



## Selective Formula as a Corrosion Inhibitor to Protect the Surfaces of Antiquities Made of Leather-Composite Brass Alloy



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### Abstract

The interactions between the metal and the surroundings are responsible for electrochemical reactions that contribute to corrosion. To mitigate or deter corrosion of exposed metal in a corrosive environment, and corrosion agent must be applied to the metal surface to prevent further oxidation and therefore the presence of corrosion materials. One of the common techniques used by professionals associated in conservation-restoration to preserve metallic cultural heritage is the corrosion inhibitors. The second section of the thesis deals with the conservation and management by using an environmentally friendly corrosion agent of the corrosion of brass composite brass leather parts from the Bulaq Museum, Cairo, Egypt. Microscope Optical and scanning electron Analysis was performed to determine the microstructure of the alloy. Determining the alloy chemical composition of the identified objects using dispersive energy spectroscopy (EDS). Using X-ray diffraction (XRD), corrosion products were established. Finally, the effectiveness of composites between industrial corrosion inhibitors and surfactant materials was identified by the positive effects of (TTA + SLS) on handling. Before and after treatments the brass surfaces were described using SEM, EDS, XRD, FTIR, and XPS.

**Key words:** Brass; Conservation; Coating; Electrochemical Characterization; Corrosion Control.

### 1. Introduction

According to its outstanding mechanical characteristics, low-cost availability and ease of manufacturing, brass alloy plays an important and significant role in ancient and modern times. The brass alloys consist mostly of Cu and Zn; the main component is copper, and zinc is between 10 and 45 percent [1, 2]. In early days, brass alloys were similarly binary alloys composed of 90 to 70 percent copper and 10 to 30% zinc. If the proportion of zinc rose, the colour of the composite becomes more yellowish [3]. The colour ranges from a red like pure copper through a pleasing yellow to white and is about 45% zinc [4]. It is well known that brass is an alloy of copper zinc and is commonly used in many fields and

incorporates certain desirable features of Cu and Zn mutually. In the modern era, particularly in the times of the Mohamed Ali family in Egypt, brass alloy was extensively applied. It was used as a composite of other components to fabricate horses' staff such as cart, saddles, and horses' frames. Since zinc is the active brass component, it tends to disintegrate leaving its surface enriched with copper. The degradation of a metallic framework is often treated as an inconvenience because over time it means a transition in the objects; this damage to a metal is caused by chemical, electrochemical or even biological reactions between the metal surface and the surrounding medium [5]. The exposition of the old object is supplemented by a change reliant on the environmental conditions, which can sometimes

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accelerate objects degradation [6-8]. To establish a control technology and enhance the consequences of safety, the study of the causes of corrosion is important. It is expected that when it is exposed to an oxygen-containing environment, a thin oxide layer (patina) is automatically formed on the surface of brass objects. The thickness of this passive oxide film is around a few nanometres only and acts in the corrosive media as a protective barrier [9]. Using inhibitors on the brass surface of the products will combine the benefit of both materials, the inhibitor bioactivity, and Brass alloy's excellent mechanical properties. Put up a physical shield to separate the metal using organic layers as an example or corrosion agent to protect against corrosion [7, 10 and 11]. The current research aims to investigate the inhibition efficacy of tolyltriazole and sodium lauryl sulphate (TTA + SLS) in brass surface interactions. The first section of the survey is dedicated to testing the inhibition performance of the chosen compounds on current brass samples, these samples have the same chemical structure of the chosen archaeological objects. The second section of this thesis is a realistic study of the Bulaq Museum, Cairo, Egypt, with the care of the same historical composite brass objects. To define the microstructure of the composite, scanning electron microscope and optical inspection were done to accomplish that. The engaged energy dispersive spectroscopy EDS with SEM technique was used to discern the structure of alloys used to produce the chosen objects. Extra X-ray diffraction technique (XRD) was used for the identification of the components of crystalline corrosion. Finally, the prior experience has been utilized for the chosen items throughout a systematic evaluation and conservation. The decay of the cyclic copper chloride can also damage or destroy archaeological artefacts of Cu and its composite. Objects stored at (RH) relative humidity are usually stable between 42 and 46 percent [12]. If the RH is higher though, further corrosion can occur. The aim of applying corrosion inhibiting compounds to material containing copper chloride is to prevent the transformation of copper (I) chloride (Nantokite) into basic copper (II) chloride (Atacamite, Paratacamite) [13, 14]. In the past, new reconstruction methods have been directly applied to archaeological content, which is now considered unethical and it is important to create a systematic testing procedure. Corrosion study uses archaeological copper and its composites, but the findings of the review have certain disadvantages: the treatment can be detrimental to the material, the treatment may be lasting, the long-term consequences are unknown, the amount of corrosion varies greatly, the variation in porosity of the combining components of the rust extract may affect the treatment [15]. The new Copper and its composite corrosion test would provide conservators with a tool for evaluating new

materials that reduce variables and do not require large facilities, usually not possible in small conservation labs. [16]. The test also focuses on the consecutive tests, allowing for comparison of experimental research. A corrosion test method has been developed to replicate the frequently encountered  $\text{CuCl}_2$  decay stratigraphy on objects [17].

## 1.2. Choosing New Sources of Corrosion Control

For the stabilization of Cu and its alloy artifacts only Benzotriazole has been generally acknowledged. Madsen suggested archaeological conservation BTA focused on comprehensive industrial study [18]. BTA has become the primary inhibitor for corrosion which used in the protection of Cu and its alloys because of its perceived advantages and satisfactory performance [19]. That has also subsidized to the omission of geological conservation work on other compounds for copper. Another corrosion inhibitor has newly been proposed for conservation inhibition of brass corrosion: An assessment of existing chemical and engineering literature was conducted to examine for other brass corrosion inhibitors [20, 21]. In no case was a ternary alloy checked like copper-tin-lead, any of the various copper alloys used in archaeological sites. Such findings made it clear that published test results provided in industrial literature were useful only for preliminary compound selection for potential use in archaeological conservation [22]. The published data provided a hint of what to expect from further conservation trials. To recognize new inhibitors directly relevant to archaeological conservation goals, a re-evaluation of existing literature from a conservation point of view was required. Throughout the arena of brass corrosion inhibitors, there are numerous industry-based comparative studies [23-25]. In water flow systems such as boilers, radiators, chemical containers and marine water systems, several publications cover corrosion safety [26, 27]. These manufacturing settings have no direct relation to the conditions that would normally be encountered in a storage area or exhibition by a handled archaeological artifact. Similar characteristics as formulations and types of compounds potentially suitable for archaeological metal artifacts have been reviewed for the studies examined. To be suitable for conservation as a brass corrosion inhibitor, the combination should meet various criteria evolving from the product, the atmosphere, and the conservatory system [28]. To avoid more metal oxidation, the polymer structure should be thick, compact and without voids. The surface of corroded brass has areas where substantially low pH was observed, such as pits corrosion since copper (I) may be has a pH of 3.5-4 [29]. The acidity at chloride pits is indicated to be much smaller. Hence the inhibition should be selective over the pH

spectrum from 2 to 8. Preferably the compound would serve as an inhibitor of anodization. The anodic areas in the most important region of the pits deliberately corrode during pitting corrosion, while the outer surface is Cathodic [30]. The greatest inhibitor in anodic and cathode-like areas will respond, considering the argument of an aggressive corroding brass product, the metallic sections act as an anode and the corrosion layers act mainly as a cathode. Corrosion pits within are also contemplated to be anodic. The borders of Cathodic and anodic sections in a corroded item are generally not transparent or distinct outstanding to the heterogeneity of an alloy and its corrosion products [31, 32]. The patina's optical appearance should not be altered by adding an inhibitor. Many of the former treatments applied in restoration, as described above, caused the outer corrosion layers to be disfigured or discoloured. Benzotriazole, as is often needed, has been discovered to dim the emergence of the erosion products, particularly in repeated application. Once used in industrial methylated spirits, AMT has been shown to cause some obscuring of metallic brass [33]. The latter is also used in restoration as a cure for the 'bronze disease'. The metallic traces left in and on the exterior of the rust products can interfere with the analytical results of studies on trace elements [34]. The industrial literature review established three key forms of inhibitors that were discovered to be highly effective in inhibiting corrosion of copper; these are inhibitors containing sulphur, phosphorus, or both. The effectiveness of corrosion inhibition was noticed to be as follows: sulphur-containing > oxygen-containing > nitrogen-containing [35]. Archaeological objects are coated in oxide deposits while the metal surfaces used in industrial tests are free of contamination; the surfaces have been washed because oxide may have hampered with test results. In certain cases, there was no indication of the pH spectrum of inhibitor solutions, or the application was within a small pH spectrum. In the situation of archaeological Cu and its composites, the pH range wherein the inhibition is successful would be as small as 2 because chloride corrosion pits are thought to form at a pH amongst 3-5 and 4 [36]. It was only stated in a few instances if an inhibitor developed cathodic, anodic, or mutually forms of defencing counter to deterioration. Clearly, inhibitors not meeting the above-mentioned criteria for archaeological metals were not considered. A list of corrosion inhibition compounds was compiled, because of the review of literature [37, 38]. This paper explores the utilization of a modern archaeological brass coating that was coated with leather. Across sometimes we can find these items and we can find a number in the Mohamed Ali family as they used it in horses' staff such as wagon, saddles, and horses' glasses. Treatment to object consisted of two different materials, one organic and one non-organic, is not easy

to make, especially the way of deterioration is different, and the materials used in treatment are not the same [39].

## 2. Materials and Methods

### 2.1. Materials

Owing to its excellent properties, brass alloy and leathers play an important and significant role in both ancient and modern times. So, we do several analyses to understand the percentage of Cu and Zn in this object alloy and the form of deterioration that arises on the metallic facade even allow leather analyses to categorize the leather type. We used (LM) and (SEM) for inspection and examination to see the brass grains and the oxidation found on the superficial, to rank the percentage of brass alloy we used SEM with EDX, and to use X-ray diffraction for corrosion products to realize the type of chemical compounds we used. Use infrared spectroscopy (FTIR) to recognize the degradation and loss of leather compounds and use light microscopy to understand the type of leather by hair follicles. Subsequent procedures were applied for care and refurbishment of the piece. Dust deposits from the initial sections of the item were removed internally and externally using mechanical cleaning methods, in particular different types of brushes that were suitable for leather and metal, then using scalpel to scrape coats of rust from the metal.

### 2.2. Methods

#### 2.2.1. Conservation Process

Numerous scientists in archaeological preservation have attempted to replicate unnaturally pre-decayed samples for research laboratory experiments. The techniques of electrochemistry were conducted to a traditional electrochemical cell containing three compartments for working (with an exposed region of 0.785 cm<sup>2</sup>), a platinum wire (0.1 cm<sup>2</sup>) counter and reference electrodes. The reference electrode was a (Ag/AgCl) saturated calomel electrode is used directly in connection together with the working solution. The trials were organized in a 150 cm<sup>3</sup> volumetric cell. The whole electrolytes were recently planned through pure chemical of analytical grade substances utilizing double distilled water. The tests were performed in stagnant aerated solutions. The experimental works were conducted to solutions of 3.5% NaCl without and with various concentrations of (TTA + SLS).

#### 2.2.2. Procedure to Check Corrosion

To check therapies that prevents corrosion, as inhibitors for corrosion, the structures including vigorous CuCl<sub>2</sub> as a corrosion product in the Cu and its alloy. Pure sheet brass was used. The sheet was

rolled to a thickness of 1 mm, as given. A standard of the BSI (British Standards Institution) recommends a sample size not less than 25 cm<sup>2</sup>, but this sample size was found too large. The humidity chamber available during the experiment could not handle samples of this size. The content was cut to the size of 20 x 50 x 1 mm on a guillotine. The size of the used sample also allows for the treatment of a greater number of coupons in one trial, thereby helping to establish the repeating of experimental findings. Measures used to formulate the coupons have to be closely controlled to eliminate differences in surface corrosion [40]. That phase of surface provision had to be meticulously selected and examined as minor changes could impact the corrosion data resulting from it. It is difficult to determine explanations for changes in corrosion levels after corrosion has occurred, because consideration must be given to so many complex interacting factors. X-ray diffraction analysis was used to test the compositions of the resulted powder and the composition of the rust layers present on the coupons. In the 1 M of copper (II) chloride solution, one sample was taken after corrosion, drying at 50° C under an infrared lamp for 5 min., exposure to 105° C in an oven for 30 min., and one-hour cooling in a silica-gel buffered polyethene case. After the surface was exposed to 95 % relative humidity for 24 hours, another sample was taken from the same specimen. The XRD study was performed on a Siemens X-ray diffractometer D5000. The sample taken following copper (II) chloride corrosion clearly indicates the occurrence of nantokite. The sample was clearly converted to and classified as paratacamite. A metallographic segment was taken to examine the corrosion layers, prior and subsequently exposure of the nantokite layer to ~100% RH. The pre-corroded coupon segment shows a 20-25 μm layer of nantokite on top of the brass substratum. This was covered with a 5-10 μm layer of what appeared to be red cuprite (copper (I) oxide, Cu<sub>2</sub>O). The coupon covered with paratacamite revealed a 10-25 μm coating of what appeared to be cuprite on top of the brass substratum, and a 160-175 μm coating of paratacamite covering the cuprite. The previous XRD examination did not find the cuprite evident in the nantokite or paratacamite based coupon specimens. That may be because of the much smaller volume of cuprite.

### 2.3. Calculation of Inhibition of Corrosion

To determine the efficacy of a corrosion inhibitor, the inhibition efficiency (I.E %) can be determined from the next formula:

$$I.E, \% = \frac{\text{uninhibited corrosion rate} - \text{inhibited corrosion rate}}{\text{uninhibited corrosion rate}} \times 100$$

The uninhibited corrosion rate is the weight of the corrosion product after a unit time on a blank specimen (a nantokite-covered sample not treated with a corrosion-inhibiting compound exposed to ~100% RH

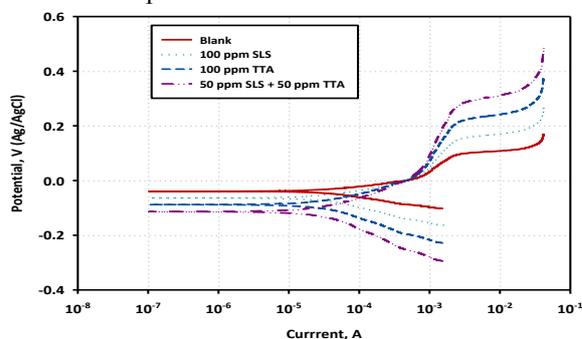
at ambient temperature for 24 hours). The inhibited corrosion rate is the comparable ratio for the inhibited coupon of corrosion (after 24-hour exposure at ambient temperature at 95 % RH).

## 3. Results and Discussion

### 3.1. Corrosion Results

#### 3.1.1. Polarization Curves

The impact of TTA and I or SLS at concentration of 100 ppm and in mixture of 50 ppm each on brass's polarization activity is seen in Fig. 1. Depending on the experimental output from their concentration, the presence of TTA reduces the rate of anodic breakdown by 3-4 orders of magnitudes. In the anodic branch exists a passive region due to the creation of a defensive film of the Cu (I) TTA complex. This passive area stops at the potential for collapse,  $E_b$ , after which the current expands exponentially as the potential becomes more anodic. Owing to the degradation of the defensive coating the sudden rise in current above  $E_b$  is caused by localized corrosion. As the concentration of TTA raises, the potential for dissolution,  $E_b$ , is becoming more favourable and the current in the passive area reduces suggesting a more stable film. The effect of sulphide ions in the inhibited TTA solution on the polarization curve of brass is shown in Fig. 1. The sulphide ions have a clear negative effect on the TTA-induced passivity. Can HS<sup>-</sup> ion concentration have the following effects? It decreases the risk for degradation by hundreds of mV, based on the concentration, increases the passive area current and the rate of anodic dissolution by magnitude commands. The free corrosion potential changes by hundreds of mV in the cathode direction. Note that a concentration of sulphide ions as low as 10<sup>-5</sup> M (0.32 ppm sulphur) raises the current on brass's polarization curve by around 100 ppm TTA in presence. This concentration of TTA (100 ppm) is 1000 times that of the sulphide ions, but it was not able to deter the assault on sulphide.



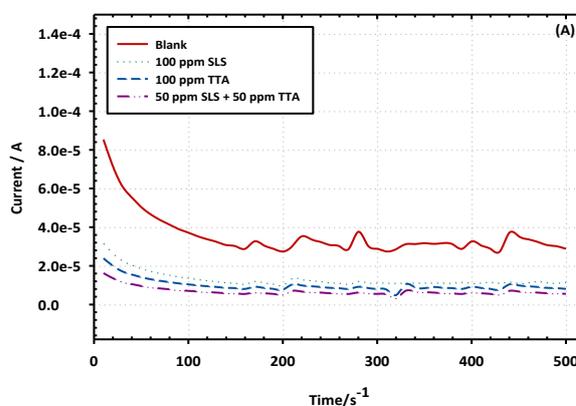
**Fig. 1:** Plots of potentiodynamic polarization curves for brass at a scan rate of 1 mV s<sup>-1</sup> in a 3.5 % NaCl

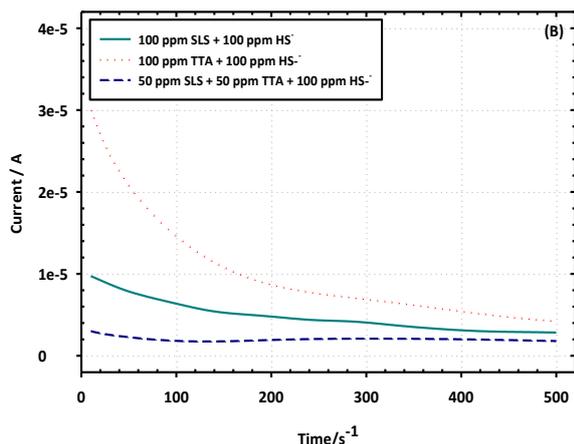
solution in the presence of 100 ppm TTA, 100 ppm SLS and 50 ppm TTA + 50 ppm SLS at 30 °C.

### 3.1.2. Current transients

Potentiostatic current transients on brass electrodes were tested at potentials in the passive region in the presence of 100 ppm concentrations of TTA, 100 ppm from SLS and 50 ppm mixture from each. Fig. 2 shows current transients estimated at a potential of 0.05 V vs Ag/AgCl (within the passive region). Note that, the initial accelerated current decline over time until the current begins to level out into a stable value. After 500 s the currents for the 100 ppm TTA, 100 ppm SLS and 50 ppm mixture from each were 1.2, 0.9 and 0.49  $\mu\text{A cm}^{-2}$  respectively. This is an example of TTA's remarkable effectiveness against brass dissolution within the passive zone. Under this ability, the fortification against corrosion is due to the development of the Cu (I) TTA complex. The decline in current over time is an example of the gradual upsurge of the Cu (I)TTA film's inhibiting performance with involvement time, see Fig. 2. The related currents in the potentiodynamic polarization curves at the same potential (0.05 V vs Ag/AgCl), (Fig. 2) are roughly 12, 9 and 0.5  $\mu\text{A cm}^{-2}$  for 100 ppm TTA, 100 ppm SLS and 50 ppm for each as mixture, respectively. Although the two currents in the presence of 100 ppm TTA are nearly the same, the steady state current in the presence of 100 ppm SLS but the mixture (0.45  $\mu\text{A cm}^{-2}$ ) is around fourfold higher than the potentiodynamic polarization curve (12  $\mu\text{A cm}^{-2}$ ) curve present. This may be due to a brass's propensity to undergo localized corrosion in the presence of low TTA concentrations. Similar tests were conducted to find out whether the pre-immersion of brass in the TTA inhibited electrolyte would also enhance its sulphide attack resistance. In each experiment a certain concentration of sulphide ions under potential in the passive region was injected into the electrolyte after different periods of brass interaction with TTA. The surface of the brass was polarized for 500 s in the presence of TTA before  $\text{HS}^-$  injections, respectively. Note that, the sudden rise in current when sulphide ions are injected that occurs in all situations, suggesting that the length of the Cu (I) TTA film growth process does not increase its resistance to sulphide attack. This is counter to well-documented finding in unpolluted media where the efficacy of inhibitors increases with the time of immersion. The extent of this rapid rise in current is taken as a measure of the sulphide attack rate upon injection of sulphide ions. Fig. 2b shows a further series of findings showing the influence of TTA concentration on the current transient reaction to the sulphide attack. One electrolyte was inhibited by 100 ppm TTA while the other was inhibited by 50 ppm

from the mixture of TTA + SLS. Note that, the fast-current rise when sulphide ions were applied to both media. Also note that in the presence of the mixture (about 260  $\mu\text{A cm}^{-2}$ ) the rise in current is more pronounced than in the case of 100 ppm TTA and/or 100 ppm SLS (about 170  $\mu\text{A cm}^{-2}$ ). This suggests that a rise in TTA concentration in order of magnitude does not eliminate a sulphide attack but only modestly decreases its strength (by around one third). The effect of the injected sulphide ion concentration on the current transient is seen in Fig. 2b for 100 ppm TTA and 100 ppm SLS in presence of  $\text{HS}^-$  sulphide concentrations in the presence of 50 ppm mixture TTA + SLS. When  $10^{-4}$  M  $\text{HS}^-$  is applied, the current raises by just around 20  $\mu\text{A cm}^{-2}$  compared with 270  $\mu\text{A cm}^{-2}$  when  $10^{-3}$  M  $\text{HS}^-$  is injected. A concern occurs here on the cause of the present spike after the sulphide ions have been injected, i.e. whether this is due to the oxidation of sulphide ions or an increase in the rate of Cu corrosion. It is possible to oxidize sulphide ions to give some potential products including elemental sulphur. Different experiments on graphite and brass electrodes were carried out under the same conditions to respond to the above question. The current transients generated by the brass and the polarized graphite electrodes in n electrolyte comprising 3.5 percent NaCl+100 ppm TTA at 0.0 V vs Ag/AgCl. The current generated by the brass electrode leaps to a value of approximately 170  $\mu\text{A cm}^{-2}$  after injection of  $10^{-3}$  M  $\text{HS}^-$  ions, and subsequently decreases with time. But after 500 s it continues moderately high (about 70  $\mu\text{A cm}^{-2}$ ). On the other hand, the graphite electrode's current leaps to around 50  $\mu\text{A}$  and gradually falls to an insignificantly small amount. Graphical integration of the loads passing under curves (for 500 s) yields values of 418.3 and 34.6 mC respectively for the brass and graphite electrodes. This suggests that sulphide ion oxidation contributes only a small fraction of around 8 percent of the load transferred upon insertion of the sulphide ions, while the remainder of the load is due to increased brass corrosion.

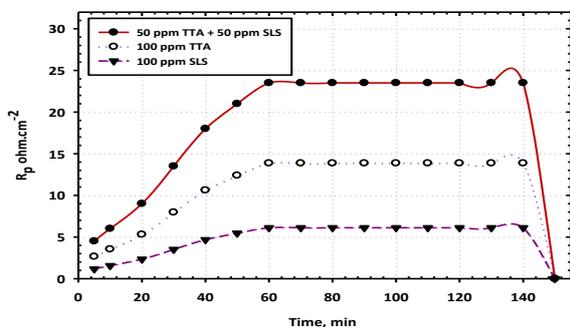




**Figs. 2a, b:** Plots of current transients estimated at a potential of 0.05 V vs Ag/AgCl for brass electrodes in (A) 3.5 % NaCl without and with 100 ppm TTA, 100 ppm SLS and 50 ppm TTA + 50 ppm SLS, (B) 3.5 % NaCl + HS<sup>-</sup> (sulphide injection) with 100 ppm TTA, 100 ppm SLS and 50 ppm TTA + 50 ppm SLS

### 3.1.3. Polarization Resistance

The incremental decline in current over time (Fig. 3), shows that tolyltriazole inhibiting efficacy improves over time. Electrochemical impedance spectra were calculated after different stages of brass immersion in the inhibited TTA medium, before and after the sulphide ions were injected. Those spectra were examined as seen before. The study yields the resistance to polarization ( $R_p$ ) which is inversely proportional to the corrosion rate, where K represents a constant for each device. The  $R_p$  vector with immersion time is shown in Fig. 3. Note the steady rise in  $R_p$  with the immersion time before injection of the sulphide ions, in line with earlier work findings. Note also the pronounced adverse effect of sulphide ions in decreasing  $R_p$  (and thus increasing the risk of corrosion). The sulphide ions have an incredibly rapid influence.

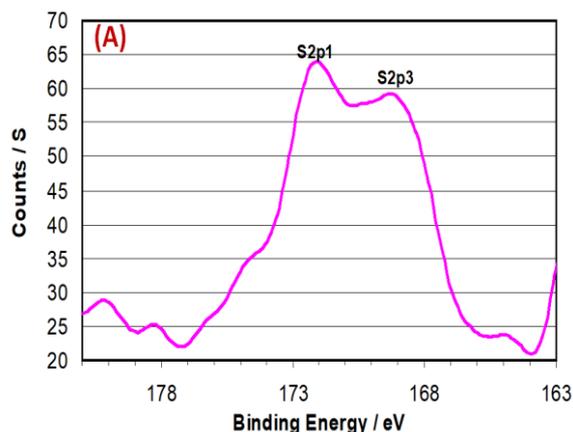


**Fig. 3:** The TTA, SLS and their mixture's inhibiting efficacy improves over time and its effect after sulfide injection.

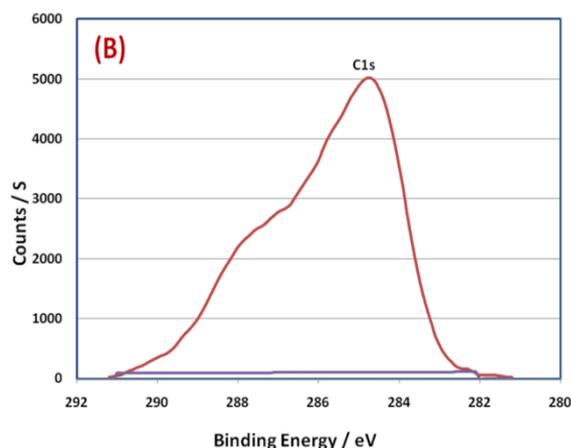
## 3.2. Surface characterization

### 3.2.1. X-ray photoelectron spectroscopy (XPS)

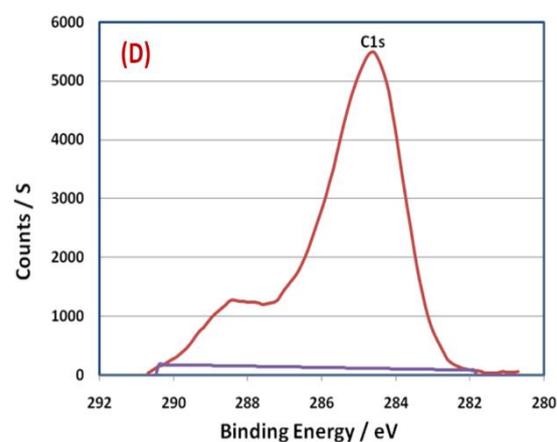
Fig. 4, displays portions of the XPS spectrum derived from the corroded surface of the brass. The electrode was polarized at 0 V vs Ag/AgCl for 17 hours in the presence of 100 ppm TTA, 100 ppm SLS and their mixture of 50 ppm for each, before injection of  $10^{-3}$  M HS<sup>-</sup>, which stayed in contact with the brass surface for 1 hr. The XPS spectrum shows the presence of N1's peak at a binding energy of 400 eV and S<sup>2p</sup> at 162.0 eV, compared to the peak of C1s at 284.6 eV. The N1s peak shows some TTA on the surface of the brass, which was corroded in the presence of sulphide ions. The S<sup>2p</sup> also shows the presence of sulphide ions in the form of copper sulphide, at a binding energy of 162.0 eV. The absence of a S<sup>2p</sup> at 164.0 eV shows that the corroded brass surface lacks elemental sulphur. This is evidence that current increases in Figs 4 and 4-7 are caused by brass dissolution under the effect of sulphide ions, rather than sulphide ion oxidation.



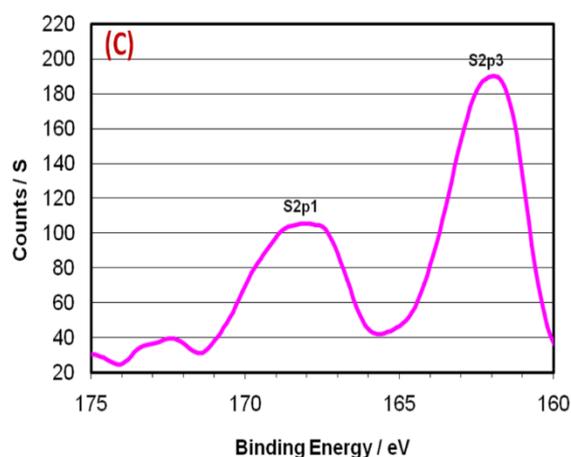
**Fig. 4a:** XPS patterns of brass in 3.5%NaCl + 50 ppm TTA + 50 ppm SLS at 0.0V, the peak of S<sup>2p</sup>1 and S<sup>2p</sup>3 at 172.63 and 169.2 respectively indicating of presence of (sulphur bearing oxygen) sulphate or sulphite ions. It means that reaction occurred on the electrode surface (oxidation of sulphur to sulphite or sulphate) and no complex formed between SLS and copper.



**Fig. 4b:** XPS patterns of brass in 3.5%NaCl + 50 ppm TTA + 50 ppm SLS at 0.0V, the peak of C1s at 284.7 exactly.



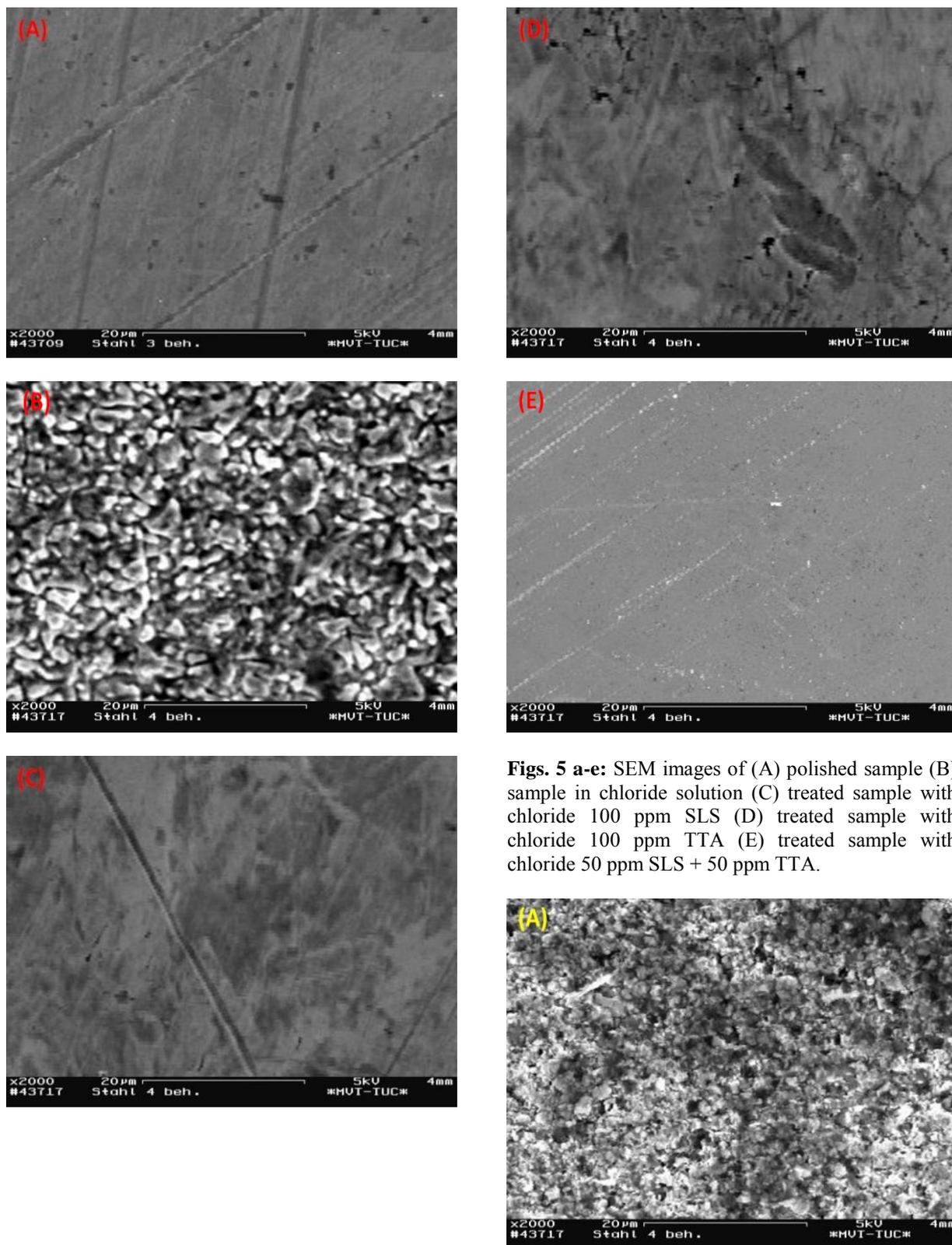
**Fig. 4d:** XPS patterns of brass in 3.5%NaCl + 50 ppm TTA + 50 ppm SLS and injection of 0.001 M HS<sup>-</sup> at 0.0V, the peak of C1s at 284.6 exactly.

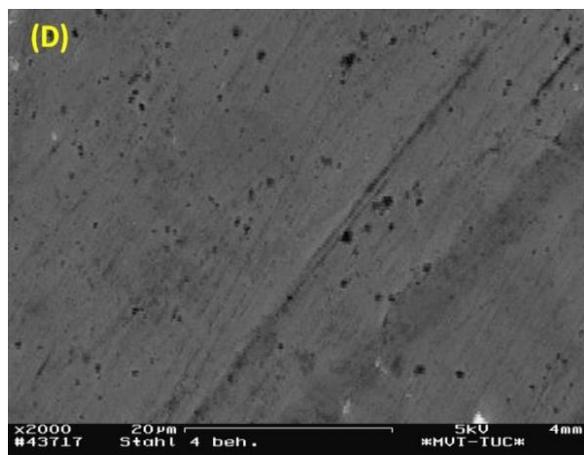
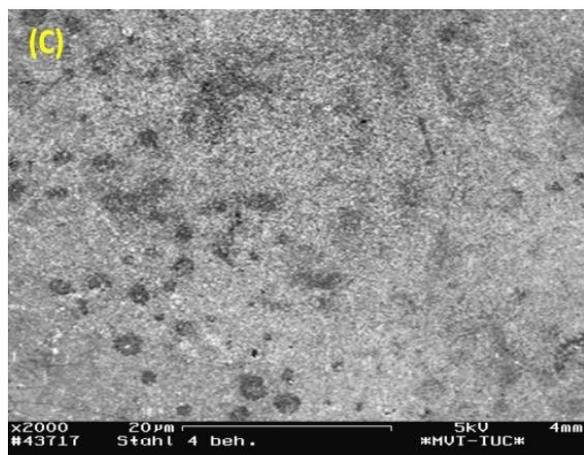
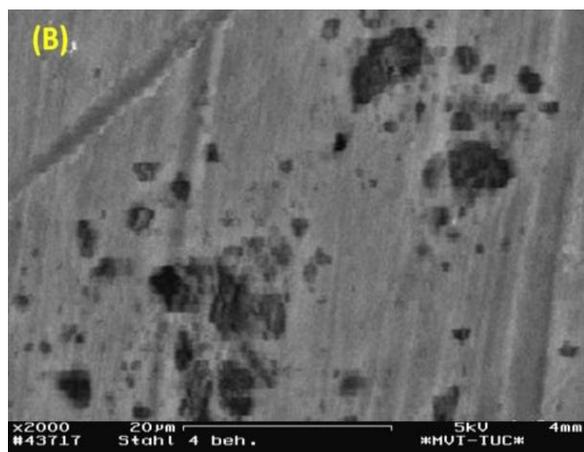


**Fig. 4c:** XPS patterns of brass in 3.5%NaCl + 50 ppm TTA + 50 ppm SLS and injection of 0.001MHS<sup>-</sup> at 0.0V, the peak of S<sup>2</sup>p1 and S<sup>2</sup>p3 at 168.1 and 161.9 respectively, indicating of presence of sulphate and sulphide ions respectively, on the electrode surface which coming from sulphide injection but presence of SLS lowering the effect of sulphide on the complex formed from TTA and brass.

### 3.2.2. SEM Out Put

Fig. 5 illustrates the SEM images of (A) polished sample (B) sample in chloride solution without inhibitor (C) treated sample with 100 ppm SLS (D) treated sample with 100 ppm TTA (E) treated sample with chloride 50 ppm SLS + 50 ppm BTA. The data represent the brass electrode (a) after polishing with SiC paper, (b) the brass electrode in case of absence of the inhibitor and it is clearly noticed that the formation of corrosion product on the brass surface, (c) in the presence of 100 ppm SLS as inhibitor at 20 °C and the surface suffered from some pitting corrosion due to the effect of chloride ion and formation of CuCl<sub>2</sub>. These data like the effect of 100 ppm TTA but the pitting corrosion seems lower that that obtained in case of SLS as seen in Fig 5d. The SEM micrograph of the corroded brass tested in a 3.5 NaCl + 10<sup>-3</sup> M HS<sup>-</sup> solution in the absence of the inhibitor as shown in Fig. 6a, it shows that the brass surface was consistently brutally harmed in the belligerent chloride and sulphide attack. In distinction, in the existence of the mixture of TTA and SLS as brass corrosion inhibitor, only few pits are formed as a localized corrosion can be noticed on the brass surface see Fig. 6d, so the occurrence of this mixture as a corrosion inhibitor altered equally the rate of corrosion and the general corrosion is disappeared just a little pitting corrosion is observed.





**Figs. 6 a-d:** SEM images of (A) untreated sample in polluted sulphide (b) treated sample with sulphide 100 ppm SLS (C) treated sample with chloride 100 ppm TTA (D) treated sample with chloride 50 ppm SLS + 50 ppm TTA.

### 3.3. Mechanism of film breakdown

In the relative stabilities of copper sulphide and the defensive Cu (I) TTA group, a reason for the observed action of sulphide ions can be sought. Although  $\text{Cu}_2\text{S}$

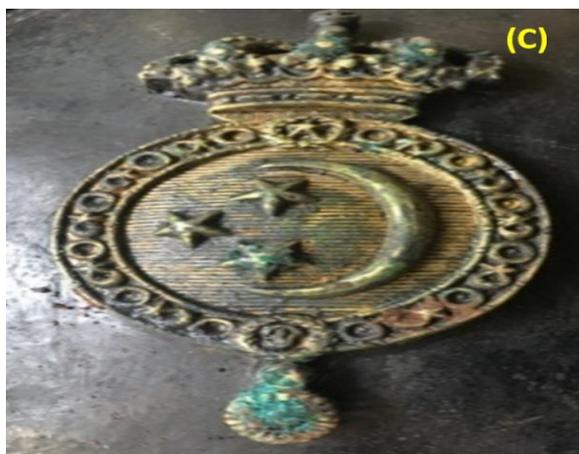
has stability constant of about 1047, Cu (I) TTA complex has a stability constant of about 102. This suggests that sulphide ions fight for Cu (I) ions under a driving force much greater than TTA. The Cu (I) ions can thus be separated from the Cu (I) TTA complex by sulphide ions. The first step is to break down the Cu (I) TTA defensive layer under the influence of the sulphide ions. This reaction contributes to some of the defensive Cu (I) TTA film vanishing and to the presence of copper sulphide. If the defensive coating wears down, there is rust on the raw surface.

## 3.2. Case Study

### 3.2.1. Description and Condition

The investigation and treatment were conducted on same composite artifacts made of brass alloy and leather. These selected objects are storage in Royal Vehicles Museum, Bulaq, Egypt. They date back to the era of Khedive Ismail (1863-1879 AD), he also considers the first ruler who built a building for Royal vehicle and horses [41]. The museum contains a rare collection, of various shapes - some bearing the names of vehicles - made of black or brown leather and each set is fitted with trinkets, some of which are brass like royal crowns, stars, crescents, while others are formations of polished or woven copper pieces. They suffered from deterioration factors and aspects such as thin green, blue and black layers of corrosion products, calcareous spots and missed parts. The selected artifacts consist of three objects as the following feedback. The first object is concerned with the eyeglasses from domo Alalai Set: A horse head has two glasses made from black leather with braided brass mastric and *on it the crown and on top of it are a lock and buckle, and on the head generally some brass motifs, including the crescent and crown, and the head has a part of glossy black leather on which a brass circle is attached to it by the crown and crescent and bears the name of a posthole speed 6, No.152, as seen in Figs 7a,b,c*. The different parts of the object suffered from the deterioration aspects of the substances such as a thin green/black layers. *The second object is concerned with the Al-Hanbal jacket (The bells): it consists of a leather strip fixed on it ten bolls (small bells) made of Brass alloy. The metallic state of the bells is very good, but they suffered from existing of a thin layers of corrosion products consists of the metal corrosion products mixed with the dirt's, dust from the leather Fig. 8*. The third object is concerned with the saddle: it consists of block leather fixed on it a group of five rings, key, two crowns and belts made of Brass alloy. The metallic state of the group is very good, but they covered with layers of corrosion products consists of corrosion products of

metal mixed with the dirt's, dust from the leather see Figs. 9, 10a, b, c.



**Figs. 7a, b, c** shows the different parts of the glass before treatment: (A) show the glass of the horse head, (B) show the buckle and (C) show the crown



**Fig. 8:** show Al-hanbal jacket before treatment



**Fig. 9** shows the saddle before treatment





**Figs. 10 a, b, c** shows the different metallic parts of the saddle before treatment

### 3.2.2. Examination and Analysis

OM, SEM and EDS examinations and analysis were utilized to examine the surfaces morphology and microstructure of the artifacts, deterioration creations were analyzed by XRD method. The examinations and analysis were performed as the following:

#### 3.2.2.1. Light Microscope

Optical microscope was used to understand the kind of leather by hair follicles see [Figs. 11, 12, 13 and 14](#).



**Fig. 11:** OM examination for a sample from the crown of the glass shows the deterioration aspects dispersed on the metal surface such as thin green/black layers of corrosion products and pitting



**Fig. 12:** OM examination for a sample from the buckle of the glass shows the deterioration aspects dispersed on the metal surface such as thin green/black layers of corrosion products



**Fig. 13:** OM examination for a sample from Al-Hanabal (the bells) shows the deterioration aspects

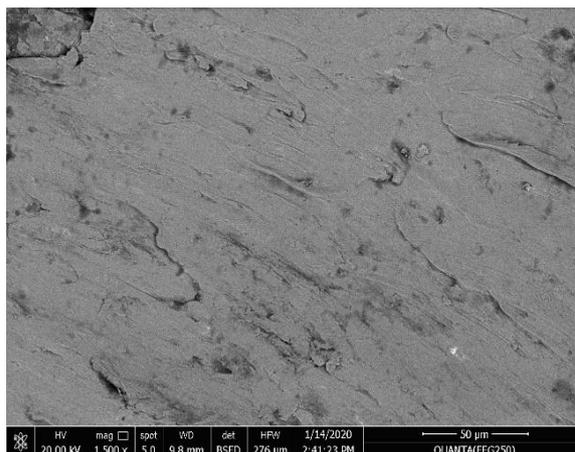
dispersed on the metal surface such as thin green/black layers of corrosion products and pitting corrosion



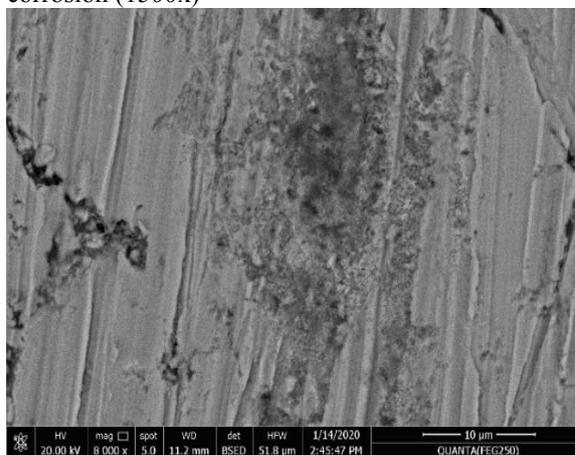
**Fig. 14:** OM image for the saddle shows the deterioration aspects on the surface of saddle

### 3.2.2.2. Scanning Electron Microscope & Energy Dispersive Spectrometry (SEM&EDS)

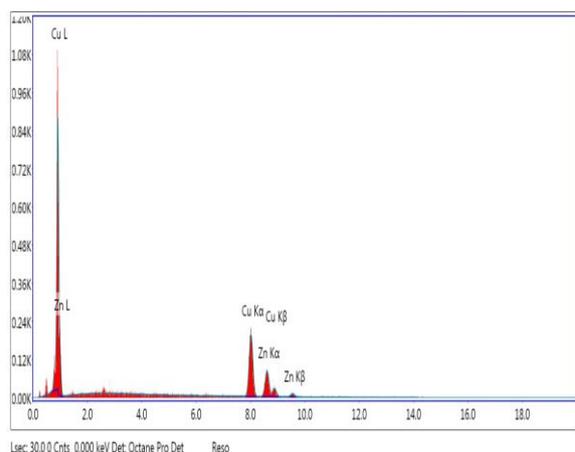
SEM&EDS examinations were detected the microstructure, the emergence of deterioration spots and the chemical arrangement of the substances, analysed by using an Inspect S50 (FEI). Figs. 15- 21 show SEM examinations and EDS of the tested objects. Fig. 15 shows the SEM ex., of the crown and the white grains of zinc dispersed in the alloy, Fig. 16 a crossed section shows the distorting and micro cracks dispersed in the alloy of the buckle and Fig. 17 shows SEM&EDS Scan for the glass metallic parts shows the constituents of the composite. Fig. 18 shows SEM examination for a sample from Al-Hanabal (the bells) shows the stress and pitting corrosion dispersed on the metallic surface of and Fig. 19 SEM&EDX Scan for Al-Hanabal (the bells) shows the constituents of the alloy [41]. Fig. 20 SEM examination for a sample from the saddle shows the stress and pitting corrosion dispersed on the metallic surface and Fig. 21 SEM&EDX Scan of the saddle shows the constituents of the composite. The chemical arrangement of the metallic components of the formed items from EDS results are recorded in Table 1.



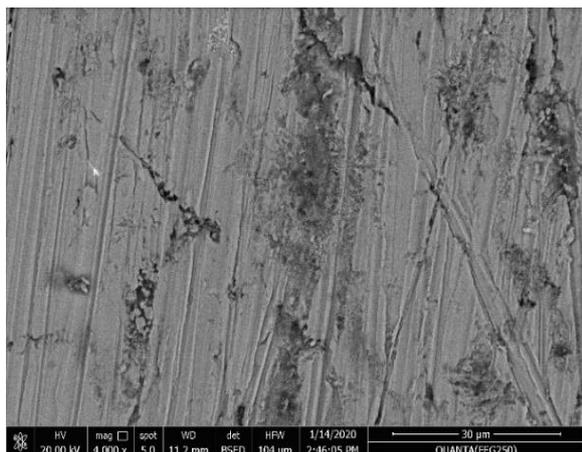
**Fig. 15:** SEM image of the crown shows the white globules of zinc dispersed in the alloy and stress corrosion (1500x)



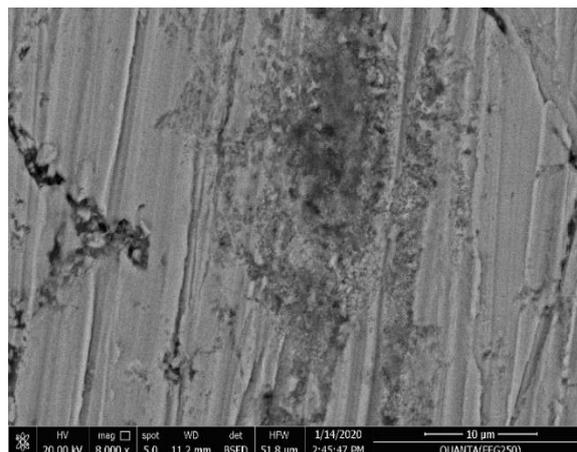
**Fig. 16:** SEM image of the buckle shows a crossed section shows the stress corrosion caused micro cracks dispersed in the alloy zinc dispersed (3000x)



**Fig.17:** EDX Scan for the glass metallic parts shows the constituents of the alloy

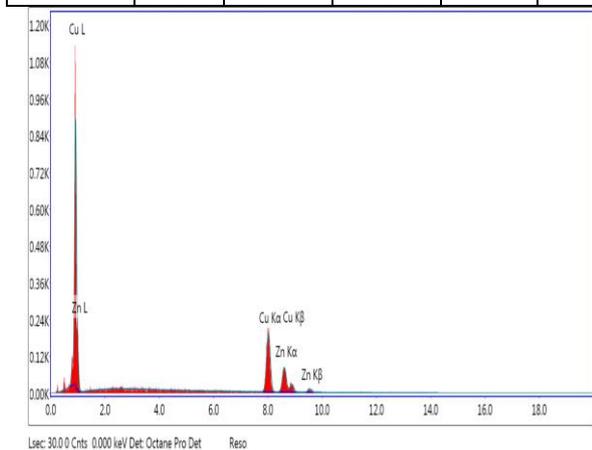


**Fig. 18:** SEM examination for a sample from Al-Hanabal (the bells) shows the stress and pitting corrosion dispersed on the surface of metal

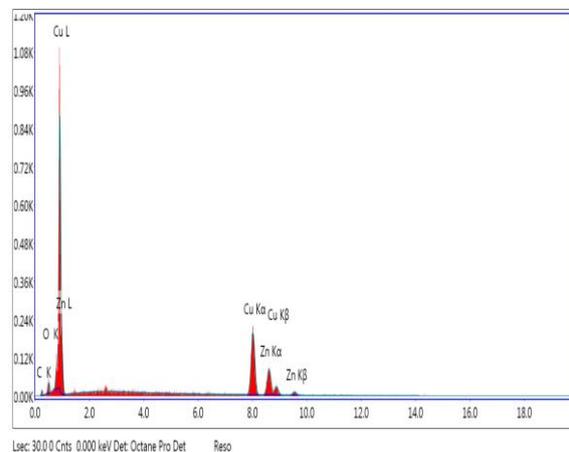


**Fig. 20:** SEM examination for a sample from the saddle shows the stress and pitting corrosion dispersed on the surface of metal

| The objects            | Element | Weight% | Atomic% | Net Int. | Error% |
|------------------------|---------|---------|---------|----------|--------|
| The head glass         | Zn      | 21.74   | 21.26   | 16.1     | 14.62  |
|                        | Cu      | 78.26   | 78.74   | 108.24   | 4.12   |
| Al-Hanabal (the bells) | Zn      | 21.6    | 21.12   | 15.88    | 15.62  |
|                        | Cu      | 78.4    | 78.88   | 107.72   | 4.3    |
| The saddle             | C       | 7.57    | 27.41   | 3.87     | 25.3   |
|                        | O       | 4.77    | 12.98   | 9.98     | 19.46  |
|                        | Zn      | 19.93   | 13.26   | 17.89    | 14.33  |
|                        | Cu      | 67.72   | 46.35   | 108.42   | 4.13   |



**Fig.19:** SEM&EDX Scan for Al-Hanabal (the bells) shows the constituents of the alloy

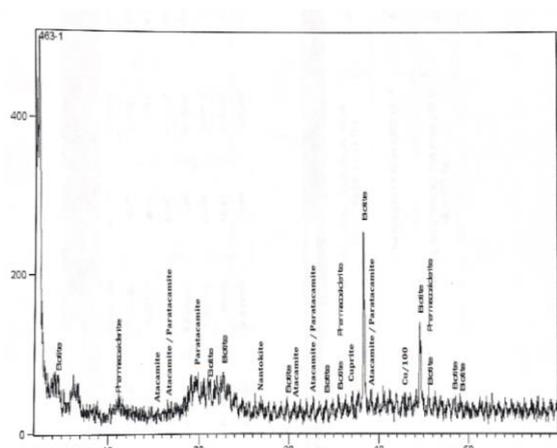


**Fig. 21:** SEM&EDX Scan of the saddle Shows the constituents of the alloy

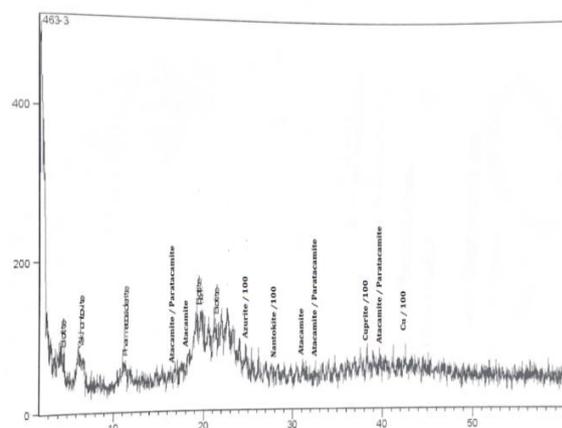
**Table 1:** shows the chemical composition of the Metallic parts of the objects formed from EDS results

### 3.2.2.3. X-Ray Diffraction Analysis

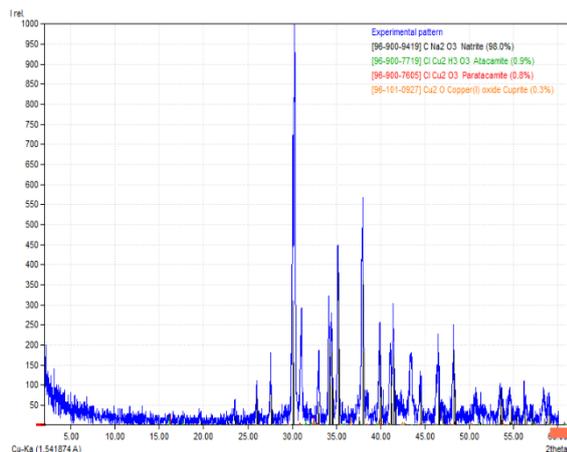
A sample from corrosion product of the item was analysed by using a Philips X-ray Diffractometer with Cu  $K\alpha$  radiation. The objective of this assessment is identification the corrosive combinations to choose whether it is reliable, steady, and appropriate to confident types of preservation behaviour. These data is able to assist in selecting the most excellent environmental display or storage for the objects. The obtained diffraction-scan given in [Figs. 22-24](#) and the identified compounds represented in [Table 2](#).



**Fig. 22:** XRD Scan for the glass metallic parts shows the composition of corrosion products



**Fig. 23:** XRD Scan for Al-Hanabel (the bells) shows the composition of corrosion products



**Fig. 24:** shows XRD scan for the corrosion products of the saddle

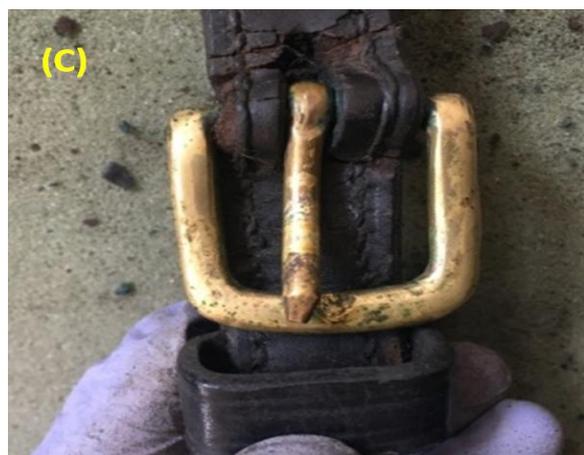
**Table (2)** shows XRD analysis results of corrosion products of the objects

| Samples                  | Compounds   |   |   |
|--------------------------|---|---|---|
|                          | Major   | Minor   | Traces  |
| The glass metallic parts | Paratacamite/<br>$\text{Cu}_2(\text{OH})_3\text{Cl}$<br>Atacamite/<br>$\text{Cu}_2(\text{OH})_3\text{Cl}$ | Nantokite/<br>$\text{CuCl}$<br>Cuprite/<br>$\text{Cu}_2\text{O}$  | Baiolet   |
| The Hanabal (the bells)  | Paratacamite/<br>$\text{Cu}_2(\text{OH})_3\text{Cl}$<br>Atacamite/<br>$\text{Cu}_2(\text{OH})_3\text{Cl}$ | Nantokite/<br>$\text{CuCl}$<br>Cuprite<br>$\text{Cu}_2\text{O}$   | Azurite/<br>$\text{Cu}_3(\text{CO}_3)(\text{OH})_2$<br>Copper /Cu |
| The saddle               | Natrite<br>$\text{Na}_2\text{O}_3$  | Atacamite<br>$\text{Cu}_2(\text{OH})_3\text{Cl}$<br>Paratacamite<br>$\text{Cu}_2(\text{OH})_3\text{Cl}$ | Cuprite $\text{Cu}_2\text{O}$                                     |

#### 4. Treatment and Conservation

Examinations and analysis proved that the objects have a good metallic state, but it was covered with dense deposits of rust products. The objects were subjected to mechanical cleaning with toothbrushes to remove dry dust and dirt. After that, an adhesive of occasioned scribble and water was used by a smooth fabric to remove the residual rouge of corrosion products. The objects were washed carefully using distilled water and dried; finally, they were isolated with TTA + SLS (Figs. 25-27).





**Figs. 25 a, b, c:** show the components of the head glasses after treatment



**Fig. 26:** show Al- Hanabal (the bells) after treatment



**Fig. 27:** show the saddle after treatment

### 5. Mode of Action

An electrical potential between the Cu and Zn, in the attendance of water, oxygen and other impurities causes an exchange of electrons resulting in intergranular corrosion, which weakens the brass and makes it especially susceptible to stress damage. Any attempt to reshape brass, such as dent removal or straightening, without prior heat treatment will result in distortion and damage, especially if corrosion-related micro-fissures already exist. Because brass must be heat-treated before working, any specific orientation in the substance due to original manufacturing techniques will be obliterated [43]. In the selective corrosion, corrosion processes cause exclusion of one and only element of alloy. A typical model of this type of deterioration is dezincification of brass, when part of the initial material, alloy of Zn and Cu, turns to spongy copper. Dezincification plays its starring role in the development of corrosion cracking of brass. All brasses having Zn content higher than 15 wt. % incline to dezincification; the process of dezincification lies in dissolution of Cu and Zn and Cu subsequently re-deposits. The dezincification often happens in waters containing chlorides and is a frequent cause of failing of the brass fittings in water circuits [44]. In this case, the corrosion is described to as discriminating corrosion. SEM examination showed the white globules of zinc dispersed in the alloy and stress corrosion, which caused micro cracks dispersed in the alloy. Stress corrosion cracking (SCC) is typical especially for brass but is less for other copper alloys. The effect appears under tension stress above a certain limit in a polluted (industrial) atmospheric environment, especially when it contains ammonium compounds. SCC affects copper alloys containing 20% or more zinc, but only rarely the other alloys [45]. The EDS qualitative analyses proved the objects were manufactured from brass alloy Table 1. As zinc content increases the brittle, ( $\beta$ ) phase begins

to appear and thus alloys with additional 50% zinc are generally avoided. Beta ( $\beta$ ) phase brasses are very much tougher than the alpha and can withstand very little cold working. The phases begins to soften at about 470°C (as the lattice changes from an ordered to a disordered state), and at about 800°C it becomes much easier to work. According to the Cu–Zn phase diagram, the solubilization of Zn in Cu can be as high as approximately 32.5 wt. %, brass composites in this assortment ( $\alpha$ -brass) are flexible, simply chilly-functioned, can be trundled into slim layers and have good deterioration opposition in a saline media [46, 47]. In general, copper, and brass alloys are highly resistant to atmospheric corrosion anticipated to the development of protective panes of rust products, which reduce the level of attack. Thickness and configuration of the rust products layer formed are governed by the relative humidity and pollution of the environment [48]. The characterization of the corrosion products of the objects by X-ray diffraction analysis revealed the existence of different minerals including Natrite  $\text{Na}_2\text{O}_3$ , Atacamite  $\text{Cu}_2(\text{OH})_3\text{Cl}$ , Paratacamite  $\text{Cu}_2(\text{OH})_3\text{Cl}$  and traces from Cuprite  $\text{Cu}_2\text{O}$  Table 2. The formation of Natrite  $\text{Na}_2\text{O}_3$ , Atacamite  $\text{Cu}_2(\text{OH})_3\text{Cl}$ , Paratacamite  $\text{Cu}_2(\text{OH})_3\text{Cl}$  and traces from Cuprite  $\text{Cu}_2\text{O}$  resulted from the interaction between the surrounding environment and the objects. The existence of basic copper chloride (Atacamite, Paratacamite) are related to the saline environment of the surrounding medium, whereas the objects were preserved. Paratacamite always found as powdery, light green secondary rust layers on the patina surface, while the compound of Atacamite occurs as a sugary-looking coating of dark green glistening crystals [49]. Often, this dark green crystalline atacamite is altered to a paler green powdery product of paratacamite [50, 51]. Cuprite is the most widely occurring alteration mineral of ancient Cu and its alloys. Most of it was concealed beneath overlying green basic salts of copper. It is formed because of reaction in the middle of the metallic surface and the existed oxygen in every environment but in different proportions. The corrosion product on the brass ancient objects is created by  $\text{Cu}_2\text{O}$  (Cuprite) and  $\text{CuO}$  (Tenorite). The metal/ interface oxide layer is relatively irregular and in a few inter-granular dispersions can be discovered. The incidence of natrite [ $\text{Na}_2\text{O}_3$ ] as a major compound on the saddle surface is most probably developed by the interaction in the middle of the metallic parts and the leather. Cleaning is one and only of the extremely familiar operations in conservation. The choice of method for cleaning depends on what is required from the item, what is made of, and the condition. It is known that the mechanical cleaning of metals is the preferred technique for eliminating disfiguring corrosion. It permits extra control and has less influence on the

metallic alloy surface. Mechanical cleaning was carried out for removing the external crust corrosion products; the objects were subjected to mechanical cleaning with toothbrushes to remove dry dust and dirt. After that, an insert of hastened scribble and water was used by a smooth fabric to remove the residual rouge of rust products. Finally, all the objects were isolated with TTA + SLS.

## 2. Conclusions

- Sulfide ions decrease the tolytriazole inhibitory activity against brass corrosion in chloride media. The magnitude of the effect depends on both species' relative concentrations. The real transients show complex associations on the brass surface between the injected sulfide ions and the TTA. An order of magnitude increases in sulfide ion concentration at a given concentration of TTA increases the sulfide attack rate by more than one order of magnitude. On the opposite, an order of magnitude increases in TTA concentration lowers sulfide attack rate by only around one third. Extended brass surface repassivation in the presence of TTA does not increase its resistance to attack by sulfides.
- SEM and XRD results show the occurrence of selective localized or general chlorine corrosion phenomena induced also by the separation of the alloy formation elements, which creates reactive electrochemical areas.
- The morphology of the surfaces and the elemental compositions of the rust products depend strongly on the chemical arrangement of the alloys.
- It is a great need to study corrosion phenomena of metal artifacts by simple and accelerating test procedures to develop proper methodologies to arrest or avoid further deterioration.
- There is a need for continued research on inhibitors for controlling corrosion and on methods to improve their adherence to a metal substrate especially for both patinated and unpatinated copper alloys and to find new non-toxic and effective compounds to be used instead of toxic corrosion inhibitors.
- A successful way to evaluate quantitatively newly selected compounds for arresting the cycle of  $\text{CuCl}_2$  corrosion was noticed to be the test procedure using brass coupons covered with a coating of nantokite and cuprite to assess brass corrosion inhibitors.
- The efficacy of the selected compounds as inhibitor for corrosion has been ranked BTA

> MBI > MBT > MBO > DB > AMT > MP > AP. The only new inhibitor that worked well was MBT, only marginally less effective than BTA. However, MBT caused the coupons to yellow, which drastically altered the presence of the corroded sheet. Due to ineffectiveness, poor visual appearance and/or damage to chloride-corroded coupons, no new corrosion inhibitors can be recommended.

- Such treatment disadvantages may be found on brass coupons that are artificially corroded, making it unnecessary to initially apply new compounds to batches of archeological products. This rapid corrosion check is a preliminary screening tool on ancient Cu and its alloys for prospective restoration treatments. It helps, too. Scientists to quantitatively compare the usefulness of inhibitor therapies or coating techniques. For this corrosion check more compounds will be evaluated in the future to be capable to substitute BTA for an inhibitor that causes less color change and is more successful on objects containing significant quantities of copper chloride corrosion.

### 3. Conflicts of interest

The authors declare that they have no conflict of interest.

### 4. Formatting of funding sources

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