CONSERVATION OF CORRODED COPPER ALLOYS: A COMPARISON OF NEW AND TRADITIONAL METHODS FOR REMOVING CHLORIDE IONS

Ian Donald MacLeod

Abstract—A comparison of new and traditional methods for stabilizing corroded copper alloy artifacts is presented, using data obtained from a variety of objects from both marine and land-based sites. The data show that there are common parameters that determine the rate at which chloride ions are removed. The choice of methods is discussed in terms of cost effectiveness and what patination changes are acceptable. The seven washing regimes, ranked in order of the rate of removal of chloride ions, show that alkaline dithionite is very much faster than thiourea-inhibited citric acid solutions, than 5 wt% sodium sesquicarbonate than 1 wt% benzotriazole than 50 vol% acetonitrile than 1 wt% sodium sesquicarbonate than distilled water. The effectiveness of the treatments in preventing 'bronze disease' is also discussed.

1 Introduction

Chloride ions are ubiquitous in the majority of archaeology sites, whether they are land-based or submerged. Corrosion of metal objects can occur in both aerobic and anaerobic micro-environments where chloride ions are involved in the fundamental nature of the corrosion process, either exerting an influence on the kinetics of the oxidation process or assisting through the formation of corrosion products [1-6]. Stabilization of artifacts after excavation is essential if the deleterious effects of moisture, increased oxygen supply and residual chlorides are to be minimized [7-10]. Because copper is a less reactive metal than iron, artifacts made of copper and its alloys are not as prone to dramatic damage, so the underlying corrosion problems have tended to receive relatively little attention.

Copper alloys are normally covered by a protective oxide film of the copper(I) oxide, cuprite (Cu_2O), which effectively slows down the overall corrosion rate [11, 12]. In the presence of chloride ions, pitting corrosion can occur when breaks in the oxide film or the build up of surface

scale change the nature of the surface [13]. The thermodynamic and kinetic stability of copper and its salts changes markedly with increasing chloride ion concentrations [5, 14]. As a metal oxidizes, the corrosion products and other adventitious materials can create a barrier to the free exchange of ions which effectively increase the chloride ion concentration at the metal surface to many times that in the overall environment [15, 16]. The increased chloride concentration within the artifact can lead to accelerated corrosion, which is readily seen when an object has 'bronze disease'.

Since its inception, the work of the conservation laboratories of the W.A. Museum has been primarily concerned with the stabilization of artifacts recovered from historic shipwrecks off our 3000km coastline. Since the majority of sites are well oxygenated and warm (mean water temperatures 17°-25°C), many of the 10,000 copper alloy artifacts were badly corroded and in need of immediate attention [17-20]. After a six-year research programme the corrosion products and corrosion mechanisms have been shown to be dependent on the composition of the alloy, the nature of the wreck site and the surface of the object [21]. With a knowledge of the above, it is now possible to predict how long any treatment will take and what changes in patination will take place during a treatment programme.

Since the major problem facing any comparative study is the marked variability of the extent of corrosion of artifacts, a set of 3600 'copper' sheathing tacks from the *Lively* (c. 1820 [22]) was examined in a series of controlled experiments. This paper reports the results of these experiments along with data from hundreds of other washing treatments. Apart from artifacts recovered from shipwreck sites, this work also shows that the stabilization of ancient Greek and Roman coins recovered from land sites is achieved using the same approach.

2 The *Lively* experiment

In 1983 some 6000 sheathing tacks were recovered from a wreck on the Rowley Shoals (16°20'S, 119°35'E), some 400km off the coast of north-west Australia. The site depth ranges from 10m to 2m and is subject to strong surges since the atoll bears the full brunt of the deep ocean swell. The water depth increases to 400m within 200m of the site. Since the mean sea-water temperature is 25·4 ± 1·6°C [23, 24] the long period of immersion, *c.* 160 years, combined with the well-oxygenated nature of the site should have produced good conditions for corrosion of the sheathing tacks [25–28]. In order to try to minimize the problems associated with other comparative studies, e.g. insufficient number of artifacts for statistically valid results and the problem of the variable nature of corrosion in apparently similar objects, a set of seven washing regimes using triplicate samples was established. Each plastic screw-top vessel contained two litres of solution and a constant weight of sheathing tacks (365·22 ± 0·48g) with a mean number of 164 ± 11 tacks. The wash solutions were sampled at regular intervals and analyzed for chloride and copper with periodic checks on the lead, tin and zinc concentrations. Chloride analyses were performed using a Buchler-Cotlove chloridometer and the metals were determined by atomic absorption spectrophotometry (VarianAA4). Periodic measurements of the solution pH and metal corrosion potentials were used to establish the aerobic or anaerobic nature of the wash solutions.

After development of the alkaline dithionite treatment method for corroded silver [29] it was decided to check on its efficacy as a way of stabilizing degraded copper, brass and bronze artifacts since experience with other media such as distilled water and sesquicarbonate had led to very long washing times [24]. The use of benzotriazole (BTA) as a standard treatment for copper-based artifacts is well established but there was little quantitative data in the literature to enable its effectiveness to be compared with other methods [30–33]. Increasing awareness of the hazards of long-term exposure to carcinogenic materials such as BTA [34] and its relatively high cost meant that alternative treatments could be of great value to conservators working with limited resources. Where restoration of patina is not of major importance, the use of thiourea*-inhibited solutions of citric acid needed to be investigated [35, 36], particularly in the post-stripping washing treatments, to see how much chloride is removed at each stage. The use of copper(I) complexing solutions, such as aqueous acetonitrile [37], needed clarification. Previous experiments on highly corroded brass have shown this to be a most efficient way of removing copper(1) chlorides from within the corroded metal-corrosion product matrix [24]. Finally, a comparison between deionized water, 1 wt% and 5 wt% sodium sesquicarbonate solutions was needed since these three solutions are commonly used in the conservation of copper, brass and bronze artifacts [38–41].

A total of eleven measurements was made on each solution at intervals which were close together at the start and up to two to three weeks apart towards completion of the 69-day wash. A set of typical data from each of the wash solutions is shown in Table 1. A quick perusal of the information shows up quite marked differences in the chloride ion concentrations in the washing solutions at any particular time. A convenient way to compare the data from various solutions is to plot the chloride concentration as a function of time, to see which solution is the most efficient at removing chloride ions. Previous reports have shown that in the most commonly used media, such as distilled water and sesquicarbonate solution, the chloride concentration is linearly dependent on the square root of the treatment time [42]. Characteristic plots of data from 5 wt% sesquicarbonate (no. 17) and deionized water (no. 7) are shown in Figure 1 where the chloride concentration increases monotonically until it reaches a plateau. When a plateau has been obtained, the wash solution is normally changed and the chlorides continue to diffuse out, but at a slower rate, until they establish a second plateau level as seen in Figure 2. A detailed discussion of the relationship between plateau levels and the chloride concentration gradient in the corroded artifacts will be given in a later paper.

Inspection of the data collected after two hours of washing (Table 1) shows that significant amounts of chloride have been released from the dithionite, citric acid and benzotriazole solu-

*Thiourea (Tu) is also known as thiocarbamide $SC(NH_2)_2$.

Table 1   Comparison of chloride release data from corroded 'copper'^{c} sheathing tacks, Lively (c. 1820)

Sample no.	Time (hr)	Deionized water [Cl] ppm (7)	Sesqui-carbonate 1 wt% [Cl] ppm (14)	Acetonitrile 50 vol% [Cl] ppm^d (2)	Sesqui-carbonate 5 wt% [Cl] ppm (17)	Benzo-triazole 1 wt%^{e} [Cl] ppm^d (4)	Citric acid 5 wt% [Cl] ppm (22)	Dithionite 5 wt% [Cl] ppm (19)
1	2	3	4	79	6	276	336	418
2	19	13	21	98	72	409	454	741
3	26	14	22	96	93	236	552	811
4	69	19	33	108	141	333	631	916
5	140	33	43	122	250	356	690	1180
6	166	52	57	136	290	431	697	1233
7	331	67	79	142	359	350	695	1240
8	451	75	84	153	396	40^a	698	555^a
9	786	88	96	153	428	55	122^b	499
10	1122	94	106	154	458	65	126	733
11	1652	92	108	141	460	78	173	143

(a) Solution changed at 331 hours.

(b) Solution changed at 451 hours to 1 wt% sodium sesquicarbonate.

(c) Composition of the sheathing tacks varied—see Table 2.

(d) Background corrections due to washing medium of 70 ppm and 40 ppm should be made to all data from 50 vol% acetonitrile and 1 wt% BTA respectively.
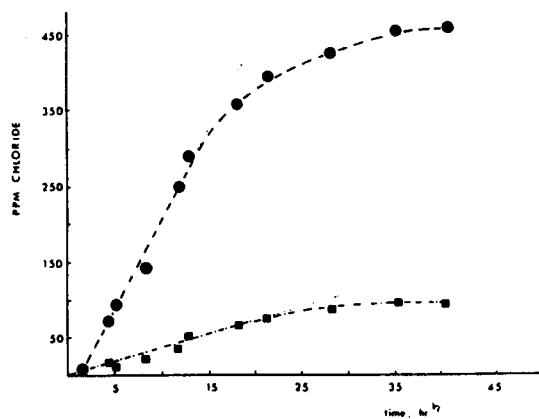
(e) 5 wt% ethanol.

Figure 1   Plot of chloride concentration vs the square root of time for treatment of copper alloy sheathing tacks from the Lively in 5 wt% sodium sesquicarbonate (●) and in deionized water (■). The solution volume was 2ℓ.
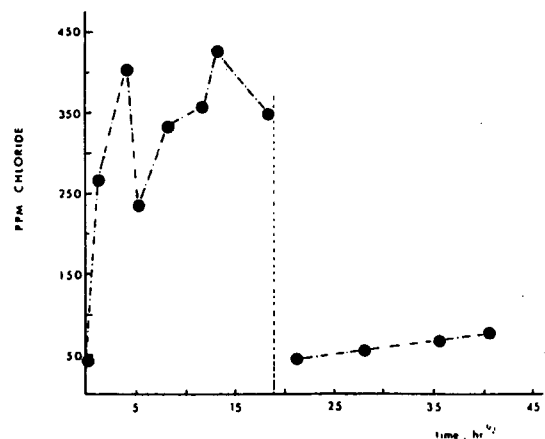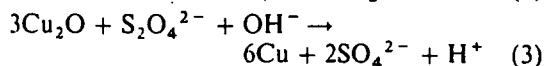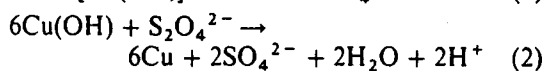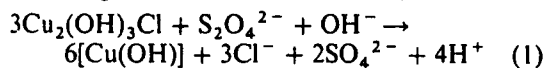
Figure 2   Plot of chloride concentration vs the square root of treatment time for washing a set of copper alloy sheathing tacks from the Lively in 1 wt% benzotriazole (5 vol% ethanol). The solution volume was 2ℓ.

tions. The large amount of chloride ions in solution after such a short interval is primarily due to a number of different chemical reactions taking place at the surface of the corroded nails. These reactions are associated with the marked changes in the patina of the objects within the

first two hours. For alkaline dithionite solutions, the colour change from the blue-green copper(II) hydroxy chlorides, through a yellowy orange transient copper(I) hydroxide, to the chocolate brown finely divided metallic copper takes place within a few minutes. The overall

reaction for removal of the corroded layers is complex but may be seen as a stepwise process involving reactions such as:

$$3Cu_2(OH)_3Cl + S_2O_4^{2-} + OH^- \rightarrow$$
$$6[Cu(OH)] + 3Cl^- + 2SO_4^{2-} + 4H^+ \quad (1)$$

$$6Cu(OH) + S_2O_4^{2-} \rightarrow$$
$$6Cu + 2SO_4^{2-} + 2H_2O + 2H^+ \quad (2)$$

$$3Cu_2O + S_2O_4^{2-} + OH^- \rightarrow$$
$$6Cu + 2SO_4^{2-} + H^+ \quad (3)$$

These reactions occur since dithionite is a strong chemical reducing agent under alkaline conditions, i.e. the standard reduction potential for the reaction:

$$2SO_3^{2-} + 2H_2O + 2e^- \rightarrow S_2O_4^{2-} + 4OH^- \quad (4)$$
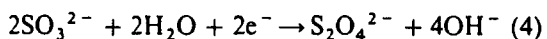
is -1.12 volts vs hydrogen [43]. From the colour changes, it is apparent that the reduction of copper(II) occurs in two one-electron steps. The dithionite is oxidized up to sulphate ions via intermediates such as sulphite (SO_3^{2-}).

With the thiourea-inhibited citric acid solutions, the nails begin to change colour within a few minutes. After two hours, a dull brown colour, due to a mixture of cuprite and absorption of thiourea on the corroded surface, is evident. If there are any carbonates or hydroxy chlorides on the patina, they will dissolve due to the moderately acid conditions, i.e. pH 0·95, and the complexing strength of citric acid through reactions such as:

$$Cu_2(OH)_3Cl + 2H_3L \rightarrow$$
$$2Cu HL + Cl^- + H^+ + 3H_2O \quad (5)$$
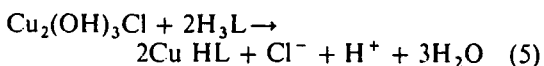
where H_3L is citric acid,
$$HOC(CH_2COOH)_2COOH.$$

Complexation of the surface copper(II) corrosion products with benzotriazole (BTA) is the primary cause of the initial rapid release of chloride ions into such wash solutions, viz.

$$Cu_2(OH)_3Cl + 6BTAH^* \rightarrow$$
$$2Cu(BTA)_2(BTAH) + Cl^- + 3H_2O + H^+ \quad (6)$$
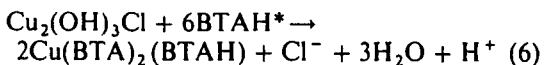
with concomitant changes in the patination of the artifacts [44-46].

The small amounts of chloride in the wash solutions for 50% aqueous acetonitrile, 1 wt% and 5 wt% sesquicarbonate and deionized water washes after only two hours of washing were not unexpected. The complexing, or solvating powers, of these media [47] are not sufficient to cause

*BTAH is the normal (protonated) form of benzotriazole.

rapid breakdown of the stable copper(II) hydroxy chlorides.

When all the data are checked for correlations between the rate of release of chlorides and a number of different time functions, the 'normal' diffusion-controlled dependence is observed for all but the dithionite and the benzotriazole solutions. In simple terms, this means that a common physical phenomenon controls the release of chloride ions from the corroded nails in deionized water, 1 wt% and 5 wt% sesquicarbonate, 50 vol% aqueous acetonitrile and 5 wt% inhibited citric acid solutions. The linear relationship between increase in chloride concentration and the square root of the washing time ($t^{\frac{1}{2}}$) implies that the chloride release is controlled by the rate of diffusion through the adherent cuprous oxide layer on the corroded artifact. This in turn is controlled by parameters such as patina thickness and the number of defects, such as micro-cracks, in the Cu_2O film. Since the data listed in Table 1 are from the same type of objects from the same environment, most of the differences in the Cu_2O layers will be overcome through having a sufficient number (164 $\pm$ 11) of objects to minimize random variations. The outer patina of copper(II) hydroxy chlorides is much less dense than the primary copper(I) oxide layer, with respective densities of $3.75gcm^{-3}$ and $6.05gcm^{-3}$ [43]; hence it has no effect on the rate-controlling step. Citric acid solutions, by their acidic nature, will dissolve a number of copper(I) and copper(II) corrosion products such as $Cu_2(OH)_3Cl$, $Cu_2(OH)_2CO_3$, CuO and Cu_2O. The presence of thiourea will mean that instead of the acidic dissolution of Cu_2O producing unstable aquated copper(I) species, a stable copper(I) thiourea complex will be formed. The interaction of copper(I) and thiourea is complicated by the formation of some polynuclear species [48]. The formation of this complex prevents the disproportionation of aquated copper(I) to copper metal and copper(II) which is commonly observed when dissolving Cu_2O in dilute sulphuric acid solutions. Citric acid also forms stable complexes with Cu(II) with a stability constant of $10^{8·68}$ [49] for the reaction no. 5 (see above). Inhibited citric acid solution will dissolve both copper(II) and copper(I), the strengths of the citrate complexes with copper(II) are greater than those with copper(I) by a factor of approximately 10^4,

Table 2   Composition of corroded sheathing tacks from the Lively *(c. 1820)*

	Cu	Sn	Pb	Zn	Cl
RS 89–1 shank	59·54	15·9	0·46	1·56	0·51
89–2 head	74·57	18·8	0·60	1·89	1·10
89–3 tail	51·80	12·5	0·42	0·90	1·13
RS 113–1 head	81·52	4·71	0·30	2·88	1·29
113–2 tail	71·75	12·14	0·59	2·0	1·78
113–3 shank	57·60	11·87	0·19	1·5	1·29
RS 48* core sample	87·08	8·53	0·79	2·97	0·05

*Other analyses included Fe 0·105%, Ag 0·080%, Ni 0·029%, As 0·01%, Sb 0·066% and Bi 0·081%.

therefore the copper(II) corrosion products will be preferentially dissolved. The presence of thiourea, as a corrosion inhibitor, further modifies the complexing ability of citric acid for copper(I) oxide through the formation of stable copper(I) thiourea complexes such as the polynuclear $Cu_2(Tu)_4^{2+}$ complex which has a stability constant of $10^{15·4}$ [48]. The net balance of all these competing reactions is that a mixed copper(I) oxide-polynuclear copper(I) thiourea remains on the artifacts immersed in inhibited citric acid solutions. Therefore, the chloride release follows the same diffusion-controlled behaviour as in other aqueous media, once the initial dissolution of the $Cu_2(OH)_3Cl$ layer has occurred.

A summary of the 21 experiments is given in Table 2. A comparison of the chloride release rates shows that alkaline dithionite is by far the most efficient method for removing chloride ions since it released 13 times as many ions in one-sixth of the time required by simple washing in deionized water. Although the chloride release data for the dithionite gives a better fit when plotted against log_{10} time (correlation coefficients 0·991–0·998), rather than against $t^{\frac{1}{2}}$ (correlation coefficients 0·975–0·990), the quality of the data does not make any clear distinction between the two rate laws. For the purposes of comparing the rates of chloride removal, we can use the slopes obtained from the plots of chloride concentration vs the square root of time for all but the benzotriazole solutions, since they are complicated by a variety of complexation and adsorption reactions. Although reasonable precautions were taken when assembling the sheathing tacks for the experiment, it was not possible to ensure that the same area of corroded metal was exposed to the wash solutions. Since

the diffusion of chloride ions through the copper(I) oxide film is essentially a two-dimensional or surface phenomenon, correction of the raw data for apparent geometric area can be made to 'normalize' the release rates. The problem of variable solution volumes (concentrations are determined as parts per million or mg per litre) is readily overcome by converting ppm to mg of chloride, copper, etc.; hence, the diffusion rate in $ppm.hr^{-\frac{1}{2}}$ can be normalized by the following [42],

$$R_N = \frac{R_{ppm} \times \text{solution volume in litres}}{\text{surface area in cm}^2} \quad (7)$$

where R_N is the normalized rate in $mg.cm^{-2}.hr^{-\frac{1}{2}}$, (or $\mu g.cm^{-2}.hr^{-\frac{1}{2}}$ for convenience) and R_{ppm} is the rate determined from the graphical plots for ppm chloride vs the square root of time. This normalization procedure improves the quality of the results of the triplicate washing experiments, since although the same weight and number of tacks were used in each experiment the approximate geometric surface areas varied by as much as 16·5% within the sets. The various washing treatments can be ranked in the order: alkaline dithionite $\gg$ citric acid > 5 wt% sesquicarbonate > 50 vol% aqueous acetonitrile $\geqslant$ 1 wt% sesquicarbonate $\geqslant$ deionized water. Since the strongly reducing environment of alkaline dithionite solutions will effectively remove the adherent Cu_2O film which overlays the corroded metal, it is not surprising that the chloride ions will be removed at a very rapid rate. The only limiting factor will be the tortuosity and length of the 'diffusion pathway' through the metal structure, which has been subject to intergranular corrosion and various other forms of preferential corrosion [50].

The inhibited citric acid solutions gave the second fastest release rates after the initial surge as $Cu_2(OH)_3Cl$ was dissolved. As previously mentioned, this is probably due to partial dissolution of the Cu_2O layer through formation of copper(I) thiourea complexes. Because of the d^{10} electronic configuration of the copper(I) ion, it can form very strong bonds with the sulphur atom in thiourea $((NH_2)_2C=S)$ through $d^{\pi}-p^{\pi}$ back bonding. This will force copper(I) chlorides, such as CuCl, to dissociate, viz.

$$CuCl + 2Tu \rightarrow Cu(Tu)_2^+ + Cl^- \qquad (8)$$
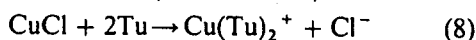
where Tu is thiourea, $(NH_2)_2CS$ (thiocarbamide).

One complication of thiourea being present is that it also forms complexes with copper(II) ions which gradually oxidize thiourea, viz.

$$2Cu(Tu)_2^{2+} + 2CS(NH_2)_2 \rightarrow$$
$$NH_2C(NH)SSC(NH)NH_2 +$$
$$2Cu(Tu)_2^+ + 2H^+ \qquad (9)$$
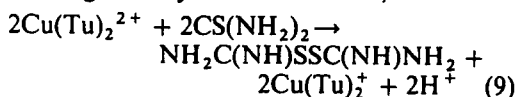
If such stripping solutions are left to stand for a few months in the open air, a yellow-brown, polymeric, tar-like film deposits on the artifact. Previous experiments using 1 wt% thiourea as a complexing agent to remove copper(I) chlorides* appeared to work very well and gave a normalized release rate of $50\mu g.cm^{-2}.hr^{-\frac{1}{2}}$. However, due to the marked solubilization of copper, i.e. $680\mu g.cm^{-2}.hr^{-\frac{1}{2}}$, such treatments were not carried out in this controlled experiment.

Removal of harmful chloride ions, and associated complexes such as $CuCl_2^-$, is the desired objective of conservation treatments designed to stabilize copper and its alloys. Apart from using thiourea as a complexing agent, the use of 50 vol% aqueous acetonitrile has been shown to be effective in stabilizing heavily corroded brasses which repeatedly showed bronze disease, despite citric acid stripping, benzotriazole impregnation, etc. [24].

In 50 vol% aqueous acetonitrile mixtures, there will be selective mobilization of copper(I) chlorides, because of the selective solvation of copper(I) by acetonitrile (MeCN) to form the stable complex, $Cu(MeCN)_4^+$ [37]. In such solutions, the solubility of materials such as

*Experiments were performed on a series of silvered bronze coins of the Emperor Probus (276–281 AD) on loan from Robert Organ [40].

$Cu_2(OH)_3Cl$ is less than in water owing to the lower dielectric constant of the mixed solvent [47]. Therefore, such materials tend to remain on the surface of the artifact. The relatively small rate of release of chlorides from the *Lively* sheathing tacks may be due to the fact that a large portion of the chloride-containing corrosion products are the poorly solvated copper(II) hydroxy chlorides, given that the fully oxygenated nature of the wreck site will tend to favour formation of copper(II), rather than copper(I) species [21]. The aqueous acetonitrile solution plateaued earlier than the 1 wt% sesquicarbonate and deionized water washes and this solution removed one-third more chloride ions than the other two treatments in approximately half the time.

The faster rate of chloride release in the 5 wt% sodium sesquicarbonate wash, compared to the 1 wt% rate, is not an effect of pH since the solutions were within 0·3 pH units of each other (see Table 3). The increase of $5·2 \pm 0·5$ in the rate of release of chloride must be largely due to the increased complexing ability of the more concentrated sesquicarbonate. The increased solubility of minerals such as atacamite, botallakite and paratacamite (the Cu(II) hydroxy chlorides commonly found on shipwreck material) [15] in carbonate media is easily seen through the marked blue coloration of the wash solution, as reactions like:

$$Cu_2(OH)_3Cl + 4CO_3^{2-} \rightarrow$$
$$2Cu(CO_3)_2^{2-} + 3OH^- + Cl^- \qquad (10)$$
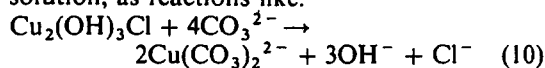
cause the release of chloride ions into solution. The mean diffusion-controlled release rates for copper are $1·38 \pm 0·18\mu g.cm^{-2}.hr^{-\frac{1}{2}}$ for 1 wt% and $27·8 \pm 4·0\mu g.cm^{-2}.hr^{-\frac{1}{2}}$ for the 5 wt% sodium sesquicarbonate, i.e. an increase of 20 times. Although the 5 wt% sesquicarbonate wash removed a total of 1007mg of chloride, compared with 235mg for the 1 wt% solution, it was at the 'expense' of over 300mg of copper, compared with 37mg from the less concentrated washing solution.

Inspection of the data on chloride release from the benzotriazole impregnation (Table 1) shows that while the changes in chloride concentrations are reproducible in the three experiments, they do not conform to the monotonic pattern seen this far. A typical set of data is shown in Figure 2 where it can be seen that there is an initial rapid rise in chloride ions, which then falls and rises

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Table 3   Effective rates of chloride removal from corroded 'copper' sheathing tacks

Medium	Diffusion rate ppm.hr$^{-\frac{1}{2}}$	Normalized rate $\mu g.cm^{-2}$ hr$^{-\frac{1}{2}}$	Time to reach plateau, days	mg of chloride[c] removed
5 wt% sodium dithionite 1M NaOH	132 ± 26[a]	296 ± 43	7	2737
5 wt% citric acid and 1 wt% thiourea	39·8 ± 4·5	84·8 ± 5·2	4	1212
5 wt% sesquicarbonate	23·0 ± 0·9	47·1 ± 2·0	33	1007
1 wt% benzotriazole (5 vol% EtOH)	(b)	(b)	4	609
50 vol% acetonitrile	4·8 ± 1·3	12·1 ± 3·0	20	314
1 wt% sesquicarbonate	3·9 ± 0·4	9·0 ± 0·8	47	235
Deionized water	4·6 ± 1·3	13·4 ± 4·6	43	211

(a) The data from dithionite solutions approximated to t$^{\frac{1}{2}}$ for purposes of comparison with rest of washing media.

(b) Data from benzotriazole experiment does not approximate to a t$^{\frac{1}{2}}$ dependence.

(c) Mean amount of chloride release at the time of reaching the first plateau (chloride levels corrected for background effects and averaged over three experiments).

again, before settling down to a plateau level. Despite this complex behaviour, the 1 wt% benzotriazole (in 5 wt% ethanol-water mixtures) is effective at quickly removing a significant amount of chloride in a relatively short space of time. Apart from the formation of complex copper(II)-BTA species [30–33], as described above [51, 52], the benzotriazole also forms very stable copper(I)-(BTA) complexes. Once the competition between desorption of chloride species and adsorption of BTA moities has equilibrated, the chloride release rate drops off to zero (it plateaus) until the solution is changed. In the fresh solution, the equilibrated film acts as a stable barrier through which entrapped chlorides can diffuse to the washing environment.

3   Choice of methods

Although there have been several reports in the conservation literature regarding the suitability of a particular treatment for corroded copper alloy artifacts, this work presents a different approach to the problems which face conservators dealing with large numbers of artifacts, all of which need some form of stabilization. Previous experience in the laboratories of the W.A. Museum has shown that simple citric acid stripping is often not sufficient in itself for long-term stabilization (i.e. greater than seven years) of the bronze artifacts, nor is vacuum impregnation

with ethanolic solutions of benzotriazole. Because of the above problems, the citric acid stripping is routinely followed by soaking in a 1 wt% sesquicarbonate solution. This not only removes more chlorides and neutralizes the acid, but also provides the right environment for the removal of significant amounts of copper as a copper(II) citrate complex [53, 24].

The choice of method should be made when all the advantages and disadvantages of each system are understood. The answer to the question 'will this treatment prevent bronze disease?' is in part based on an understanding of the electrochemical nature of this form of accelerated corrosion. A detailed discussion of how chloride ion activities effectively destabilize copper has been previously reported [14, 54].

At chloride ion activity levels above 10,000ppm, there is a large amount of copper mobilized in the form of $CuCl_2^-$ ions. Under such conditions, accelerated corrosion of copper is thermodynamically favoured. The estimated amount of residual chloride ion in the sheathing tacks, after the various washing regimes, is shown in Table 4. If one considers the average residual chloride level, it can be seen that dithionite, citric acid, 5 wt% sesquicarbonate and benzotriazole generally produce residual chlorides at a level below that theoretically required for 'active bronze disease', whereas the aqueous acetonitrile, 1 wt% sesquicarbonate and

Table 4   Comparison of washing regimes for removal of chloride ions

Washing regime	wt% chloride extracted	% extracted of maximum Cl content[a]	Residual chloride ppm	
			Minimum	Maximum
Alkaline dithionite	1·50	94·3	0	940
Citric acid, 1 wt% sesquicarbonate	0·72	45·3	500	8,740
5 wt% sesquicarbonate	0·55	34·6	2,200	10,400
1 wt% benzotriazole[b]	0·38	23·9	3,900	12,100
50 vol% acetonitrile	0·17	10·7	6,000	14,200
1 wt% sesquicarbonate	0·13	8·2	6,400	14,600
Deionized water	0·12	7·5	6,500	14,700
No treatment	0·00	0·0	7,736	15,940

(a) Maximum chloride content based on mean chloride analysis of total dissolution of six sections of corroded sheathing tacks plus one standard deviation (Table 2).
(b) Benzotriazole dissolved in 5 vol% ethanol/95% water mixtures.

deionized water leave higher amounts of chloride in the artifacts.

If the patina of the object is of no great significance, and if the appropriate sealed vessels are available, then the use of *alkaline dithionite* may be the preferred option since it effectively removes the bulk of the total chloride in the shortest time. This technique has been used to treat several sets of Graeco-Roman bronze coins which were very badly corroded and had no discernible inscriptions on them (see Figure 3).
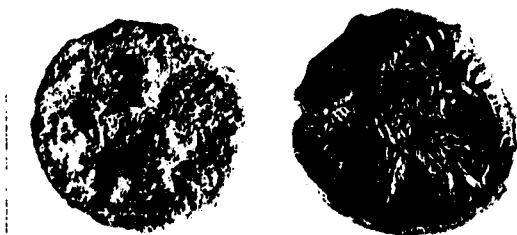

Figure 3   Typical photographs of Graeco-Roman coins recovered from a land site, before and after treatment with alkaline dithionite (30 days in 1M NaOH, 5 wt% Na₂S₂O₄). The treated coin was identified as an Alexandrian tetradrachm of Gaudian III (238–244 AD).

After dithionite treatment, the pustular growths had been reduced to a loose copper powder which could be brushed off to reveal the original surface inscription. As in the case of the sheathing tack experiments, monitoring of chloride, copper, tin, lead and zinc levels was periodically

performed and significant amounts of tin were found to be dissolving from the corroded matrix and reporting to the wash solution. Analysis of the tin concentration and washing time in dithionite showed that there was a linear increase in tin with t^3 (time in hours) with an average induction period of $11·4 \pm 1·7$ days before any tin was in solution. Similar behaviour was observed when treating a series of heavily corroded, massive bronze door-hinges from the *Batavia* (1629). In strongly alkaline media, the dissolution of tin oxides, such as SnO_2, to form soluble stannates, such as $Sn(OH)_6^{2-}$, is well documented and the kinetics (dependence on t^3) are consistent with the shrinking sphere mechanism [42, 55]. Measurement of the corrosion potential, E_{corr}, of the artifacts during treatment showed average values of $-0·89 \pm 0·087$ volt vs NHE at pH 13·0. Under these reducing conditions, SnO_2 is in equilibrium with SnO_3^{2-} (1100 $\pm$ 200 ppm). Tin metal, contained in the artifact, is immune to corrosion under these conditions of Eh and pH [56].

We have found that alkaline dithionite treatments can consolidate heavily corroded bronzes and 'reform' the original surface, though care should be exercized when cleaning the redeposited layers. The normal follow-up for objects, after dithionite treatment, involves washing in deionized water for up to 48 hours to remove residual caustic solutions.

Inhibited citric acid stripping, followed by a sesquicarbonate wash, is the most commonly

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used method for treating large objects such as bronze rudder gudgeons, capstan pall traces and some heavily concreted bronze cannon. The cost of large airtight containers and the cost of sodium dithionite ($5.00 per kg cf. citric acid BP crystals $3.50 per kg), as well as the hazards of dealing with large amounts of foul-smelling solutions,* are some of the reasons why citric acid cleaning tends to be popular. Although the patina of the object is destroyed in citric acid stripping, this technique often reveals inscriptions on artifacts which are of vital significance to the archaeologists. Without the follow-up rinse in sesquicarbonate, substantial amounts of both copper and chloride ions remain trapped in the corroded object. This can lead to renewed outbreaks of bronze disease in four to six years. Since post-washing efflorescence has been observed on objects washed in 5, 4 and 3 wt% sodium sesquicarbonate solutions, the use of 1 or 2 wt% solutions for highly corroded brasses and bronzes is recommended. During the alkaline wash, the sickly pale yellowy brown surface of the artifacts reverts to the richer brown hue which is characteristic of bronzes.

Benzotriazole impregnation is a method that enjoys a good deal of popularity because of the remarkable corrosion resistance it imparts to the object. The relatively high cost of benzotriazole, particularly if bought in quantities less than 10kg, tends to preclude its use in many laboratories which operate under extreme fiscal constraints. The ability of BTA to displace a large proportion of chloride-containing corrosion products through formation of stable Cu(I) and Cu(II) complexes, together with the effective inhibiting properties of the copper-BTA films, provides the basis for its efficacy [46, 51, 52]. The reason why many BTA treatments fail after five or so years may be insufficient impregnation time. Rather than soaking for periods of a few days, a few months of washing may lead to longer-term corrosion resistance. Due to the carcinogenic nature of benzotriazole, it should be handled with care (avoid inhaling dust and wear gloves) [34].

Aqueous acetonitrile is a very effective com-

plexing agent for copper(I) corrosion products. For objects suffering from active bronze disease, the use of 50 vol% acetonitrile-water mixtures has been shown by the author to be very effective at removing cuprous chloride and thereby stabilizing the object [24]. Analysis of the colourless wash-solutions shows that the molar ratio of chloride to copper ions is 1:1 which indicates that the following reaction is dominant [37, 47]:

$$CuCl + 4MeCN \rightarrow Cu(MeCN)_4^+ + Cl^- \quad (11)$$

Long-term (greater than six weeks) washing in such solutions can lead to a darkening of the blue-green patina as the black copper(II) oxide, tenorite, is formed. Due to the greater solubility of molecular oxygen in the mixed solvent there is a tendency for copper(I) oxide to be further oxidized to CuO. The use of aqueous acetonitrile washes necessitates a well-ventilated space, or sealed containers, since the acetonitrile vapour is moderately toxic [57].

Sodium sesquicarbonate solutions of various concentrations still remain one of the most tried methods of stabilizing corroded bronzes. Earlier literature reports established that for certain objects a 5 wt% solution of sesquicarbonate was the optimum for removing chloride ions [39]. Although the 5 wt% solution removes chloride ions at an initial rate of five times that for a 1 wt% solution (see Table 2), it does so at the expense of removing more copper from the artifact. If retention of the original patina is of paramount importance, then the choice of less concentrated sesquicarbonate solutions should be made. The inherent longer wash times are not a major problem. The objects need only periodic checking. Post-treatment washing to remove excess carbonate and bicarbonate from extensively corroded objects is only needed for washing solutions greater than 1 wt% sodium sesquicarbonate.

Distilled or deionized water will gradually wash out chloride ions from corroded brass and bronze artifacts without changing the patina of the objects. However, there will normally be insufficient driving force to remove significant amounts of chloride ions. As a consequence, the object may remain susceptible to further breakouts of bronze disease. Effective stabilization in deionized water can be attained if washing periods of two to four years, at ambient (19·5 ± 5·5°C) temperatures, are used.

*Impurities in commercial grade sodium dithionite are very pungent. Spent dithionite solution should be allowed to oxidize before disposal into the sewage system since its oxygen scavenging ability will upset the microbiological balance.

4 Weight loss and corrosion control

When a washing treatment is used to stabilize an object, it is important to monitor the solution and the artifact itself to ensure that no untoward reactions, such as accelerated corrosion, are taking place. By measuring parameters such as chloride ion concentration, metal ion levels and the pH of the solution, a guide to the 'health' of the artifact is given. The use of corrosion potential measurements in the field has been shown to be of immense benefit in the understanding of the microenvironment of metal artifacts and can be used to help design appropriate post-excavation treatments [17]. Most conservation laboratories have access to a high impedance multimeter and suitable silver/silver chloride reference electrodes can be manufactured at little or no cost from broken pH electrodes if funds are not available to purchase commercially made electrodes. A 2cm length of moderate gauge platinum wire can be soldered/spot welded to a piece of electric cable and the join encapsulated in an epoxy resin to make a cheap working electrode. The voltage measured at the platinum electrode is called a mixed or corrosion potential. At this potential the rate of the oxidation (metal corrosion) and reduction (oxygen consumption) reactions are the same. Detailed discussions on the nature of corrosion potentials can be found in standard electrochemistry text books [58].

A summary of the microenvironments of the seven wash solutions at the end of the experiment is given in Table 5 and illustrated in Figure 4, which is the Eh-pH Pourbaix diagram for the $Cu-H_2O-Cl$ system at 25°C [2]. The major difference between the alkaline dithionite and the other wash solutions is that the former is strongly reducing, with E_{corr} at -1.014 volts vs AgCl. The other solutions have corrosion potentials in the range -0.061 to $+0.049$ volts, which is typical of normal aerobic solutions. The air-saturated solutions have potentials and pHs which have copper in the passive zone on the Pourbaix diagram, i.e. copper is corroding at a slow but steady rate (see Figure 4). Based on an average Tafel slope of 48mv for the oxidation of copper(0) to copper(I) [52, 59], the difference of 110mv in the corrosion potential of the nails in deionized water and in benzotriazole indicates that the corrosion rate of Cu is lowered by a factor of 200. Whilst the interpretation of corrosion potentials is dependent on many parameters and requires some knowledge of electrochemistry, it is nevertheless a very useful and cheap adjunct to the tools already available to metal conservators.

Apart from removing chloride ions, the seven washing treatments also resulted in varying amounts of copper, tin, lead and zinc going into solution. The reason why the alkaline dithionite solutions dissolve tin corrosion products has already been discussed—no other treatment resulted in significant loss of tin oxidation prod-

Table 5 Mean values of solution parameters after 70 days washing[a]

	$Ecorr$[b] volts	pH	Cl	Cu	Sn	Pb	Zu
5 wt% dithionite	−1·014	12·98	163[c]	5	892	0·8	1·6
5 wt% sesquicarbonate	−0·050	9·32	518	53	1·3	15·6	20·4
1 wt% sesquicarbonate	−0·021	9·65	122	101	2	5·3	0·08
5 wt% citric acid, followed by	−0·437[d]	1·2	675	2194	19	83	55
1 wt% sesquicarbonate	−0·045	9·26	164	211	2·6	1·0	0·3
50 vol% acetonitrile	+0·036	9·20	161	38	9·7	n.d.	n.d.
Deionized water	0·049	8·62	108	0·36	n.d.	1·0	0·2
1 wt% benzotriazole	−0·061	7·04	142[c]	0·30	n.d.	1·3	0·05

(a) Mean of three sets of data for each solution, concentrations of ions in ppm (mg per litre).
(b) Volts vs Ag/AgCl (1M KCl) reference electrode.
(c) Second wash solution, first wash average 1397 ± 121 ppm chloride for dithionite, 318 ± 16 BTA.
(d) Corrosion potentials measured at t = 451 hours.
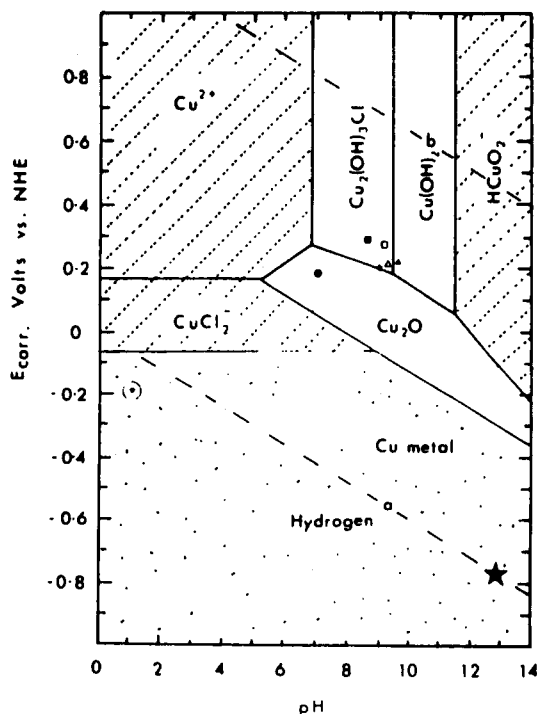n.d. Below detection limit.

*Figure 4   Pourbaix diagram for copper in sea water[2] showing corrosion potentials of sheathing tacks at the end of the treatment programmes. The data points relate to the following regimes: *5 wt% sodium dithionite (1M NaOH), △ 5 wt% sodium sesquicarbonate, ▲ 1 wt% sodium sesquicarbonate, ⊛ 5 wt% citric acid (inhibited with 1 wt% thiourea), + 1 wt% sodium sesquicarbonate post citric acid pre-treatment, □ 50 vol% acetonitrile water, ■ deionized water and ● 1 wt% benzotriazole.*

ucts from the surface of the corroded sheathing tacks. The only wash solution that led to significant amounts of copper, lead and zinc corrosion products being changed into soluble species was the two-stage wash of thiourea-inhibited citric acid solution followed by 1 wt% sesquicarbonate (see Table 5). Since oxidation of the leaded bronze sheathing tacks (see Table 2 for composition) would have resulted in corrosion products such as Cu_2O, $Cu_2(OH)_3Cl$, SnO_2, $ZnSO_4 \cdot 4H_2O$, $PbSO_4$, $Pb(OH)_3Cl$, $Pb_2(OH)_2(CO_3)$ [15], the mildly acidic citric acid solution will dissolve the hydroxy chlorides and hydroxy carbonates forming a series of soluble metal (M^{II} ions) citrate complexes [49]. The release of lead and zinc into the wash solutions closely followed $t^{\frac{1}{2}}$ kinetics with correlation

coefficients of the order 0·99987 for the least squared fit. The diffusion-controlled release rates for copper, tin, lead and zinc during the citric acid stripping are 170, 1·2, 1·6 and 2·8 ppm.hr$^{-\frac{1}{2}}$ respectively. Previous studies have shown that under fully aerobic conditions, the copper-rich phases of bronzes and brasses tend to corrode selectively [21, 59]. Since the *Lively* wreck site is on the edge of a coral reef and is subject to a heavy surge, it is not surprising to find that the surface corrosion products are copper-rich [60]. The molar ratio of the release rates for copper and chloride ions is 2·1 ± 0·8 which also indicates that a major source of the ions is the corrosion product, $Cu_2(OH)_3Cl$. During the sesquicarbonate rinse, there is no further mobilization of tin, lead and zinc corrosion products. The blue coloration of the wash solution has an absorption maximum at 746nm which is characteristic of copper(II) carbonate complexes. The molar ratio of the release rates for copper and chloride in the alkaline stage of the treatment is 0·20 ± 0·07 which indicated that the major cause of chloride ions are the copper(I) corrosion products. Solvent extraction of the blue solution in diethyl ether and subsequent analysis showed that copper citrate was also one of the species present in the sesquicarbonate rinse.

5   Tests for bronze disease

One of the standard tests for bronze disease is to place the object in a sealed bag for a few weeks at 100% RH to see if 'green spots' break out on the surface of the object. It has been the experience of this author and many colleagues that the above test does not always give a true guide to the long-term stability of corroded copper alloys, since the objects that failed to show 'active bronze disease' in a few weeks were found to be actively corroding several years later. In order to see what effects the atmosphere (air or nitrogen) and relative humidity had on the corrosion of copper artifacts, sheathing tacks from the *Rapid* (1811) were placed in heat-sealed plastic bags filled with air or nitrogen (commercial grade) at relative humidities of 100% (water), 60% (saturated potassium iodide solution) and 32% (saturated calcium chloride solution).* The

experiment ran for approximately four years (1500 days) during which time the tacks were periodically removed and re-weighed before the original atmosphere was restored prior to heat-sealing. The results are summarized in the plot of increased weight % vs time, shown in Figure 5. Two distinct features can be seen. The increase in the weight of the tacks (oxidation or corrosion) is greater in the air than in the nitrogen atmospheres for the same humidity, and the behaviour of the 100% RH experiments is markedly different to the 60% data. The data from the 32% RH experiment are not shown in Figure 5 since the solution spilt after only 156 days (before the first measurement) and the surface of the tacks was contaminated with saturated calcium chloride. This resulted in the solubilization of some of the copper, for the nails lost 1.52 ± 0.12 wt% copper after 371 days in $CaCl_2$ solution. After removing the spent solution these tacks were replaced at 32% under air and nitrogen and the weights monitored as with the remaining four samples.
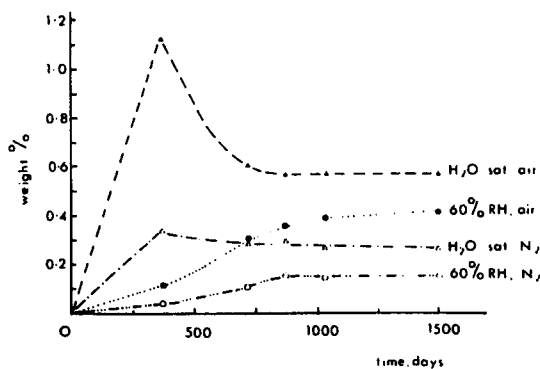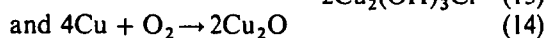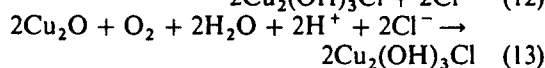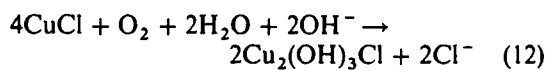

Figure 5   Plot of the effective increase in weight (wt%) vs time for sets of copper sheathing tacks exposed to different microenvironments. ▲ 100% RH in air, △ 100% RH in nitrogen, ● 60% RH in air and ○ 60% RH in nitrogen. The tacks were from the wreck of the American China Trader Rapid *(1811).*

The only cases where the characteristic blue-green pustular outgrowths associated with bronze disease were observed concerned the tacks which had been immersed in the saturated calcium chloride (12·7M) for 156 days, and subsequently held at 32% RH. The weight increase with time for these sheathing tacks was similar to that observed with the 60% RH environment, i.e. a gradual increase in weight. Although

significant increases in weight did occur, there were no obvious symptoms of the underlying corrosion for the other four sets of tacks. For the 100% RH environments, the peaks in weight increase after one year may be due to micro-droplets of water adsorbed on the corroded nails by hygroscopic copper(I) chloride species. Oxidation reactions such as:

$$4CuCl + O_2 + 2H_2O + 2OH^- \rightarrow$$
$$2Cu_2(OH)_3Cl + 2Cl^- \quad (12)$$
$$2Cu_2O + O_2 + 2H_2O + 2H^+ + 2Cl^- \rightarrow$$
$$2Cu_2(OH)_3Cl \quad (13)$$
and $4Cu + O_2 \rightarrow 2Cu_2O$ \quad (14)

will all result in an increase in the weight of the corroded nails. Since the copper(II) hydroxy chlorides are not as hygroscopic as the copper(II) chlorides, reactions such as (12) will take place at high RH and then the relative weight increase will diminish as excess water is desorbed from the copper(II) corrosion products. The fact that corrosion of the nails occurred under a nitrogen atmosphere is due to inward diffusion of oxygen through the 0·2mm-thick polyethylene film and the fact that in a high chloride environment, copper(II) is a sufficiently powerful oxidant to corrode the underlying copper to produce copper(I) chlorides, which are then subject to hydrolysis reactions [14]. The most practical implication of the above experiment is that the oxygen concentration and moisture level both have an effect on the chloride-induced corrosion of copper alloys. It could be argued that the testing of the sheathing tacks from the *Rapid* is an unfair experiment since the presence or absence of bronze disease in essentially pure copper objects *does not relate* to corroded bronzes. Wet chemical analysis of the tacks showed that the core material was 99·5% Cu, 0·22% Sn, 0·14% Pb, 0·01% Zn, 0·10% Sb and 0·015% Ag. The corroded nails were treated by the alkaline dithionite method for 10 weeks at the end of the corrosion experiment and gave mean values of 1.02 ± 0.23 wt% chloride for the 100% RH and 60% RH tacks, and 2.93 ± 1.39 wt% for those contaminated with the saturated $CaCl_2$ solution. Metallographic examination of cross-sectioned sheathing tacks from the *Rapid* show that corrosion products containing chloride are *concentrated* in the outer layers of the metal. This 'concentration' effect raises the chloride level well above the critical concentration (i.e. 10,200

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ppm), and should leave the metal in an inherently unstable state, i.e. subject to accelerated corrosion.

The reason why so many corroded copper objects do not suffer from bronze disease lies in both the kinetics and the altered thermodynamics of the oxidation reactions. At chloride ion activities above 1,778 ppm (5×10^{-2}M), the oxidation reaction

$$Cu^{2+} + Cu + 4Cl \rightarrow 2CuCl_2^{-} \qquad (15)$$
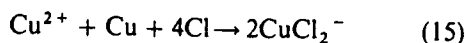
is thermodynamically favourable (i.e. ΔG reaction is negative at $Cl > 10^{-2}$M), hence bronze disease could occur. In practice, the natural electrochemical resistance of the corrosion products to electron transfer reactions will mean that higher chloride levels are needed to drive the reaction forward. Since the oxidation reactions are occurring at 'molecular surfaces' the effects of trace elements can be quite marked, e.g. the small amounts of tin and antimony in the sheathing tacks (0·22 and 0·10 wt% respectively) can concentrate along grain boundaries and lower copper metal activities through the formation of intermetallic phases [61, 62]. Although the precise model for 'bronze disease' is still subject to debate, it is readily apparent that the ability of the Cu_2O film to function as a bipolar electrode will be inhibited by the presence of impurities such as arsenic and antimony, which are very common in most historic artifacts. An example of this effect is seen with the addition of small amounts of nickel to the Cu_2O film. The electrical resistance of a Cu_2O film is changed from $5·5 \times 10^{13}\Omega.cm^{-2}$ to $23·5 \times 10^3\Omega.cm^{-2}$ at a level of 10 wt% nickel [63].

6 Conclusion

A series of experiments on shipwreck and land-based archaeological materials has established the diffusion-controlled nature of the release of chloride ions in a variety of aqueous and non-aqueous washing solutions. The normally observed differences between the extent of corrosion of similar objects from the same site have been overcome through using large numbers of objects in triplicate experiments to obtain statistically reliable data. The results of the washing regimes showed that the rate of release of chloride ions in alkaline dithionite ≫ citric acid > 5 wt% sesquicarbonate > 1 wt% benzotriazole >

50 vol% acetonitrile water > 1 wt% sesquicarbonate > deionized water. The effectiveness of the different washing solutions at removing chloride ions was shown to be dependent on the oxidizing/reducing strength of the medium as well as on their ability to form stable and soluble copper(I) and copper(II) complexes. The use of pH and corrosion potential measurements as a monitor of the metal microenvironment has been demonstrated. The choice of washing methods is discussed in terms of capital, equipment and aesthetic constraints. Interpretation of a long-term corrosion experiment illustrates the importance of factors such as relative humidity, oxygen levels, chloride ion activity and the presence of trace metals on the accelerated corrosion of copper and its alloys.

Acknowledgements

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Ian Donald MacLeod (1948), BSc (Hons), PhD. Prior to joining the W.A. Museum in 1978, research included the electrochemistry of copper in aqueous-organic mixtures at Murdoch University, Perth. Current areas of research interest include the study of the interaction of metals with marine organisms and the effects of long-term sea burial on the degradation of metals, wood and ceramics. Currently in charge of the W.A. Museum's Department of Material Conservation and Restoration. *Author's address: Western Australian Maritime Museum, Cliff Street, Fremantle, WA 6160, Australia.*

Résumé—En se basant sur les résultats obtenus sur une variété d'objets provenant de sites tant marins que terrestres, on présente une comparaison des méthodes nouvelles et des méthodes traditionelles de stabilisation des objets corrodés en alliage de cuivre. Les résultats montrent que des paramètres communs déterminent la vitesse à laquelle les chlorures peuvent être extraits. Le choix des méthodes est envisagé en fonction tant de leur rapport qualité/coût du traitement que du point de vue de l'obtention d'une patine acceptable. Si l'on classe les sept traitements de lavage par ordre de vitesse d'extraction des ions chlorure, il apparaît que la dithionite alcaline est beaucoup plus efficace que les solutions de thiourée inhibées par

l'acide citrique, puis viennent les solutions de sesqui-carbonate de sodium à 5% en masse, les solutions à 1% en masse de benzotriazole, l'acéto-nitrile à 50% en volumes, le sesquicarbonate de sodium à 1% en masse et enfin l'eau distillée. On discute l'efficacité des trai-tements dans la prévention de la 'maladie du bronze'.

Auszug—Ein Vergleich neuer und traditioneller Methoden zur Stabilisierung korrodierter Kupferlegierungsgeräte, bei dem von vielen ver-schiedenartigen Objekten sowohl aus Meeres- als auch Landfundstätten erhaltene Daten benutzt wur-den, wird präsentiert. Die Daten zeigen, daß es gemeinsame Parameter gibt, welche die Ge-schwindigkeit bestimmen mit der Chorionen beseitigt werden. Es wird die Wahl der Methoden hinsichtlich Kostenwirksamkeit und der Patinationsänderungen, die akzeptabel sind, erörtert. Die sieben in der Reihenfolge der Beseitigungsrate von Chlorionen geordneten Waschverfahren zeigen, daß alkalisches Dithionit weitaus schneller wirkt als mit Thioharnstoff inhibierte Zitronensäurelösungen, als 5 Gewichts-% Doppelsalz von Soda und Natriumhydrogenkarbonat, als 1 Gewichts-% Benzo-triazol, als 50 Volum-% Azetonitril, als 1 Gewichts-% Doppelsalz von Soda und Natriumhydrogen-karbonat, als destilliertes Wasser. Die Wirksamkeit der Behandlungen bei der Verhinderung von 'Bronzekrankheit' wird ebenfalls erörtert.