hallstatt Period*, **Revista de Chimie**, **64**(2), 2013, pp. 152-157.
- [35] D.A. Scott, *A Review of Copper Chlorides and Related Salts in Bronze Corrosion and as Painting Pigments*, **Studies in Conservation**, **45**(1), 2000, pp. 39-53.
- [36] D.A. Scott, **Copper and Bronze in Art: Corrosion, Colorants, and Conservation**, Los Angeles: Getty Publications, 2002.
- [37] O. Papadopoulou, P. Vassiliou, S. Grassini, E. Angelini, V. Gouda, *Soil-induced corrosion of ancient Roman brass – A case study*, **Materials and Corrosion**, **67**(2), 2016, pp. 160-169.
- [38] R.F. Tylecote, *The effect of soil conditions on the long-term corrosion of buried tin-bronzes and copper*, **Journal of Archaeological Science**, **6**(4), 1979, pp. 345–368.

- [39] W. Gerwin, R., Baumhauer, *Effect of soil parameters on the corrosion of archaeological metal finds*, **Geoderma**, **96**(1-2), 2000, pp. 63–80.
- [40] D.A. Scott, *Bronze disease. A review of some chemical problems and the role of relative humidity*, **Journal of the American Institute for Conservation**, **29**(2), 1990 pp. 193–206.
- [41] M. Finšgar, I. Milošev, Inhibition of copper corrosion by 1,2,3-benzotriazole: A review, **Corrosion Science** **52**(9), 2010, pp. 2737-2749
- [42] V. Argyropoulos, S. Mavroforaki, M. Giannoulaki, S.C. Boyatzis, T. Karabotsos, A. Zacharopoulou, E. Guilminot, **New Approaches in Stabilizing Chloride-Contaminated Ancient Bronzes Using Corrosion Inhibitors and/or Electrochemical Methods to Preserve Information in the Patinas**, Getty Conservation Institute, <http://www.getty.edu/publications/artistryinbronze/conservation-and-analysis/38-argyropoulos/> [accessed on 17/3/2020].
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