Synergistic effects of corrosion inhibitors for copper and copper alloy archaeological artefacts

S. Golfomitsou and J. F. Merkel

Abstract

Benzotriazole (BTA) is one of the most widespread treatments used at present for the stabilisation of bronze disease. Unfortunately, BTA does not always work effectively when applied to heavily corroded copper and copper alloy archaeological artefacts. Combinations of corrosion inhibitors are extensively used in industry to retard copper corrosion. When two or more corrosion inhibitors are used, the inhibition efficiency of the mixture may be improved. This paper presents data that indicate the mixture of BTA with other inhibitors for chloride-containing corrosion products improve corrosion prevention under accelerated testing conditions. The six selected compounds. 5-Amino-2 Mercapto-1, 3, 4-Thiadiazole (AMT), Benzylamine (BZA), Ethanolamine (ETH), 1-Phenyl-5-Mercapto-Tetrazole (PMT), Potassium Ethyl Xanthate (KEX) and Potassium Iodide (KI) were tested individually and in combination with BTA. Factors such as concentration of the solution, time of immersion and solvent (de-ionised water, and ethanol) were examined. The inhibitors were applied initially on artificially corroded copper coupons and accelerated corrosion tests were assessed. The treated coupons were analysed using Scanning Electron Microscope (SEM-EDS) to examine the effects of such combinations. The results indicate that the combination of BTA with AMT improves the inhibitive efficiency at lower concentrations with ethanol or deionised water as a solvent. Finally, the combinations of BTA with AMT and BTA with PMT were applied on archaeological objects from the excavations of Kaman Kalehöyuk in Turkey and Mochlos in Crete, Greece. Treated objects have been monitored on an annual basis to investigate their long-term performance.

Keywords: Benzotriazole, 5-Amino-2 Mercapto-1, 3, 4-Thiadiazole, copper corrosion inhibitors, synergistic effect, accelerated corrosion testing.

1: Introduction

Although a number of chemical compounds can be used as corrosion inhibitors for copper, only a few have been tested for conservation and even fewer are currently in use. Research related to inhibitors for copper is largely dependent on industrial research. Unfortunately, inhibitors used in industry where copper is relatively free of corrosion have different aims and restrictions than those in conservation. For example, corrosion products can be viewed as part of the object's history and also often constitute a part of or even the whole of an object. The use of inhibitors for

conservation is also restricted by factors such as composition alterations, colour changes, toxicity and inhibitor film stability.

The main corrosion inhibitor used for the stabilisation of copper and copper alloy archaeological artefacts is benzotriazole ($C_6H_5N_3$); a nitrogen-containing organic heterocyclic compound. Benzotriazole (BTA) was first used by Madsen in 1967 and has been used widely in the field since then (Madsen, 1967: 163-166). For years the use of BTA was based on empirical assessment and the application methodology varied accordingly.

Although the inhibition of copper corrosion using BTA is one of the most thoroughly investigated processes, there is no comprehensive theory on its exact mode of action. Different analytical methods such as XPS, FT-IR, SERS, SIMS and electrochemical methods have been employed to examine the formation and protective action of the copper-BTA complex. BTA acts as a cathodic inhibitor retarding the cathodic reactions and as it has been also reported it acts predominantly as an anodic inhibitor (Dugdale and Cotton, 1963, Fox et al, 1979, Fiaud 1995).

Another controversy concerning BTA regards the properties of film formation. The film formed can be the result of either physisoption or chemisorption. BTA is thought to be physically adsorbed on the surface reacting with copper to form a polymeric film that acts as a physical barrier (Poling, 1970). Another theory is that BTA is chemisorbed on the metal surface and the film that is formed mainly prevents the adsorption of oxygen and slows down, or stops the initial corrosion reaction of

copper: $2Cu + O_2 \leftrightarrows CuO_2$ (Mansfeld *et al.*, 1971: 293).

BTA efficiency as well as film formation depends on a number of factors including the pH of the solution. In low pH values the adsorption of BTA on copper is weakened (Musiani and Mengoli, 1987: 201). This might explain why BTA fails to inhibit corrosion of heavily corroded copper artefacts where the pH level is very low, such as in the case of pitting and active bronze disease.

Brusic *et al.* (1991) reported that BTA increases the corrosion potential, retarding the corrosion rate of copper. This implies that benzotriazole primarily blocks the exodus of copper ions and acts as a barrier to oxygen diffusion. The kinetics of the film formation, its thickness and the degree of polymerisation depend on the pH of the solution. In very acidic solutions (pH<2) a thick film (up to 25 nm) grows quickly following a dissolution-precipitation mechanism and, as such, the polymerisation is not complete. Therefore, although the film is thick, it is not that protective. At a pH of around 7, the film grows more slowly in a self-inhibiting manner. It is thinner (0.5-4 nm) and is completely polymerised providing the best protection. Therefore the degree of protection is found to be proportional to the degree of polymerisation. Finally different oxides give different films, and the structure of the film is dependent on the copper oxides formed (Brusic, 1991: 2253).

Archaeological artefacts are often covered with thick corrosion layers that hinder access to the remaining metal. The corrosion products often include anions such as chlorides or chloride containing corrosion products (i.e. nantokite) that impede inhibition. These anions contribute to a low pH (<3.5) resulting in a less effective partly polymerised film.

The aim of this paper is to examine whether the combination of different compounds could improve the effectiveness of BTA when treating archaeological copper and copper alloy artefacts. The properties of complex corrosion product compositions are beyond the range of BTA control alone.

In industry, it is very common to use more than one chemical compound to retard the corrosion process of a metal or alloy. When two or more corrosion inhibitors are added to a corrosive environment of a metal or an alloy, the inhibition efficiency of the mixture may be greater than the sum of each one of the additives. This is a synergistic effect (Rozenfeld, 1981: 110).

There are obvious benefits of the use of synergistic effects for the corrosion inhibition for archaeological copper and copper alloy artefacts. In most cases, the additives alone are not very effective inhibitors, but present good inhibitive properties when combined utilising different inhibitive features. For example, a combination of anodic and cathodic inhibitors could result in slowing down both the anodic and cathodic reactions of the electrochemical process.

The exact mechanisms of the synergism of inhibitors are not always clear. Some additives (e.g. halides) may modify the surface characteristics of a metal, assisting in the adsorption of the inhibitor. For example halide anions (Cl^-, Br^-, and I^-) act synergistically in the corrosion inhibition of iron, altering the properties of the surface, making possible the adsorption of organic cations on the metal surface (Kuznetsov, 1996: 40).

The combinations used have already been tested for industrial purposes. The selected combinations and their mode of action are shown in table 1.

Name	Formula	Mode of Action	*Main Advantages*	*Main Disadvantages*
Benzotriazole (BTA)	$C_6H_5N_3$	Cu-BTA complex	*Easy to apply, does not cause much colour change*	*Not effective on heavily corroded artefacts* *Not stable in acidic conditions* *Toxic*
2-Amino-5-Mercapto-1,3,4-Thiadiazole (AMT)	$C_2H_3N_3S_2$	Dissolve the Cl^-, forms a thin polymeric film	*Effective in very low concentrations*	*Causes colour alterations* *Moisture sensitive compound* *Toxic*
1-Phenyl-5 Mercapto-Tetrazole(PMT)	$C_7H_6N_4S$	Cu(I)-PMT complex	*Very good inhibitive properties in H_2SO_4*	*Possibly not effective in Cl^- containing environments*
Ethanolamine (ETH)	C_2H_7NO	Acts synergistically with BTA	*Not very effective when used alone*	*Toxic*
Benzylamine (BZA)	C_7H_9N	Acts synergistically with BTA forming mainly cupric compounds	*Not very effective when used alone*	*Toxic*
Potassium Ethyl Xanthate (KEX)	$KC_3H_5S_2O$	Acts synergistically with BTA	*Effective inhibitor for copper*	*Toxic, Causes colour alterations*
Potassium Iodide (KI)	KI	Acts synergistically with BTA, different theories on its mode of action, formation of Cu(IBTA)	*It is not an inhibitor alone*	

Table 1. Inhibitors tested and their observed general effects.

2: Research methodology

In order to examine the synergism of BTA with other compounds for the inhibition of archaeological copper and copper alloys, experiments were undertaken in both laboratory and field conditions. The initial laboratory experiments were performed on clean and pre-corroded copper coupons for comparison. The effectiveness of the selected treatments was assessed using weight change measurement and accelerated corrosion tests in relation to the copper substrate (clean, corroded), the concentration of inhibitive solution and the time of immersion. The topography and distribution of the inhibitive compounds was investigated foremost Scanning Electron Microscopy-Energy Dispersive Spectrometer (SEM-EDS). Following this, the more effective combinations were tested on archaeological artefacts.

2.1: Coupon preparation

The preparation of standard coupons was imperative to obtain consistent and comparable results. Several researchers in archaeological conservation have tried to reproduce artificially pre-corroded specimens for laboratory experiments (Angelucci et al, 1978; Faltermeier, 1995; Brostoff, 1997; Brazil, 1999).
To keep margins of errors within the same scale for all experiments, the coupons used had the same composition, size, and shape. Electrolytic copper (99.9% Cu) coupons (20x50x1mm) were corroded and treated following the technique proposed by Faltermeier (1995) as an easily reproducible and reliable method for routine production of pre-corroded surfaces for testing inhibitors. The coupons were air-abraded with glass beads to remove surface oxides, degreased in acetone in ultrasonic bath, weighed (±0.0001g) and immersed in 25 ml of 1M aqueous cupric chloride solution (dihydrate $CuCl_2.2H_2O$ in deionised water) for 24 hours at an ambient temperature (20-25°C). The coupons were washed in deionised water for an hour (in three 20-minute baths of 100 ml for each coupon) and, after a quick immersion in ethanol, dried under an infrared lamp (approx. 50°C). Following this, the coupons were placed in an oven and exposed to 105 °C for an hour. Nantokite and cuprite corrosion products were formed on the surface as confirmed by X-ray Diffraction (XRD) analysis. XRD of the coupons was undertaken using a Siemens D5000 Theta/2 Theta X Ray Diffractometer at the Chemistry Department at University College London. For every experimental run, at least three coupons were chosen as the minimum number of replicates statistically required to assess possible errors (Carter, 1982: 27).
The clean copper coupons used for the testing were treated within a few hours of air abrasion and degreased in acetone ultrasonic bath.
Accelerated corrosion testing aimed to assess and compare the properties of the different compounds in a reproducible corrosive environment.
Humidity testing at 25°C and 95% RH (±5%) was undertaken in a Fisons climate chamber with a Eurotherm 910D dual loop thermostatic controller.
The evaluation of the treatments was based on weight-gain measurements. The assessment of the corrosion by means of weight changes is valid when applied to specimens with uniform corrosion, as was the case for the ones produced for the purpose of these experiments. The formation of corrosion products results in a net mass increase and the weight uptake is related to the thickness of the corrosion

(Heitz, 1992: 12). Consequently, the mass change over time is associated to the corrosion rate and can be measured using the following formula (Skerry, 1985: 5):

$$IE\% = [(CR-CR_i)/ CR] \times 100$$

Where
        IE is the inhibitive efficiency,
        CR is the weight changes of the untreated coupons, and
        CR_i is the weight change of the treated coupons.

Because of the humidity fluctuation in the chamber that could result in different corrosion rates of the exposed coupons, untreated control coupons were placed alongside the treated coupons and were used to calculate the inhibitive efficiency. It is remarkable how even small changes affect corrosion rates. The comparison of results of accelerated corrosion treatment testing is valid only if selected independent variables are controlled within known parameters (e.g. in attempt to control RH variation, coupons exposed to climatic chamber concurrently).
The treated coupons placed in the humidity chamber were monitored by weighing (±0.0001g) after 24, 48, 168, and 504 hours of exposure, and some at 840 hours.
The pH of aqueous solutions of the inhibitors used was measured to examine any relationships between the effectiveness of an inhibitor and the pH. A Corning pH meter 240 at the Chemistry Department of UCL was used. The values measured in the aqueous solutions are shown in Table 4.

SOLUTION	pH	COLOUR OF SOLUTION
BTA 0.1M, pure	5.8-5.5	Clear
BTA 0.1M,, 1h time of immersion	4.1-4.2	Clear, some green sediment
BTA 0.1M, 24h	3.5-3.6	Clear, some green sediment
BTA 0.1M, 1h/1h	4.1-4.0	Clear, some green sediment
BTA 0.1M, 1h/24h	3.5	Clear, some green sediment
BTA 0.1M, 24h/1h	3.7	Clear, some green sediment
BTA 0.1M, 24h/24h	3.2	Clear, some green sediment
BTA 0.01M, pure solution	5-5.1	Clear
BTA 0.01M, 1h	3.6-3.7	Clear, some green sediment at the bottom of the beaker
BTA 0.01M, 24h	2.75-2.8	Opaque/ light green
BTA 0.1M + AMT 0.01M, pure solution	4.1-4.2	Clear
BTA 0.1M + AMT 0.01M, 1h	4.1-4.2	Clear
BTA 0.1M + AMT 0.01M, 24h	3.9-4	Clear
BTA 0.01M + AMT 0.01M, pure solution	3.9-4.0	Clear
AMT 0.01M, pure solution	4	Clear
AMT 0.01M, 1h	3.3	Clear yellow with yellow sediment
AMT 0.01M, 24h	2.7	Yellow opaque, sediment
BTA 0.1M + ETH 0.1M, pure solution	9.6	Clear
BTA 0.1M + ETH 0.1M, 1h	9.6	Clear
BTA 0.1M + ETH 0.1M, 24h	9.5-9.6	Clear
ETH 0.1M PURE SOLUTION	11	Clear
ETH, 1h	10.7	Clear purple
ETH, (LOWER CONC.)	9.5	Purple
BTA 0.1M + KI pure solution	5.3	Clear
BTA + KI, 1h	4.3	Clear
BTA + KI, 24h	4.2	Clear
KI, PURE	7.0	Clear
KI, 1h	9.7	Whitish opaque and white sediment
BTA + BZA, pure solution	8.1	Clear
BTA + BZA, 1h	8.1	Clear
BZA, PURE	10.8	Clear
BZA, 1h	10.2	Semi-opaque with light green sediment
BTA + KEX, pure solution	7.4	Yellow/semi-clear
BTA + KEX, 1h	7.4	Yellow/ semi-clear
BTA + KEX, 24h	7.4	Bright yellow, semi opaque

Table 4. pH values of aqueous solutions of the inhibitor treatments.

3: Experimental design

The inhibition process is complex and affected by many interrelated variables. To evaluate each variable individually as well as, the interactions between the different variables, statistically designed experiments were employed. This way the effect of the variables and their interactions could be assessed using balanced experiments. One of the advantages is that possible experimental errors could be easily detected (Box et al, 1978: 7). The experiment outcome or response used to evaluate the results was the weight change % which is inversely proportional to the effectiveness of a treatment. In general, the higher weight uptake represents the less effective treatment.

The variables chosen were: additive with BTA solutions, concentration (of both BTA and the other compounds), time of immersion and solvent. The inhibitor concentrations selected were the ones recommended in the literature. Higher concentrations were also tested, because theoretically the more corroded an object, the higher inhibitor concentration is needed in order the treatment to be effective for archaeological copper alloys.

Minitab 12.1 was used for the experimental design and analysis. Small factorial experiments are very useful as they can reduce the amount of experiments needed by showing which factors have a significant effect in the process and which do not. The effect and the evaluation of the examined factors as well as possible interactions between factors are expressed in graphs based on mathematical formulae (Montgomery, 1997: 228).

Table 2 shows the colour changes of the copper coupons after the treatments.

Treatment	Clean copper	Pre-corroded copper	Comments after 840-hour exposure of pre-corroded copper coupons to 95±5%RH, 25°C
BTA 0.1M/H_2O	No colour changes/Metallic appearance	No colour changes although some transparent spots due to the slow evaporation of water can be seen.	Coupons covered with 'bronze disease' corrosion.
BTA 0.1M/EtOH	Metallic appearance. Some transparent inhibitor sediment at 24 hours of immersion	Coupons turned dark green.	Coupons covered with 'bronze disease' corrosion (but film still adhered on the surface).
BTA 0.25M	Metallic appearance. Some transparent inhibitor sediment at 24 hours of immersion	Coupons turned dark green with a lighter olive green residue.	'Bronze disease' overall, film still adhered on the substrate.
BTA + AMT	Coupons keep metallic appearance.	No colour changes except some few green or yellowish spots.	Surface darkened and there are some areas of 'bronze disease'.
BTA + BZA	Metallic appearance after 1h of immersion, but covered with a semi-transparent green layer after 24 h of immersion.	Coupons became slightly darker.	Only few areas of 'bronze disease' on coupons.
BTA + ET	Coupons immersed for 1h keep metallic appearance. After 24h immersion, they are almost wholly covered with a green layer.	Coupons became darker. At 24 hours of immersion there is a semi-transparent residue.	'Bronze disease' overall, film not adhered on substrate.
BTA + KEX	Coupons lose metallic appearance. Covered with a dark green/black/iridescent layer. After 24 h of immersion the film is flaking.	Coupons did not change colour after 1 h of immersion, but became slightly darker brown and yellowish after 24 hours.	Bronze disease overall, film not adhered on substrate.
BTA + KI	The coupons keep metallic appearance when immersed for 1h in all combinations. After 24h of immersion there is deposition of a light green semi-transparent residue.	The coupons become darker especially the BTA 0.25M and KI 0.1M were brown with some light yellowish brown residue.	The inhibitor film turned green and it is flaking and not well adhered on the substrate.
BTA + PMT	The coupons keep their metallic appearance.	Slight darkening of the surface which is more prominent after 24 h of immersion.	Coupons covered with a flaking layer of the film and there is BD overall the surface.

Table 2. Observations on colour changes induced by the selected treatments.

4: Results of Accelerated Corrosion Testing

4.1: BTA and AMT

AMT was tested as a corrosion inhibitor for archaeological copper and copper alloy artefacts by Ganorkar *et al.* (1988), Faltermeier (1995) and Uminsky and Guidetti (1995).

Ganorkar *et al.* proposed that AMT first reacts with copper chloride found on the metal surface and dissolves all the chlorides from the corrosion products. Following this, a thin polymeric layer is formed where copper ions are bonded to the sulphur (Ganorkar *et al.*, 1988: 97-100).

Uminsky and Guidetti (1995) tested AMT as a reagent to dissolve chloride ions from artificially corroded bronze plates and found that it cannot effectively remove copper chloride. They also stated that treated coupons appeared discoloured; grey-green with brown spots (Uminsky and Guidetti, 1995: 274-278). This is in direct contrast to earlier results (Ganorkar *et al.*, 1988: 97-100).

Faltermeier (1995) also tested AMT on artificially corroded copper coupons as well as on archaeological copper alloy artefacts and found that its inhibitive efficiency varied in different values of relative humidity. AMT was more protective than BTA, when tested for 24 and 48 hours at 95% relative humidity but it was less effective than BTA at long-term tests at similar RH values. He also mentioned colour changes on the copper surface, after the treatment. Copper coupons appeared to be brown-yellow. The discoloration was greater in higher concentrations and for immersion longer than 24 hours.

Ganorkar et al suggested that heavily corroded objects should be treated with both AMT and BTA. Faltermeier (1995) also used both AMT and BTA for the stabilisation of objects but not concurrently with satisfactory results (Ganorkar: 1988, Faltermeier: 1995).

Three factors were initially taken into account: the BTA concentration, the presence of AMT and the solvent. The factors and their levels (values) are shown in table 3. The results indicate that for the first 504 hours of exposure the most important factor is AMT whilst both BTA concentration and solvent are insignificant. After that both the concentration and the solvent become significant. Still the combination of BTA and AMT resulted in higher inhibitive efficiency throughout the exposure.

Factors / Level	-1	1
BTA	0.01M	0.1M
AMT	No	0.01M
Solvent	Water	Ethanol

Table 3. Factors and the values of their levels for the BTA-AMT experiment

Another set of experiments examined the combination of the inhibitors in relation to the concentration of BTA (0.25M and 0.1M) and the time of immersion (1 and 24 hours). All combinations of BTA with AMT were found to be highly effective. In all cases the BTA efficiency improves. From those the best was found to be the treatment of 0.25M BTA with 0.01M AMT immersed for one hour.

Graph 1 shows the average inhibitive efficiency of the different BTA-AMT treatments
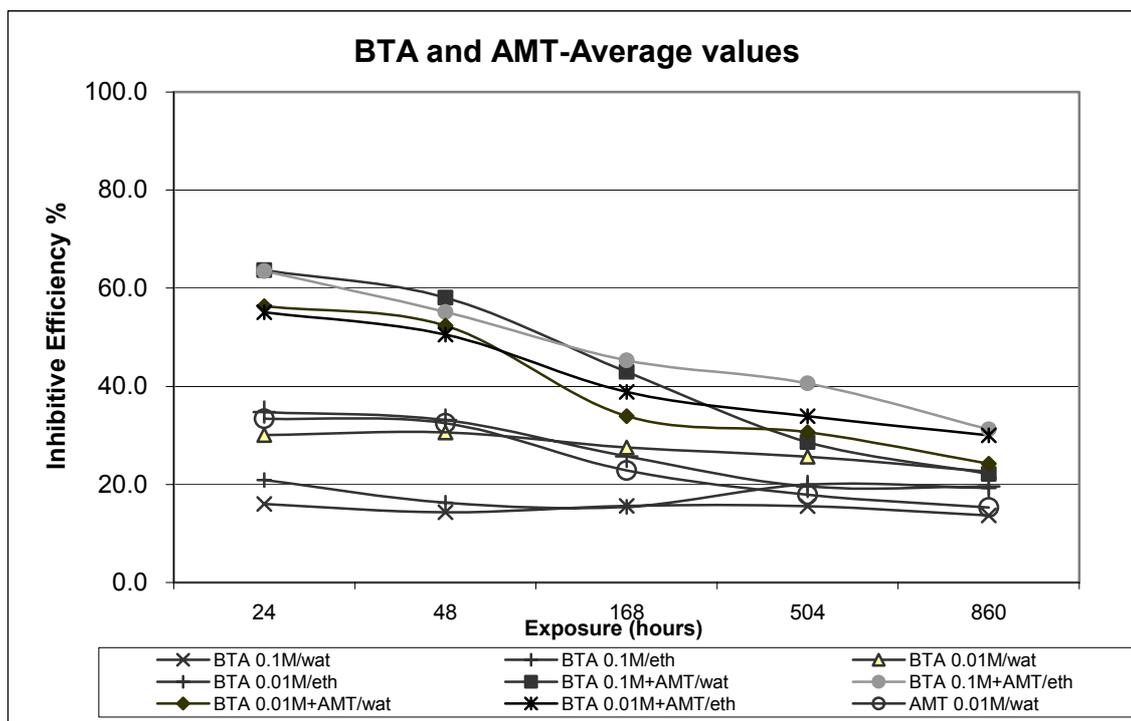
Graph 1. Average values of inhibitive efficiency for the BTA-AMT combinations.

4.2: BTA and BZA

In contrast, from the accelerated corrosion testing one can conclude that the combination of BTA with BZA had a negative effect on the inhibitive process. Instead of slowing down the corrosion of copper, it actually caused acceleration of the corrosion rate. Another disadvantage of this mixture was the colour changes caused on copper, especially in higher concentrations. After 24 hours of immersion, clean copper lost its metallic appearance due to the precipitation of a green residue, whilst the corroded coupons turned darker.

Although the pH of the solution was slightly alkaline after the addition of BZA (pH $\approx$ 8), the inhibitor film formed was not protective. Fleischmann et al (1985) suggest that BZA added to BTA solutions influences the kinetics of the film formation, one which is formed faster is less porous and highly protective. Since they did not find any adsorption of BZA on copper, it therefore affects the formation of the film itself (Fleischmann et al: 1985).

The analysis of the experimental designs confirms that whilst both BTA and BZA are significant in the inhibition process, BTA increases copper corrosion resistance but the presence of BZA causes an increase in the corrosion rate. The results were similar even when higher concentrations of both BTA (0.25M and 0.1M) and BZA (0.1M) in ethanol were used. The adjustment of pH to near neutral or slightly alkaline values did not result in the formation of a protective inhibitor film in this case.

4.3: BTA and ETH

Similarly to BZA, ethanolamine results in faster film formation when added into BTA solutions. BTA-ETH films were found to be more stable than those of BTA alone retarding both the anodic and cathodic corrosion reaction of copper (Wang and Zhang, 1987).

The presence of ETH in the BTA solutions adjusted the pH to alkaline values (9.5-10) affecting the process by decreasing the weight uptake. Still, the presence of inhibitive efficiency of the BTA-ET mixture was not much different than that of the BTA alone. The analysis of the results showed that there is no significant interaction between the inhibitors. In higher concentrations this mixture was less effective than BTA alone.

4.4: BTA and KEX

The presence of KEX into BTA solutions in a chloride containing environment was found to form a more compact film causing shifting of corrosion potential towards more positive values. Also, the presence of KEX results into a hydrophobic surface impeding the reacting of copper with moisture from the environment. The Cu-KEX film is porous with small holes that can result in local corrosion. The presence of BTA seals these holes creating a more protective layer (Gonzalez et al, 1993).

The experimental results of the 0.01M BTA and 0.01M KEX in deionised water, showed a slight improvement in the BTA effectiveness, however this dropped dramatically after 168 hours of exposure into 95±5 %RH. Similarly, in higher concentrations the overall efficiency was similar or less than that of BTA alone. Graph 2 illustrates the inhibitive efficiency of BTA, KEX and their combination.
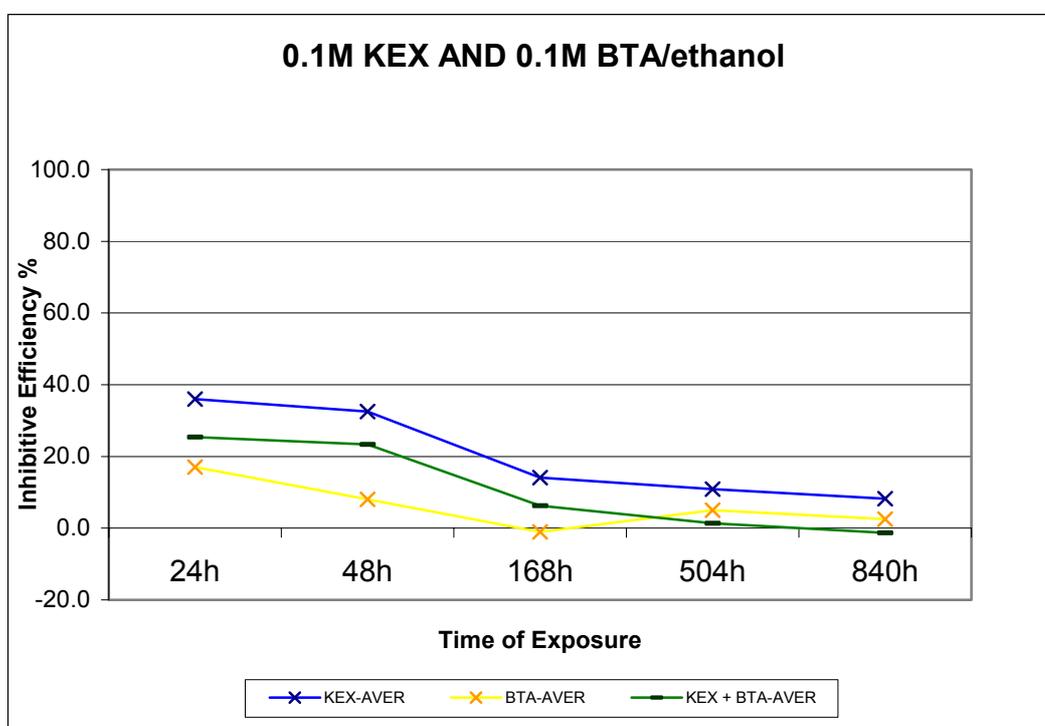
Graph 2. Inhibitive efficiency % for 0.1M BTA and 0.1M KEX and their combination in ethanol.

Moreover, the presence of KEX caused considerable colour alterations of the metal coupons.

4.5: BTA and KI

Wu et al (1993) suggested that the presence of iodide ions in the BTA solution improves the adsorption of the inhibitor on copper. The presence of KI in the BTA solution results in the formation of a thicker polymeric Cu(IBTA) film affecting the anodic reaction (Wu et al, 1997).
The combination of BTA with KI was tested taking three factors into account: BTA concentration, KI concentration and solvent (deionised water and ethanol). The experiments showed that the results and the possible synergistic effect between BTA and KI depend on their concentration and the solvent used. Consequently, the treatment of copper with this combination can lead to improved inhibition or increase of the corrosion rate. The mixture of 0.1M BTA with 0.01M KI in deionised water increased the efficiency of BTA, whilst in other cases the mixture accelerated corrosion. When a higher concentration of BTA was used, the presence of KI did not cause any significant effect in the process.

4.6: BTA and PMT

PMT reacts with cuprous ions to form a complex insoluble and compact film (Ye et al, 1998). PMT is a compound with low solubility in water. It was decided to test PMT alone and within BTA solutions to test possible synergism. PMT alone presented a good inhibitive efficiency, close to that of BTA (although a little bit higher). The combination of the compounds did not result in increased efficiency (0.005M was used for both inhibitors). When higher concentrations of BTA (0.1 and 0.25M) and PMT (0.1M) in ethanol were used, the results indicated that BTA alone is more effective than the mixture. There is no observed synergism between the compounds.

4.7: Colour changes

Table 2 shows the colour changes observed on the coupons after the treatments with the respective solutions. Some of the treatments are not acceptable for conservation purposes as they alter dramatically the colour of the copper/copper oxide. Still it is obvious that factors such as the time of immersion affect both the film formation and the colouration of the surface. In general, it was found the higher the time of immersion, the more the colour alteration. Some treatments caused total loss of the metallic appearance of the clean coupons especially in higher concentrations (e.g. KEX)
All the experiments performed on both clean and pre-corroded copper coupons. No results were obtained from the clean coupons, as the testing time (35 days) and the type of accelerated corrosion test used (humidity test) were not sufficient for this purpose. Still the application was valid for analytical purposes.

4.8: SEM-EDS analysis of copper-inhibitor complexes

The analysis took place on both clean and pre-corroded coupons and examined the same factors examined in the accelerated corrosion tests. The analysis carried out at the Wolfson Scientific laboratories of the Institute of Archaeology, UCL using a JEOL JSM-35CF with Link ISIS microanalysis system. The aim of the analysis was to obtain information regarding the topography and the structure of the copper-inhibitor films. The samples were not carbon-coated as the coupons were treated with organic compounds (inhibitors). Linescans were taken (elemental analysis across a line) which provided information about the distribution of the elements in comparison to copper.

From the images it is evident that some inhibitors follow the crystal formation of the corroded copper surface, forming a thin film (e.g. AMT, BTA, ETH), whilst in others (BZA, KEX, KI, PMT) the copper crystals are not distinctive anymore, as the surface is covered with a thick porous non-uniform layer. Figures 1-3 illustrate SEM images of corroded copper coupons treated with BTA, BTA and AMT and BTA and KEX respectively (Figs. 1-3).
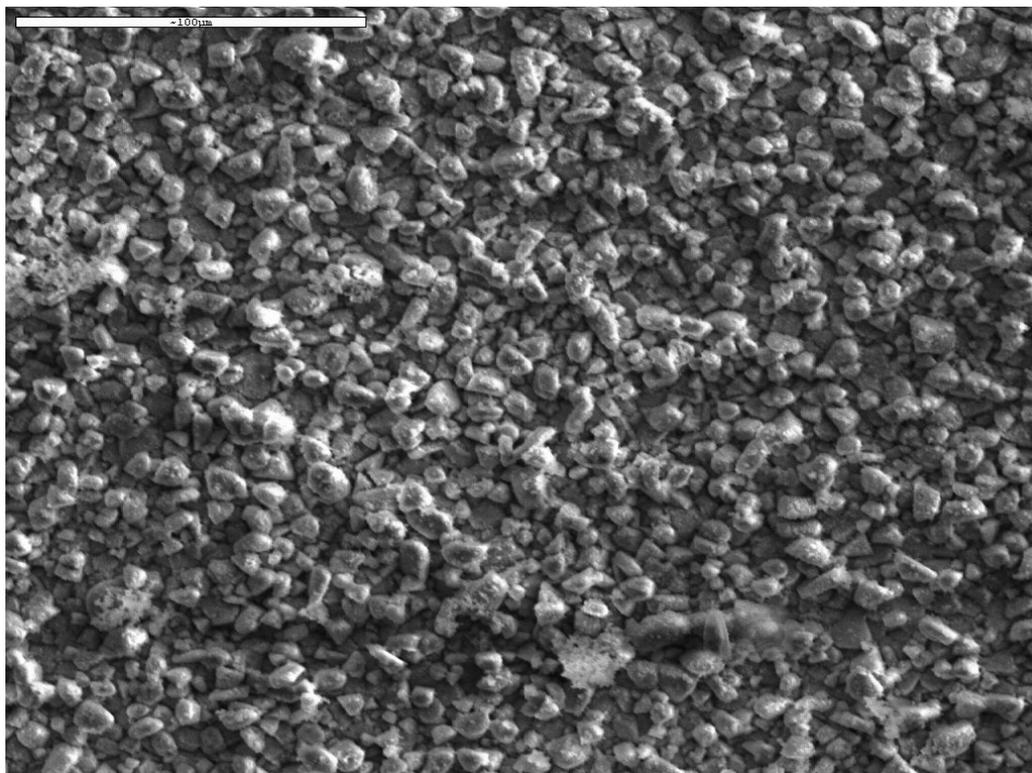

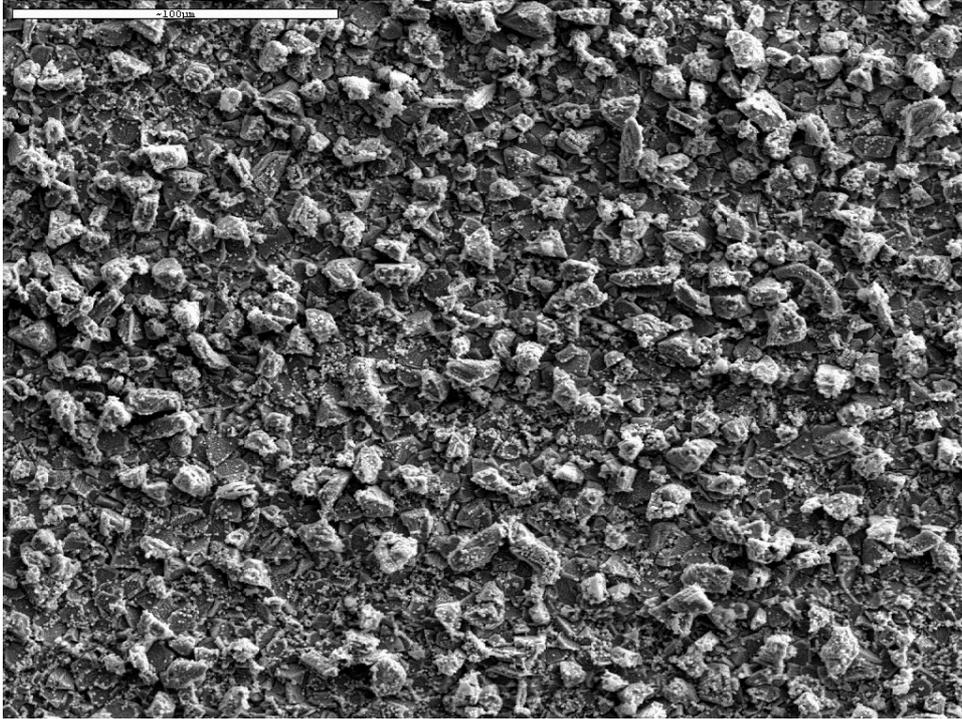Figure 1: Corroded copper treated with 0.1M BTA in ethanol.

Figure 2: Corroded copper treated with 0. 1M BTA and 0.1M AMT in ethanol
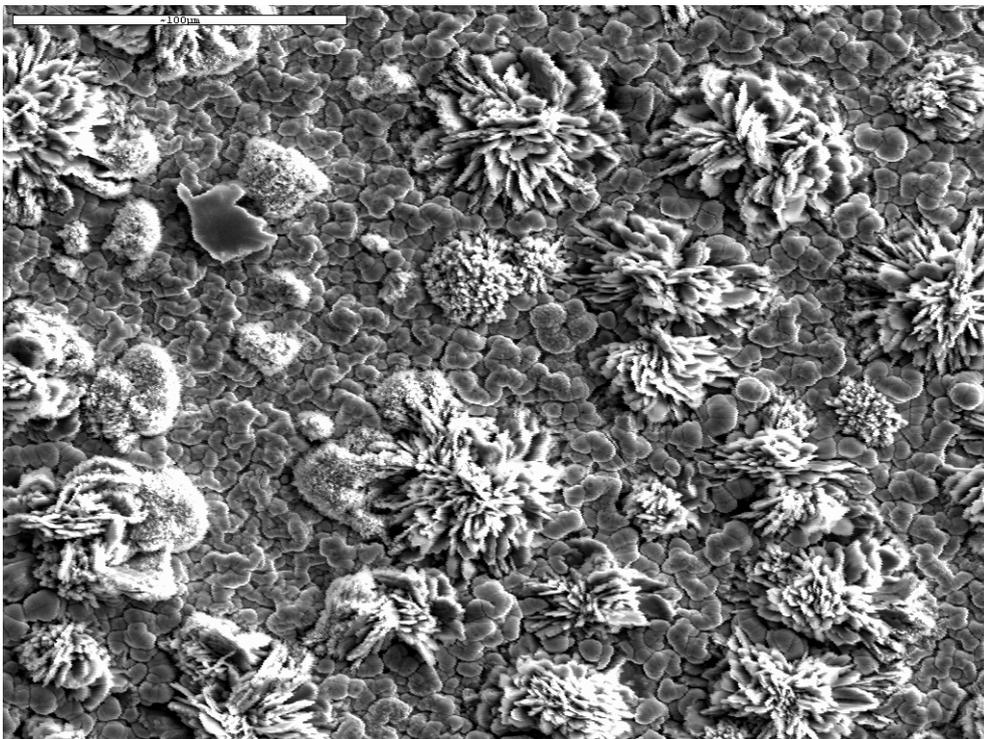

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Figure 3: Corroded copper treated with 0.1M BTA and 0.1M KEX in ethanol

In the linescans the inhibitor film is represented by the elements it contains (e.g. C, N, S, K, I). Their distribution in comparison to copper shows that in general they follow the topography of the surface. In case of KI applied on copper, the distribution of I follows copper in reverse, when copper is low, I is high. The same was found on the linescans of the combination of BTA and KI. In case of BZA, carbon is distributed in a thicker layer, without following the copper, whilst the its combination of BTA shows both C and N following the copper distribution, which could be an indication about the complex formed. Similar results were found in the ETH and BTA and ETH combination, whilst KEX shows a better distribution of C, N and S in relation to copper both when applied on each own and in combination with BTA (Graph 3).

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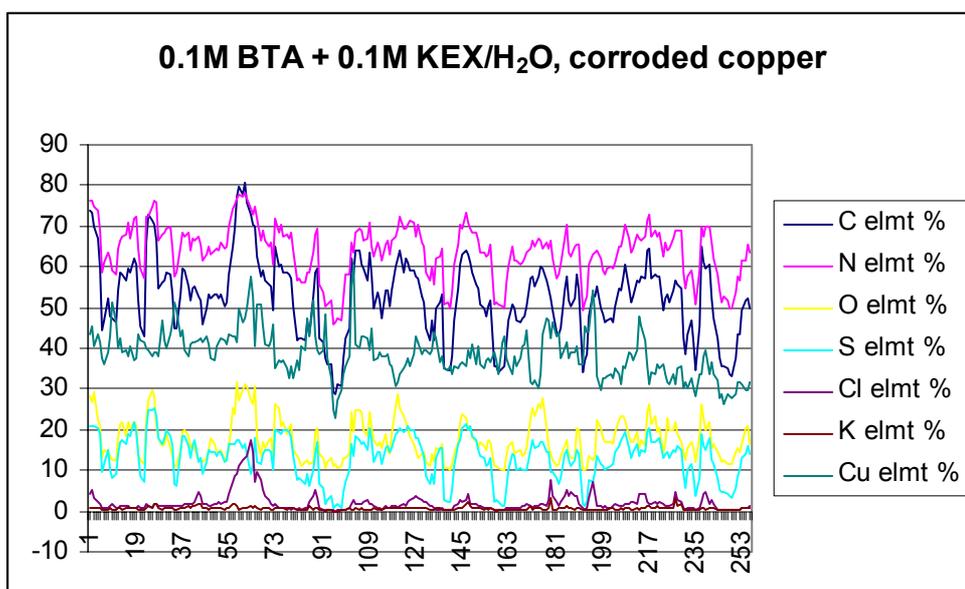
Graph 3. Linescan of 0.1M BTA and 0.1M KEX in deionised water, time of immersion 1h, superimposed elements

AMT linescans show a very low content of sulphur, whilst the BTA and AMT combination presents a better distribution of C, N as well as higher concentration of sulphur.

5: Testing of selected inhibitors on archaeological artefacts

The archaeological sites of Mochlos, Crete in Greece (Minoan period) and Kaman Kalehöyük, Turkey (dating from early Bronze Age to the Ottoman period) were chosen for the testing of inhibitors. Both sites have brought to light a significant number of copper alloy objects most of which are found heavily corroded. The site of Mochlos is located close to the sea and the soil has very high chloride content, whilst Kaman Kalehöyük is inland with alkaline environmental conditions which also result in poor preservation of metal artefacts (Merkel: 2002, Omura, S: 2000, Soles, : 2004).

Following the experimental results from the laboratory experiments, the inhibitors and inhibitor combinations which performed best (BTA and AMT, AMT, BTA and PMT, PMT) were applied on archaeological copper/copper alloy objects. The objects were mechanically cleaned and treated with the solutions then subjected to high relative

humidity (approx. 100%) for 24 hours. All the objects were heavily corroded and suffered from bronze disease.

Because of the complexity of the corrosion forms and diversity of the corrosion products present, weight changes were not valid in this case.

A method that is used is by choosing one form of corrosion in a fail/pass test (e.g. if an object presents bronze disease signs, the treatment fails). The method chosen for the evaluation was based on the visual observation of the objects under stereomicroscope recording bronze disease signs. The simple nominal scale (or fail/pass test) was of little use in this case as it does not give an objective picture about the treatment. The degree of the new corrosion is of greater importance. Consequently, a scale was created taking into account not only the presence of bronze disease but also the extent of bronze disease outbreaks on an object.

Clearly, the scale cannot take into account all the factors affecting the result. However, the number of the objects used (e.g. 10 for each treatment at Kaman Kalehöyük tests) can give a close approximation about the efficiency of the treatments.

The scale has 4 levels depending on the extent of bronze disease outbreaks found on the objects. The evaluation of a treatment takes into account both the number of objects with bronze disease and the severity and extent of the active corrosion (number of pits).

Each level (table 5) has a different number of significance. The evaluation takes place by multiplying the number of objects at each level by the number of significance and finally the numbers from each level are summed. The final number is a subjective way to assess how effective a treatment is and it is valid only when compared to experiments carried out under the same conditions and evaluated using the same scale and method.

The results were analysed using one-way ANOVA (Analysis of Variance).

Level	Degree of corrosion	Degree of significance
I	Minimum BD outbreaks (up to 4 small spots)	1
II	Few BD spots (>4)	2
III	BD in a larger extent	3
IV	BD overall	4

Table 5. Scale used for the evaluation of the testing on archaeological copper and copper alloys from Kaman Kalehöyük.

5.1: Kaman Kalehöyük

The testing took place during two summer field seasons (July-August 2000 and 2001). The objects selected came from different strata and periods. Some of them were freshly excavated and not treated before, whilst others had been excavated in past years and previously treated with BTA (3% in 1:1 ethanol:water) under vacuum. Most of the objects selected were bronzes. XRD analysis on six bronze fibulae performed by Twilley showed tenorite (CuO), cuprite (Cu_2O) and cassiterite (SnO_2) (Twilley, 1996: 239). XRF analysis on some of the objects showed leaded bronzes.

The procedure followed was the same as the treatment protocol of the lab, established by G.Wharton.

The objects, after mechanical cleaning, were classified into three groups, depending on the degree of corrosion. The first class included objects in good condition with metal core present, the second class included more corroded objects that had some metal core left, and the third class included heavily corroded objects most of which were totally mineralised, but still showing active corrosion.

The objects were cleaned mechanically, degreased in acetone for one hour and immersed in the inhibitor solutions. The application methodology followed in the lab is to immerse the objects for 3 hours under 40mmHg vacuum (Wharton, 2000). Some groups were treated using the same procedure, whilst others were only immersed in the solutions for one hour to examine if the application methodology affects the result. To eliminate experimental errors because of the diversity in factors such as composition, corrosion forms and products, the treatments were applied in batches of 10 objects (3, 3 and 4 from each class). The objects were photographed and all the observations from the treatments were input into a database designed purposely.

After the treatment, the objects were subjected to high RH (approx. 100%) for 24 hours to evaluate the treatment efficiency. After the testing, the objects were allowed to dry, they were then photographed and examined under a stereomicroscope for outbreaks of bronze disease.

The treatments tested, observations after the immersion into the inhibitive solutions (i.e. colour changes), the number of objects in each group with bronze disease and the evaluation of the treatments (ranking) can be seen in table 6.

Group	Treatment	Factors examined	Colour changes after treatment	Number of objects with BD	Ranking
VI	BTA 0.1M + AMT 0.01M/EtOH	Synergism BTA-AMT, BTA concentration, solvent, application	No colour changes	0/10	**0**
VII	BTA 0.1M + AMT 0.01M/H$_2$O	Synergism BTA-AMT, BTA concentration, solvent	No colour changes	4/10	**6** (2xI and 2xII)
XXI	BTA 0.25M/EtOH	BTA concentration, solvent used, application	Darkening of the surface, few BTA crystals on surface	7/10	**8** (6x1 and 1xII)
VIII	BTA 0.25M + AMT 0.01M/EtOH	Synergism BTA-AMT, BTA concentration, application		7/10	**9** (5xI and 2xII)
XVIII	BTA 0.1M + AMT 0.01M/H$_2$O	Synergism BTA-AMT, BTA concentration, solvent	No colour changes	6/10	**12** (2xI, 2xII and 2xIII)
XIX	BTA 0.01M + AMT 0.01M/EtOH	Synergism BTA-AMT, BTA concentration, solvent	No colour changes	9/10	**13** (5xI and 4xII)
IX	BTA 0.1M + PMT 0.1M/EtOH	Synergism BTA-PMT, BTA concentration	White inhibitor residues that was easily brushed off	8/10	**14** (3xI, 2xII, 1xIII and 1xIV)
XVII	BTA 0.1M + AMT 0.01M/EtOH	Synergism BTA-AMT, BTA concentration, solvent, application	No colour changes	7/10	**15** (2xI, 3xII, 1xIII and 1xIV)
XIV	BTA 0.1M/ EtOH	BTA concentration, solvent used, application	No colour changes	7/10	**17** (2xI and 5xIII)
III	BTA 0.25M/ EtOH	BTA concentration, solvent used, application	Darkening of the surface, some BTA crystals formed on the surface	9/10	**19** (1xI, 6xII and 2xIII)
II	BTA 0.1M/H$_2$O	BTA concentration, solvent used, application	No colour changes	9/10	**20** (1xI, 3xII, 3xIII and 2xIV)
XVI	BTA 0.25M + AMT 0.01M/EtOH	Synergism BTA-AMT, BTA concentration, application		10/10	**20** (3x1, 4xII and 3xIII)
I	BTA 0.1M/ EtOH	BTA concentration, solvent used, application	Slight darkening	9/10	**23** (1xI, 3xII, 4xIII and 1xIV)
XX	BTA 0.01M + AMT 0.001M/ H$_2$O	Synergism BTA-AMT, BTA concentration, solvent	No colour changes	9/10	**23** (2xI, 2xII, 3xIII and 2xIV)
XIII	BTA 0.1M/H$_2$O	BTA concentration, solvent used, application	No colour changes	9/10	**24** (3xI, 3xIII and 3xIV)
IV	AMT 0.01M/EtOH	AMT, application		9/9	**26** (1xI, 2xII, 3xIII and 3xIV)
V	PMT 0.1M/EtOH	PMT	Surface covered with a thin white layer (which was brushed off)	10/10	**26** (1xI, 4xII, 3xIII, 2xIV)
XII	Controls (XII)	-	-	10/10	**27** (Ix2, 3xII, 1xIII and 4xIV)
XI	Controls (XI)	-	-	8/9	**29** (3xIII and 5xIV)

Table 6. Ranking of the treatments tested at Kaman Kalehöyük using the scale indicated in Table 5. The factors examined, colour changes and the number of objects with bronze disease are also shown.

As aforementioned the number given in the ranking column is not an absolute
number. This number represents the extent of corrosion after the exposure and the
lower the value, the more effective the treatment. The treatments on table 6 are placed
according to their efficiency, starting from the most effective treatment and finishing
with the least effective (which in this case are the two control groups).
There was only one group of objects that did not have any signs of active corrosion.
This is group VI in which the objects were treated with the combination of BTA 0.1M
and AMT 0.01M in ethanol (applied by immersion for 3 hours, under vacuum). Group
VII treated with the same combination in the same concentrations but using de-
ionised water as a solvent presented very good inhibition with only four out of ten
objects having bronze disease. From the results one can see that all the factors tested
(time of immersion, the application methodology, concentration of the solution,
solvent and combination of inhibitors) affect the process.
These results are in agreement with the results obtained from the laboratory
experiments where again the combination of BTA 0.1M with AMT 0.01M in both
ethanol and water as solvents performed the best (see graph 1). During summer
fieldwork season of 2001,a survey was conducted for the objects treated during
summer 2000, this confirmed a continued the level of success regarding these
treatments.
For the purposes of this research the objects were not covered with a protective
coating. They are currently stored in silica gel containing polyethylene boxes.

5.2: Observations/colour changes

BTA is known to cause darkening of the surface. Because of the time of immersion
used (1 and 3 hours) no colour changes were observed, with the exception of 0.25M
where the objects darkened slightly. Also some of the objects treated with BTA
0.25M had BTA crystals formed during drying. These were removed by swabbing
with ethanol. These crystals were not observed on objects treated with lower BTA
concentrations.
The treatments of BTA and AMT did not induce colour changes, except where
nantokite was exposed where there was a yellowish precipitant which was brushed off
easily.
The objects treated with PMT were covered with a thin whitish precipitant which was
swabbed off with ethanol. The objects treated with the combination of BTA and PMT
showed the same white precipitant.

5.3: Mochlos

This project took place in two phases, the first of which was completed in 1999 and
included the documentation and cleaning of the selected objects and the second was
the application of the treatments and was carried out during August 2000. Only the
combination of BTA with AMT in two different concentrations was tested on this site.
The objects (CA-108 and CA-109) were mechanically cleaned and were stored for
one year without any treatment to observe if any signs of new corrosion would
appear. Although the objects were stored in a specially designed room for the storage
of metals with a controlled environment (dehumidifier set at 35-45 % RH and 18-
20°C) they presented extensive bronze disease after one year.

Figure 4: The CA-108 and CA-109 bronze bowls were found one inside the other. The objects were seperated during mechanical cleaning and were treated with the BTA and AMT

The powdery corrosion products were removed mechanically and the objects were immersed for 24 hours in the inhibitive solutions. No great colour changes were noticed except for the yellowish precipitation where nantokite had been exposed. Following this, the objects were exposed to higher RH (approx 100%) for a further 24 hours. None of the objects presented any signs of new corrosion. The objects were not covered with a protective coating and were stored as in the previous year. Unfortunately, during the winter of 2002-2003 the dehumidifier broke down for an unknown period of time causing damage to most of the metal artefacts stored in there. The objects were examined during July 2003 and it was found that CA-109, treated with BTA 0.1M and AMT 0.01M in ethanol, had only a few signs of active corrosion. CA-108 presented extensive active corrosion (figure 5). However, CA-108 had more nantokite and than CA109. Nonetheless, these objects were found in a better state than the untreated objects.

The objects were cleaned and degreased in acetone and were re-treated by a one-hour immersion in a BTA 0.1M and AMT 0.01M solution in ethanol. No signs of active corrosion were observed during the 2004 survey.

Figure 5: CA-108 after the treatment with BTA and AMT.

6: Conclusion

This paper is an assessment of experiments undertaken to investigate the synergism between selected inhibitive compounds. Based upon industrial publications, all the combinations tested had the potential to increase the inhibitive efficiency of BTA. However, the use of some of them was found to be ineffective, and in some extreme cases, the corrosion rate was increased after the treatment. There are various reasons that suggest the use of concentration and combinations are outside the effective range for the particular case. Depending on their mode of action, inhibitors can sometimes cause acceleration of the corrosion process if used in unsuitable concentrations (either higher or lower than required).

However, from the aforementioned results it is apparent that the combination of BTA with AMT increases the inhibitive efficiency of BTA. The concentration required is less than that commonly used in conservation (3% w/v). The use of water as a solvent can also be of great advantage in conservation, as it is less volatile, therefore safer for the user. Another advantage is that the cost is minimised with the use of both smaller concentrations of the inhibitors and the use of de-ionised water as a solvent.

These experiments investigated the use of different characteristics of chemical compounds to improve the BTA efficiency for archaeological copper and copper alloy objects. The results showed that there is a lot of potential when using the synergism between different inhibitors. Even the less effective combinations could be effective when used in different concentrations.

One of the main drawbacks of the use and combination of corrosion inhibitors for archaeological copper alloys is their toxicity. In these experiments, use of BTA and other additives has followed health and safety protocols for toxic substances.

More research is necessary to examine more combinations and to utilise more characteristics that might lead to more successful treatments. The research should focus more on new, less toxic, inhibitors that could retard corrosion. There are compounds that could be tested and could be effective inhibitors either on their own or in combination with other additives.

Scientific analysis carried out using FT-IR, XPS and Cyclic Voltammetry examined further how several factors affect the Cu-BTA complex formation as well as Cu-BTA-additives reactions and film formation. The results of the analysis will be presented in a future publication.

The archaeological objects treated with the BTA and AMT will be monitored in future years at Kaman Kalehoyuk and Mochlos to examine their performance in the long term. Field trials under real conditions and in real time will show if the initial results were accurate, and where research should focus next.

Materials

BTA, copper chloride and PMT were supplied by Sigma-Aldrich, AMT by Fluka, KEX by Lancaster, BZA and ETH by BDH.

Minitab 12.1 was used for the statistical design and analysis of the experiments. Link-ISIS was used for the SEM-EDS analysis.

References

Madsen, H B, 1967. A Preliminary Note on the Use of Benzotriazole for Stabilizing Bronze Objects, *Studies in Conservation,* **12**(4), 163-166.

Dugdale, I and Cotton J B, 1963. An Electrochemical Investigation on the Prevention of Staining of Copper by Benzotriazole, *Corrosion Science*, **3**, 69-74.

Fox, P G, Lewis G and Beden P J, 1979. Some Chemical Aspects of the Corrosion Inhibition of Copper by Benzotriazole, *Corrosion Science*, **19**, 457-467.

Fiaud, C, 1995. Inhibition of Copper Corrosion. The Complementary Role of Oxides and Corrosion Inhibitors. *Proceedings of the 8th European Symposium on Corrosion Inhibitors (8SEIC)* , 929-49, Ferrara, Italy.

Poling, G W, 1970. Reflection Infrared Studies of Films Formed by Benzotriazole on Copper (or Cu), *Corrosion Science*, **10**, 359-70.

Mansefeld, F, Smith T, and Parry E P, 1971. Benzotriazole as Corrosion Inhibitor for Copper, *Corrosion*, **27**, 289-294.

Musiani, M M, Mengoli G, Fleischmann M, and Lowry R B, 1987. An Electrochemical and SERS Investigation of the Influence of pH on the Effectiveness of Some Corrosion Inhibitors of Copper, *Journal of Electroanalytical Chemistry,* **217**, 182-202.

Brusic, V, Angelopoulos M, and Graham T, 1997. Use of Polyaniline and Its Derivatives in Corrosion Protection of Copper and Silver, *Journal Of the Electrochemical Society*, **144**, 436-442.

Rozenfeld, I L, 1981. *Corrosion Inhibitors*. USA: McGraw-Hill Inc.

Kuznetsov, Y I, 1996. *Organic Corrosion Inhibitors of Metals*. New York: Plenum Press.

Angelucci, S, Fiorentino P, Kosinkova J, and Marabelli M, 1978. Pitting Corrosion in Copper and Copper Alloys: Comparative Treatment Tests, *Studies in Conservation*, **23**, 147-156.

Faltermeier, R B, 1995. *The Evaluation of Corrosion Inhibitors for Application to Copper and Copper Alloy Archaeological Artefacts*. PhD Thesis, University College London, London.

Brostoff, L.B. 1997. Investigation into the interaction of Benzotriazole with copper corrosion minerals and surfaces. In Metal 1995. MacLeod, I.D., Pennec, S.L., Robbiola, L. (ed). James and James.

Brazil, R. 1999. Corrosion inhibitors of archaeological iron. PhD thesis, Institute of Archaeology, UCL, London.

Carter, V.E. 1982. Corrosion Testing for Metal Finishing. Butterworths (Published in Association with The Institute of Metal Finishing).

Heitz, E. , Henkhaus, R. , and Rahmel, A. 1992. Corrosion Science, an Experimental Approach. (translators: Dr. Waterhouse, R.B, transl.editor Dr. Holnes, D.R.). England: Ellis Horwood Limited.

Skerry, B S, 1985. How Corrosion Inhibitors Work, in S Keene (ed), Corrosion Inhibitors in Conservation, *Occasional Paper*, **4,** 5-12.

Box, G.E.P. Hunter, W.G and Hunter, J.S. 1978. Statistics for experiments: an introductionto design, data analysis, and model building. John Wiley & Sons: New York.

Montgomery, D.C. 1997. Design and analysis of experiments. 4th ed. John Wiley & Sons: New York.

Ganorkar, M C, Panditrao V, Gayathri P and Sceenivasa Rao T A, 1987. A Novel Method for Conservation of Copper-Based Artifacts, *Studies in Conservation* **33**, 97-101.
1988,

Uminski, M, and Guidetti V, 1995. The Removal of Chloride Ions from Artificially Corroded Bronze Plates, *Studies in Conservation*, **40**, 274-278.

Fleishmann, M, Hill I R, Mengoli G and Musiani M M, 1983. The synergistic Effect of Benzylamine on the Corrosion Inhibition of Copper by Benzotriazole, *Electrochimica Acta* **28**, 1325-1333.

Wang, X. and Zhang, Y. 1987. The synergetic effect of Ethanolamine and Benzotriazole on the corrosion inhibition of copper. *In10th International Congress on Metallic Corrosion*, Vol. III, 2799-2806.

Gonzalez, S, Laz, M M, Souto, R M, Salvarezza, R C and Arvia, A J. 1993. Synergistic Effects in the Inhibition of Copper Corrosion. In *Corrosion*, **49**(6), 450-456.

Wu, Y C Zhang P Pickering H W and Allara D L. 1993. Effect of KI on Improving Copper Corrosion Inhibition Efficiency of Benzotriazole in Sulfuric Acid Electrolytes. *Journal of the Electrochemical Society*, **140**(10), 2791-2800.

Ye, X R, Xin, X Q, Zhu, J J and Xue, Z L. 1998. Coordination Compound Films of 1-Phenyl-5-Mercaptotetrazole on Copper Surface. In *Applied Surface Science*, **135,** 307-317

Merkel, J.F. 2002. Soil and corrosion research at Kaman Kalehöyük, progress report. In Kaman Kalehöyük 11. Anatolian Archaeological Studies, Vol. XI, Japan, 167-171.

Omura, S. 2000. A preliminary report on the 14th excavation at Kaman Kalehöyük. In Kaman Kalehöyük 9. Anatolian Archaeological Studies, Vol. IX, Japan, 1-35

Twilley, J. 1996. Scientific analysis of six bronze fibulae from Kaman-Kalehöyük. In Kaman Kalehöyük 5. Anatolian Archaeological Studies, Vol.V, Japan, 237-250.

Wharton, G.E. 2000, Kaman Kalehöyük, conservation lab protocol for the treatment of copper and copper alloys.

Soles, J.S. 2004. Mochlos IC: Period III. Neopalatial Settlement on the Coast: The artisan's quarter and the farmhouse at Chalinomouri. The small finds. The Institute for Aegean Prehistory Press, Prehistory Monographs 9.