STABILIZATION OF CORRODED COPPER ALLOYS : A STUDY OF CORROOSION AND DESALINATION MECHANISMS

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SUMMARY

A study of more than 12,000 objects recovered from maritime and terrestrial archaeological sites has shown that there are several parameters that determine the rate of release of chloride ions during conservation treatment. Factors such as metallographic structure, salinity and dissolved oxygen levels during burial, give rise to a series of characteristic chloride release rates that enable treatment times to be calculated. The data relates principally to desalination in deionized water and sodium sesquicarbonate solutions and secondly, to sodium dithionite solutions.[1] The results show that stabilization of badly corroded objects can be achieved through extended wash log programmes. The physical basis for such treatments is described in terms of a model that also permits calculations on the apparent depth of corrosion.

INTRODUCTION

In an ideal situation a conservator has ample opportunity to properly assess what type of treatment is needed to stabilize a corroded object made of copper, brass or bronze. Factors that influence the choice are the presence or absence of 'Bronze Disease' and what changes in patination (if any) are acceptable. The decision also depends on the composition of the parent alloy and on the lead time before the object is to be returned for display or further examination. Ways of overcoming some of the problems associated with the choice of treatments have recently been reported[1] and this paper will address the area of predicting how long the overall treatment takes, and how to cope without the aid of sophisticated monitoring equipment.

The conservation of more than 12,000 copper-based artefact over the past eight years forms the database from which the mechanisms controlling the rate of desalination have been deduced. Because the variability of the extent of corrosion within an individual archaeological site can be quite marked, it was necessary to collect information from a number of locations in order to maximise the reproducibility of results. Most of the objects examined have come from ten shipwreck sites off the West Australian coast which date from the *Batavia* (1629) to the *Macedon* (1883). The warm tropical to sub-tropical waters[2] range in temperature from mean annual values of 17° to 25^oC and the sites are generally well oxygenated. These conditions favour extensive corrosion of metals. Coinage recovered from Graeco-Roman land sites has also been examined and the results are essentially the same as those found for objects recovered from the sea.

Inspection of objects previously treated in the W.A. Museum's laboratories had shown that many of the bronzes were subject to further corrosion under storage in ambient conditions, 20±4°C and 55±15% relative humidity. The objects had been given 'short' treatments of a few weeks duration and this was manifestly insufficient to effect stabilization of extensively corroded materials. It was decided to carry out a series of extended washing regimes to effect stabilization of the objects. In order to ascertain when chloride removal had been "completed" the wash solutions were regularly monitored for chloride and copper ions. Periodic determinations of the concentration of lead, tin and zinc in the washes were also made. The importance of monitoring treatment solutions has previously been demonstrated.[3] Corrosion reactions, particularly those involving brasses, can take place without there being any readily apparent change in the degraded object. A detailed analysis of the rates at which chloride ions are released into deionized water and sesquicarbonate solutions has established the basis of a physical model which adequately explains why the treatments are diffusion controlled. The time taken to remove the available chloride from the object is also reported and it is dependent on the composition of the parent alloy and the microenvironment from which the object was excavated.

<u>Results and Discussion: Model for chloride removal</u>
Most of the treatments investigated in this programme were based on desalination in deionized (distilled) water or in sodium sesquicarbonate solutions because of their minimal effect on patination and because they are still the most commonly adopted methods. The results of this work are therefore of major relevance to the majority of objects conservators.

The basic behaviour of archaeological copper alloy objects is clearly demonstrated by two bronze door pintles from the *Batavia* (1629) which were treated by traditional "strip" in 10 wt% citric acid (2 wt% thiourea) for two weeks then washed in 2 wt% sodium sesquicarbonate for 40 weeks. Two other *Batavia* door pintles had been previously treated by the same method but without the extended washing and they had subsequently showed signs of extensive corrosion despite their coating of Incralac. The chloride release data is conveniently displayed as a function of concentration and the square root of treatment time. Inspection of the graph (Figure 1) shows that the chloride concentration increases monotonically until a plateau is reached and, once the solution is changed, the chlorides are released at a slower rate until a second and lower plateau is obtained. If necessary, further solution changes can be made and the process repeated until no more chlorides report to the wash solution. The cause of the extensive corrosion of these bronze fittings is partly due to the high level of iron impurities (2.1 wt%). A discussion on the long-term corrosion effects of such impurities has previously been reported.[4]

The chloride release rates, based on the linearly increasing sections of the graph, are 3.73 ± 0.15 ppm. $hr^{-1/2}$.and 2.49 ± 0.81 ppm.$hr^{-1/2}$ for the first and second washes respectively. The scatter of the data is due to errors associated with sampling (insufficient mixing of the 80 litres of wash solution) and with chloride determinations using a Buchler-Cotlove chloridometer.
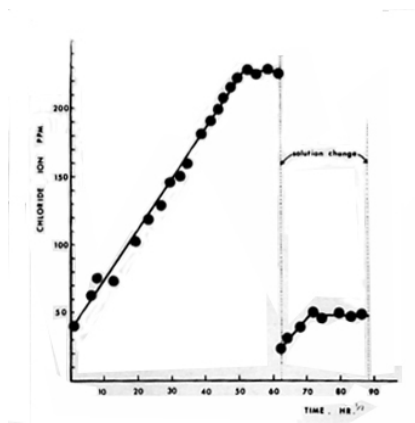

Fig. 1: Plot of chloride ion concentration versus the square root of treatment time (hr½) for two bronze door pins from the Batavia (1629) in 80 l of 2 wt% sodium sesquicarbonate. The composition of the bronze is given in Table 1

The data was analysed using a linear regression programme on a Texas Instruments (T1-55) calculator.

The bronze door pintles were given further washing in 1 wt% sesquicarbonate solutions for an extra 234 days to see if significant amounts of chloride remained behind after a total period of 280 days in the 2 wt% solutions. A total of 30 grams of chloride (0.07 wt% of the original mass) was removed during the sesquicarbonate washing and of this, some 65% came out in the first wash and a further 15% in the second wash. The treated pintles show no signs of corrosion after four years in ambient storage conditions which shows that the extended washing will stabilise extensively corroded objects with minimal changes to their patination.

Small differences in the basic behaviour outlined above will occur if secondary corrosion products or other materials precipitate on the surface of the object and effectively hinder the outward diffusion of chloride ions. Precipitation from sesquicarbonate solutions of the deep blue crystals of chalconatronite $Na_2Cu(CO_3)_2\ 3H_2O$, can slow down the release of chloride ions. Occasionally unusual corrosion products can form on objects during extended washing, e.g. a film incorporating Na_3BiO_4 was found on the surface of the *Batavia* bronze door pins, but these films are often readily removed by chemical stripping or careful brushing.

The fact that hundreds of objects give the same type of response as shown by the bronze door pintles from the *Batavia* indicates that common phenomena control the removal of chloride ions. One common factor is that all the copper brass and bronze objects have an adherent and relatively dense cuprous oxide layer (Cu_2O) on their surface adjacent to the corroded metal. The outer blue-green layers of copper (II) hydroxchlorides such as paratacamite ($\gamma\ Cu_2(OH)_3Cl$) have much lower densities, 3.75 $g.cm^{-3}$ c.f. 6.06 $g.cm^{-3}$ for Cu_2O[5], and will not be rate determining.
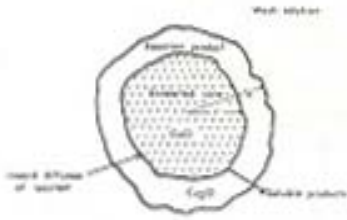

Fig. 2: Schematic cross-section through a corroded metal artefact with diffusion through the remnant structure, or products of reaction, as the rate-controlling step.

The long reaction periods of six months or more to remove the chloride ions are somewhat akin to the slow reactions associated with heap leaching of copper from mineral dumps[6] where there is slow ingress of reacting solutions, through a reaction product layer, into low grade ores in which the copper mineral is dispersed. For corroded copper alloys we can equate the reaction product layer ore as the chloride containing corrosion products disseminated within the residual metal structure. The model assumes that the reacting species (copper (I) chlorides) are evenly dispersed through spherical grains of the host matrix, which is the corroded metal artefact. A cross-section of the object and r is the radius at the reaction boundary, which moves inwardly as transport through the chloride depleted (reacted) layer which lies between the reacting front and the outer regions, and by the rate of reaction within the reaction zone. If the major hydrolysis product in the corroded metal zone is cuprite than there will still be 'gaps' left for the chlorides to diffuse through since reactions such as

$$2CuCl + 20H^- \rightarrow\ Cu_2O + 2Cl^- + H_2O \tag{1}$$

will leave the intergranular or interdendritic space more open since although nantokite (CuCl) has a similar volume of 23.9 cm^3 to cuprite (Cu_2O) at 23.65 cm^3, the stoichiometry of equation 1 shows that the void space would be increased if such reactions occurred. A combination of oxidation and hydrolysis of copper (I) chlorides, could result in dissolution of the corrosion products, as shown in equation 2

$$4CuCl + O_2 + 8HCO_3^- \rightarrow 4Cu(CO_3)_2{}^{-2} + 4H^+ + 4Cl^- + 2H_2O \tag{2}$$
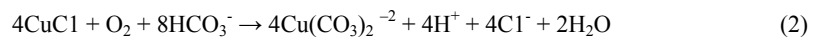
If the remnant structure or products of the hydrolysis occupy roughly the same volume as was dissolved during the chloride removal, then a special solution can be obtained[7] where the total flux is given by

$$\frac{dn}{dr} = 4\pi\ r^2\ D\ \frac{dc}{dr} \tag{3}$$

where n is the number of moles of chloride, r is the radius of the reacting front (see Figure 2), D the diffusion coefficient and c the surface concretion. The washing experiment approximates to steady state conditions in which the rate of diffusion through the pores in the shell outside the reaction zone equals the rate within the reaction zone. Under these conditions there will be a constant flux of materials across the values of r between r and r_o which changes equation 3, upon integration, to the form where the rate of increase in the number of moles of chloride, $\dfrac{dn}{dt}$, is given by the expression.
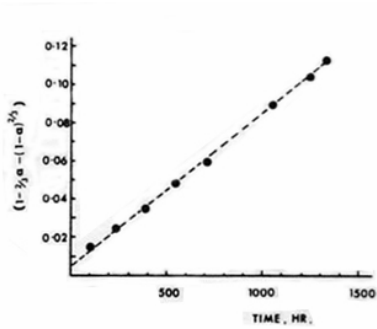
$$\frac{dn}{dt} = \frac{-4\ DCr.r_o}{(r_o - r)} \tag{4}$$

Fig.3: Diffusion model correlation of data for chloride extraction from *Batavia* bronze door pins in 2 wt% sodium sesquicarbonate solutions at 22ºC and pH 10.0 ±0.1
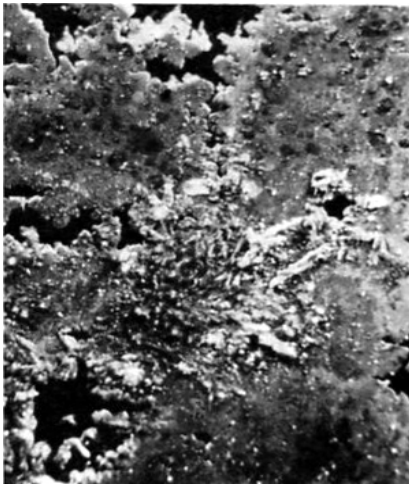

Fig 4: Metallographic transverse of section of leaded brass rudder pintle pin from *Cumberland* (1830) showing active corrosion. The surface of the section was 5 mm from the tip of the pin. The analysis of the pin is shown in Table 1. Full width of image 5.58 mm.
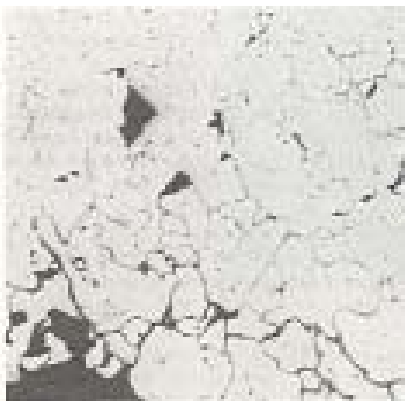

Fig. 5: Metallographic structure of a longitudinal section of the shank of a corroded brass nail from the *Rapid* (1811) after etching in 2 wt% alcoholic ferric chloride. The nail had been hot worked after casting. Full width of image 753 μm.

under the boundary conditions that c, the reaction surface concentration is small compared with C, the bulk concentration of reactant. The rate at which the reaction front radius changes is given by

$$\frac{\partial r}{\partial t} = -\frac{VDCr_o}{r(r_o - r)} \tag{5}$$

where V is the molar volume of the reacting (mineral) species. The above expression can be formulated in terms of α, the fraction of the reaction completed the time t, to give

$$\frac{\partial \alpha}{\partial t} = \frac{3VDC}{r_o^2} \frac{(1-\alpha)^{1/3}}{[1-(1-\alpha)^{1/3}]} \tag{6}$$

which results in $1 - \frac{2}{3}\alpha - (1-\alpha)^{2/3} = (2vDC/r_o^2)t$ (7)

for the condition that α = 0 at t = 0

Thus a plot of the function $1 - \frac{2}{3}\alpha - (1-\alpha)^{2/3}$ versus time should give a straight line with zero intercept and a slope of $(2vDC/r_o^2)$ if the model accurately describes the chloride removal process. Data from the first stage of the sesquicarbonate washing of the *Batavia* bronze pintles was used to test the model and the results are shown in Figure 3 for the first fifty days of the treatment. The relationship between the alpha function and time was given by

$$1 - \tfrac{2}{3}\alpha - (1-\alpha)^{2/3} = 0.0000803t + 0.00484 \tag{8}$$

which had a correlation coefficient for the least squares fit of 0.9993, where the time is in hours. The intercept value of 0.00484 is essentially zero, as intercepts would be found in cases where there was surface chloride, e.g. when sea water had evaporated to dryness on the surface of the corroded fitting and rapidly dissolved as soon as the object was placed in the wash solution. The zero intercept also supports the observation that reactions of the type,

$$Cu_2 (OH)_3 Cl + 4CO_3^{2-} \rightarrow 2Cu(CO_3)_2^{2-} + 30H^- + Cl^- \tag{9}$$
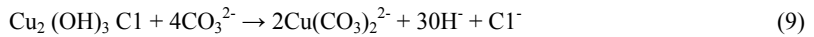
do not occur to any significant level in 1 wt% and 2 wt% sesquicarbonate solutions, viz., the blue-green patina is largely unaffected by the washing process. The value of the slope was 8.03 x 10^{-5}hr^{-1} or 2.23 x 10^{-8} sec^{-1} and can be used to calculate values of r_o, the radius of the 'untreated' artefact. If we assume that the reacting species is the hydroxide ion as shown in equation 1, then at pH 10.0,C will be 1 x 10^{-4} M, V, the molar volume of CuCl is 23.9cm^3 and D, the diffusion coefficient of the reacting ion through the Cu$_2$O layer is approximately 5 x 10^{-6} cm2. sec^{-1},[8] then r_o will have a value of 1.03cm. Such a value for r_o implies that the reaction zone, the area with copper (I) chlorides dispersed through it, is 1 cm deep into the object which is entirely consistent with the observed corrosion phenomena. Although the bronze sampled for chemical analysis was apparently solid and was predrilled to a depth of 5 mm prior to the core sample being taken, the total metal content (copper, tin, lead, zinc, etc. as show in Table I) amounted to only 98.24% which is consistent with significant mineralization at the depth range 5-10 mm. Further evidence of the depth of chloride penetration into bronze artefacts was seen when a section was cut through a corroded leaded brass pintle pin from the wreck of the *Cumberland* (1830) and was left exposed in the laboratory for three weeks. A series of concentric corrosion spots appeared approximately 1.5 cm in from the former sea water-metal interface. Active 'Bronze Disease' broke out on the polished section from the tip of the pin (see Figure 4) which was 0.5cm into the object. Despite outward appearances of a relatively sound casting, there were many defects such as casting porosity in the centre of the pin and chloride ions and penetrated several cm into the metal structure over a period of 155 years in fully oxygenated sea water at 18.5±4.6ºC.[2]

Detailed analysis of rate of chloride release from a series of aerobically corroded copper, brass, and bronze objects and one cathodically protected bronze swivel cannon from the Zuytdorp (1712) all conformed to the relationship that

$$1 - \tfrac{2}{3}\alpha - (1-\alpha)^{2/3} = \left(\frac{2vDC}{r_0^2}\right) t$$

With the mean value of the slope being (153±70) x 10^{-6} hr^{-1} which would give a mean r_o value of 7.43±3.4 mm which is consistent with typical values for depth of intergranular / interdendritic corrosion found in samples analysed metallographically, as shown in the polished section of a nail from the *Rapid* (see Figure 5) where intergranular corrosion has penetrated 7.3 mm.

A dramatic example of the depth of corrosion penetration was seen during wet chemical analysis of some leaded bronze sheathing tacks from the *Lively* (c.1810)[1]. In order to determine how much chloride was in the total mass of the nail, a number of sections were dissolved in 10 wt% nitric acid. Digestion of the samples resulted in hollow cores of creamy-white cassiterite (SnO$_2$) remaining in the acid solution (see Figure 6). Analysis showed that although some tin (IV) corrosion products dissolved, most of the matrix remained, whereas the corroded copper rich phases and all the uncorroded core were dissolved in the warm acid solution. The total chloride content of the untreated nails was 1.18±0.37 wt% or 24 times the amount in the 'uncorroded' core.

Effects of composition and on-site microenvironment on chloride release rates

In order to understand why objects took different times to stabilize and why apparently similar alloys from the same wreck site had corroded in different ways, a systematic study of the effects of on-site microenvironment was made. A number of objects were sampled for wet chemical analysis[9], electron microprobe studies[10], corrosion products[11] and the associated concretions were also studied[12]. The results show that the corrosion of copper and its alloys with oxygen and metallographic structure. Since the salinity of the Western Australian shipwreck sites were all in the range 37-35 ppt and the mean annual temperatures varied from 25.5 to 18.3°C,[2] the other factors of metal structure and on-site microenvironment were seen to be of major significance.

It has been shown that the corrosion mechanism [10,11,13] of bronzes changes with the depth of burial. If an object is lying proud on the seabed and in well oxygenated waters there is kinetically controlled oxidation of the copper rich α phase. This results in objects having an apparently sound structure and will give rise to a typical blue-green patina overlying the red-brown cuprous oxide layer. Bronzes that lie buried under several centimetres of sand corrode in a very different manner since the oxygen diminished environment results in selective corrosion of the tin rich phases, such as the α + δ eutectoid. The corrosion mechanism is under thermodynamic rather than kinetic control. Objects recovered from these 'partly aerobic' conditions have a more open surface structure which is more friable and consists of a large amount of tin (IV) and some tin (II) corrosion products intermixed with Cu_2O and copper (II) hydroxy chlorides. If the objects have been buried in anaerobic conditions the corrosion products will be principally metal sulphides. The fourth type of microenvironment is found for objects that have been cathodically protected by galvanic action by a more reactive metal such as iron. Bronzes which are normally free of concretion are found to be covered with a thin (2-3mm) calcareous layer that is hard and impervious. Once the concretion has been removed the objects appear to be in a sound condition and are normally covered with a Cu_2O or a mixed Cu_2S/Cu_2O patina.

Since we have shown that the diffusion controlled release of chlorides is largely dependent on the microstructure of the object and the copper (I) oxide layer on the surface, it is now possible to rationalize the data from more than 50 washing experiments. Plots of the raw experimental data give chloride release rates in parts per million per hour$^{\frac{1}{2}}$ (ppm hr$^{-\frac{1}{2}}$) simply because of the choice of analytical procedures used in the laboratory. A convenient way to minimise variations in apparent release rates is to correct for the solution volume and geometric surface area of the objects. The 'normalised' release rats are given by the formula

$$R_n = \frac{R_{ppm}.x}{y} \tag{10}$$

where χ is the solution volume in litres, y the surface area in square centimetres and R_{ppm} is the release rate in ppm.hr$^{-\frac{1}{2}}$. Normalised rates will have the units of mg.cm^{-2}.hr$^{-\frac{1}{2}}$. Since the data obtained is normally small fractions of a mg.cm^{-2}.hr$^{-\frac{1}{2}}$ it is reported for convenience in the units of μg.cm^{-2}.hr$^{-\frac{1}{2}}$.

Whilst it is realized that real surface areas will be considerably greater than those determined geometrically, the improvement in the quality of the data by using the former values would probably not justify the amount of work involved in such measurements.[14] Since each of the data sets relates to the treatment averaged out. The mean values of the normalised release rates for copper, brass, bronze and composite objects recovered from different microenvironments are shown in Table 2. Inspection of the data shows that there are significant differences in the chloride release rates for the various alloys. Because of the limited on-site documentation of artefacts microenvironment for some wreck sites, we are not able to further define the aerobic category into fully oxygenated and partly oxygenated. However, it is readily apparent that chloride ions are removed from aerobically corroded bronzes at a much greater rate than for brasses which in turn are faster than copper. Such trends reflect the differences in the way the metals corrode.

Copper degrades primarily through erosion and intergranular corrosion. The treated objects had copper contents of greater than 98%[9] and their metallographic structure consists of single phase α solid solution with various impurities and inclusions such as droplets of lead and particles of Cu_2O[4]. Brass objects generally had a single phase α brass structure[15] but some had enough zinc to give significant amounts of the zinc rich β phase. Many shipwreck brasses have been subject to dezincification[16] and selective corrosion of the zinc rich β phase. As the microstructure is "opened up" during corrosion, chloride ions will diffuse into the matrix and form relatively insoluble copper (I) chlorides which will be 'trapped' inside the Cu_2O layers. Metallographic examination of shipwreck bronzes[10,15,17] has shown that they are often subject to selective corrosion of the tin rich phases such as the (α + δ) eutectoid. Electromicroprobe studies of sectioned metals shows that there are significant amounts of tin (IV) and zinc (II) corrosion products within the degraded structure. Since chloride ions are readily abundant in sea water it is not surprising to find that greater amounts of chloride had diffused into bronze and brass objects to 'balance' the Zn^{2+} and Sn^{4+} ions than into the single phase copper objects where the major corrosion products are copper (I) compounds. Typical values of the amount of chloride extracted during sesquicarbonate treatment are 0.064 wt% for bronze and brass and 0.026 wt% for copper.

Fig. 6: Residual structure of corroded leaded bronze sheathing tacks, *Lively* (c. 1810), after digestion of tacks in warm 10 wt% nitric acid. The creamy-white solid was identified by XRD as cassiterite, SnO_2. The chemical composition of the tack is listed in Table 1. Full width of image 6.6 mm.

Objects having higher concentrations of chloride in them would be expected to release them at a faster rate. For example, materials such as iron and glass have higher release rates partly because they have a greater amount of chlorides in them. The amount of chloride in the untreated objects is in the order of 0.8wt% or some twelve times the amount typically extracted from bronzes. Details of chloride and sulphate removal for glass and ceramics are reported elsewhere.[18] Because degraded glass does not have such a coherent diffusion barrier as the Cu_2O layer in copper and its alloys, chlorides will tend to diffuse out at a much greater rate than commonly found in aerobic washing regimes.

When copper corrodes in an anaerobic environment the corrosion products are dominated by copper sulphides which range from Cu_2S through $Cu_{1.93}S$ and $Cu_{1.8}S$ to CuS.[12] Chloride ions are present mainly as CuC1 along grain boundaries. Although sulphides are present as corrosion products on bronze objects, they are mainly found in the outer corrosion layers with chlorides being found deeper within the metal structure. Objects that had been subject to cathodic protection from corroding adjacent iron components are included in this category since the microenvironment under the protective thin calcareous layer is essentially anaerobice.[12] The release rates found for objects recovered from anaerobic conditions can be rationalized in the same way as was used for the aerobic data.

Prediction of treatment times

Using the information outlined in the preceding section, it is now possible to predict with reasonable confidence how fast chloride ions will be released from corroded copper alloys when they are first placed into sesquicarbonate wash solutions. It is of major importance for those concerned with laboratory management to know how long an overall treatment will take so that appropriate budgeting of resources and charges for clients can be made. If an object is suddenly required for display, a conservator needs to have guidelines by which one can gauge whether or not it is safe to temporarily interrupt the treatment.

In an attempt to see if there were any systematic trends in the amount of chloride released at each stage of the stabilization process, the concentrations at which plateaus occurred were noted and the results indicated that there was no apparent order. By comparing the ratios of concentrations at which the plateaus occurred, problems associated with variable solution volumes are overcome. The ratios of subsequent plateau levels to the initial value are summarized in Table 3 for the different types of alloys and treatment programmes. Inspection of the data clearly shows that the behaviour of copper, brass and bronze is the same, but that composite materials are somewhat different. The reason why the plateau ratios are the same for copper, brass and bronze lies in the fact that the same mechanism controls the removal of chloride ions. The different ratios found for composite materials are a reflection of the influence of the rate determining steps associated with chloride release from degraded glass and/or iron. On the basis of the data in Table 3 it is now possible to predict how much of the "available" chloride is removed in each stage of desalination. For copper and its binary alloys, the first wash will generally extract approximately 73% of the total, the second wash about 21% and the third wash the remaining 6% (see Table 3).

Although the ratios of plateau levels and the percentage extraction in each wash showed remarkably little variation, the same cannot be said for the treatment times. For copper objects, two months is normally required to remove 72±4% of the chlorides when washing in 1-2 wt% sodium sesquicarbonate. The apparently shorter time required to plateau in deionized water is partly a reflection of the fact that deionized water will not necessarily extract the same total amount of chloride out of a given object as will other treatments.[2] All washing experiments had a ratio of wash volume to object volume of greater then ten. Bronzes and brasses normally contain larger amounts of chloride ions (see previous section for discussion) and so it is not unexpected that they will take slightly longer to reach the same level of removal than copper objects. With composite materials the first plateau is reached earlier than for the parent alloys since chlorides are removed more rapidly from glass than bronzes.[18] Since several sets of objects required only two washes to stabilize them, there is insufficient data to obtain statistically valid mean values for the times taken to reach the second and third plateaus. Inspection of the data in Table 3 for total treatment times, shows that all types of objects should be stabilized within a period of nine months, with simple copper artefacts typically taking three months and brass-bronze objects taking roughly five months.

Alternative Treatments

Because of time constraints many conservators need to be able to speed up the treatment programmes, especially if they are working in private industry. The problem of how to choose the more appropriate technique has recently been discussed[1] but simple comparison of sodium sesquicarbonate and alkaline sodium dithionite shows that, in the absence of aesthetic and materials constraints, the former is roughly ten to fifteen times slower than the dithionite method. Under the action of the alkaline dithionite solution the Cu_2O layer on the surface is reduced to copper metal and this makes the surface structure much more porous. Copper corrosion products within the metal matrix are also reduced to the metallic state and so the major limitation to the rate of chloride removal is the tortuosity (dimensionless path length) of the host material. Under d.c. electrolysis similar chloride release rates to alkaline dithionite

are observed. With a direct current, the "reducing power" comes from a source external to the solution.

Conclusion

A mechanism controlling rhe release of chloride ions from corroded copper / copper alloys has been described and shown to give theoretical values of corrosion depth that are supported by experimental observations. Analysis of the data obtained from treating some thousands of objects has established a series of characteristic chloride release rates that relate to alloy composition and the on-site microenvironment. It is now possible to assess with a high degree of confidence how much of the available chloride ions will be released at each stage of the desalination process. The data base established through analysis of the treatment programmes enables prediction of how long the overall stabilization process will take.

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Table 1
Chemical analyses of objects recovered from shipwrecks

	Cu	Sn	Pb	Zn	Fe	Sb	As
Batavia door pintles	92.7	1.4	1.1	0.5	2.1	0.3	0.14
Cumberland pintle pin	63.0	2.37	13.6	20.5	0.82	0.10	n.d.
Lively sheathing tacks	87.08	8.53	0.79	2.97	0.105	0.066	0.01

Table 2

Normalised chloride release rates for stabilization of artefacts during the first wash in deionized water and 1-2wt% sodium sesquicarbonate solutions in $\mu g.cm^{-2} hr^{-\frac{1}{2}}$

Composition	Microenvironment	Mean values of Normalised release rates	No. of data sets
Copper	aerobic	5.9 ± 2.6	12
Brass	aerobic	14.2 ± 5.7	8
Bronze	aerobic	50.1 ± 17.4	7
Composite+	aerobic	380 ± 227	4
Copper	anaerobic	1.7 ± 0.6	3
Bronze	anaerobic	12.9 ± 7.0	5

+ Composite materials included *Batavia* (1629) composite iron-copper-brass-solder cannon,[19] and brass portholes with glass windows from the Georgette (1876) and *Xantho* (1872).

Table 3
Mean plateau ratios and treatment times for desalination of copper and its alloys

	Copper aerobic	Brass-Bronze aerobic	Brass Bronze anaerobic	Composite aerobic
Second wash ratio	0.216±0.031	0.23±0.03	0.23±0.03	0.370±0.065
Third wash plateau ratio	0.071±0.020	0.065±0.020	0.065±0.020	0.130±0.065
Length of initial wash (days)	64±19[1] 41±15[2]	79±18[1] 79±33[2]	40.3 ±5.6	50.2±16.4
Total treatment (days)	105±71	218±111	166±61	283±12
% CI extracted 1st wash	72.0 ±3.8	74.8±6.7	-	69.7±7.0
2nd wash	21.8±4.7	20.1±6.0	-	22.4±4.2
3rd wash	6.3 ±0.8	7.4±3.2	-	7.6±2.9

[1]Treatment in sodium sesquicarbonate solutions
[2]Treatment in deionized water