CONSERVATION, APPLIED SCIENCE AND WHY TREATMENTS MUST BE MONITORED

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SUMMARY
The importance of monitoring wash solutions during aqueous stabilization procedures has been demonstrated over a five year research programme that involved treatment of more than four thousand objects. Most of the data pertain to the removal of chloride ions from corroded metals recovered from historic shipwrecks. Studies on the stabilization of textiles impregnated with metal corrosion products have shown that the removal of such stains is often controlled by complex kinetics that involve a diffusion controlled process. The conservation methods are described through a series of case studies which give details of the nature of the materials used in the fabrication of the objects and how each problem was examined and solved. The techniques used include chemical analysis by atomic absorption spectrophotometry, x-ray diffraction, scanning electron microscopy, infra-red spectroscopy and measurements of electrochemical potentials. It is often necessary to use all of the above techniques to develop an appropriate conservation treatment. The phenomena that control release of chloride ions from shipwreck materials are the same as those involved in the stabilization of material from land-based archaeological sites in the Middle East.

INTRODUCTION
Conservators are often in a dilemma when faced with a range of alternative stabilization procedures as to which one should be followed. Given that costs of chemicals, availability of equipment, and safety aspects have been rationalised the choice often seems to follow the course that is "familiar".

While innate caution is a laudable characteristic in a conservator the criteria used in choosing a particular technique are often tenuous. To adopt a procedure simply because somebody from another institution uses it is not good enough unless the objects have come from a similar environment, are made of the same materials and present the same conservation problems.

This paper will demonstrate that the majority of chemical stabilization methods are controlled by some form of diffusion of the reacting species and as a consequence the treatments show a linear dependence on the square root of elapsed time. By monitoring parameters, such as the concentration of iron released for stain treatment of metal objects, it can be ascertained when wash solutions unnecessary expenditure of time and materials is incurred. The Appendix provides details of the analytical techniques used in monitoring solutions.

Chemical reactions such as metal corrosion can occur in a wash solution without any readily apparent change in the appearance of the object and if such solutions are not monitored significant damage may occur. Examples of secondary mineralization (deposits forming on objects during conservation procedures) and its effects on subsequent treatments will be discussed. The observations reported are based on a research program carried out over the WA Museum and cover the treatment of more than four thousand artefacts. Although the majority of materials examined were from shipwrecks our experience with land based objects has shown that the same phenomena control the requirements for their stabilization. Before commencing work on an artefact that needs a novel treatment a thorough study of the object should be made and samples of mineral deposits (stains, corrosion products, concretion, fibres etc.) should be obtained for research purposes.

Since the data on objects have been collected as a result of individual treatments they will be presented as a series of case studies.

STABILIZATION OF CORRODED ALUMINIUM AND MINERALIZED CANVAS

A seaplane float from a Junkers W33 aircraft arrived at a laboratory for treatment after 46 years of corrosion on the beach in the NW of Western Australia. Inspection of the object showed that it was in an advanced state of degradation and that the metal was actively corroding. A metallographic and mineralogical survey showed that the original metal was a Duralumin alloy (92.8% Al, 4.12% Cu, 0.44% Mg, 0.31% Fe, 0.77% Mn and 0.03% Pb) which had undergone general corrosion. Some of the blue-green copper corrosion products had reacted with the underlying metal with the result that patches of metallic copper were bonded to the present alloy. This meant that the copper was acting as cathodes of pitting corrosion cells that were responsible for the perforation of large areas of metal.
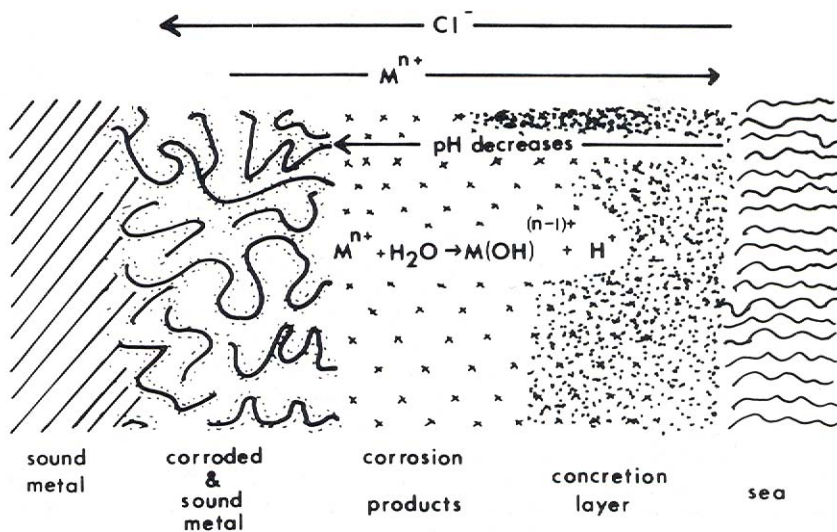

Figure 1   Schematic diagram of a cross section of a corroded metal object in sea water showing directions of diffusion of chloride and metal ions.
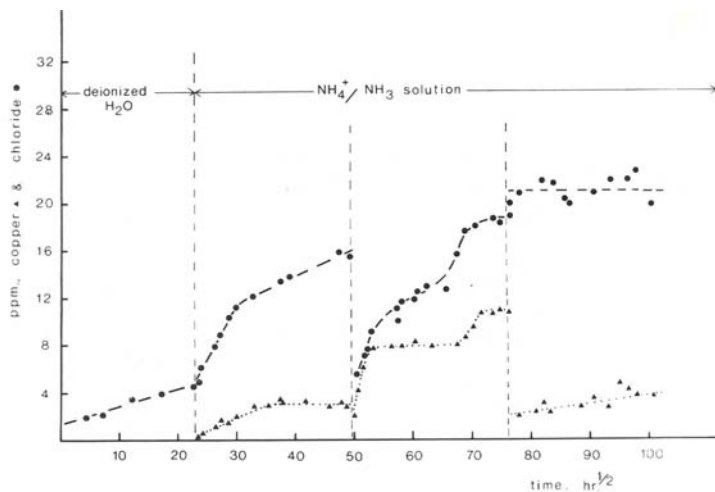

Figure 2   Plot of the amount of chloride (●) and copper (▲) released during washing of the sea plane float, against the square root of elapsed time (hours ½). Solution volume approximately 3100 litres.

The conservation problem was twofold: firstly, the redeposited metallic copper had to be removed from the float without dissolving more of the Duralumin, and secondly, the chloride ions present in the corrosion products and the corroding pits had to be removed in order to effect stabilization of the residual metal structure.

When a metal object corrodes in the sea or in a marine environment an insoluble layer of corrosion products can form on the surface and this in turn is often covered by a layer of calcareous material, Fig. 1. Underlying the corrosion product layer is a zone of partly corroded metal which often contains high concentrations of chloride ions which have diffused in to balance the charge of the metal ions that are formed as a result of the corrosion process. Chloride ions are known to increase the rates of many metal corrosion reactions so it is essential that their concentration in the partially corroded metal zone be reduced to a level where the metal exhibits no corrosion activity under normal storage conditions. The concretion layer is normally removed from an object to increase the chloride ion release rate. In the case of the seaplane float no attempt was made to remove the aluminium oxide/hydroxide layer on the metal since it is normally protective and in many parts it acted as a matrix to hold together fragments of the original metal. The major aluminium corrosion product on the float was the aluminium hydroxide gibbsite $(Al(OH)_3)$ with small amounts of felsobanyaite, a hydrated basic aluminium sulphate $Al_4SO_4(OH)_{10}.5H_2O$, and an unidentifiable light blue copper containing material with a distorted alumina structure. The major form of calcium in the concretion was gypsum, $CaSO_4.2H_2O$, and there were small amounts of calcite, $CaCO_3$. The concretion was bound together with pindan – a characteristic mixture of red clay soils of the Kimberley region of WA.

The treatment of the float involved the removal of the concretion by scrubbing with a stiff bristle brush followed by 14 months washing in solutions of 0.25 M-NH_3/0.125 M- $(NH_4)_2SO_4$ at a pH of 9.6 ± 0.1. During treatment the chloride concentration (determined with a Buchler-Cotlove chloridometer) and the coper concentration in solution) determined by atomic absorption spectrophotometry) were monitored and the results are shown in Figure 2. To ensure that no corrosion of the remaining metal occurred during immersion, the voltage (corrosion potential) of the float and the solution voltage were periodically measured. During the initial three weeks washing in deionized water ($0 < t^{1/2} < 22.5$ hr$^{1/2}$) only chloride was being released but after the ammonia/ammonium sulphate had been added both copper and chloride occurred in solution. Several points concerning the treatment are worth noting. Firstly the release of both copper and chloride is diffusion controlled as is shown by the linear response in concentration with the square root of time. Only when the copper had plateaued was there any need to change the solution. Since the solution volume is 3000 litres and the bath took 50 kg of $(NH_4)_2SO_4$ and 50 litres of 0.880 ammonia to create the right leaching conditions there are obvious savings in not having to change the solution too frequently. The release data are consistent with there being two modes of chloride release, both of which are diffusion controlled, but only one of which is associated with the dissolution of surface copper and copper corrosion products. A more detailed discussion [1] of the changes in the chloride and copper release rates is given.

The ammonia /ammonium sulphate wash solution was chosen because the combined effect of ammonia and oxygen dissolves copper (II) corrosion products and any copper metal on the surface of the float. The protective aluminium oxide film is normally stable over the pH range of 4.7 to 9.7 [2]; at lower pH the film dissolves as Al^{3+} ions while at high pH the soluble aluminate (AlO_2^-) ion is formed. Although the pH of 9.6 ± 0.1 established by the ammonium sulphate / ammonia buffer system is moderately high for the stability of the aluminium surface film, it has been found [3] that such solutions do not actively corrode aluminium.

The dissolution reaction for the surface copper metal can be written as
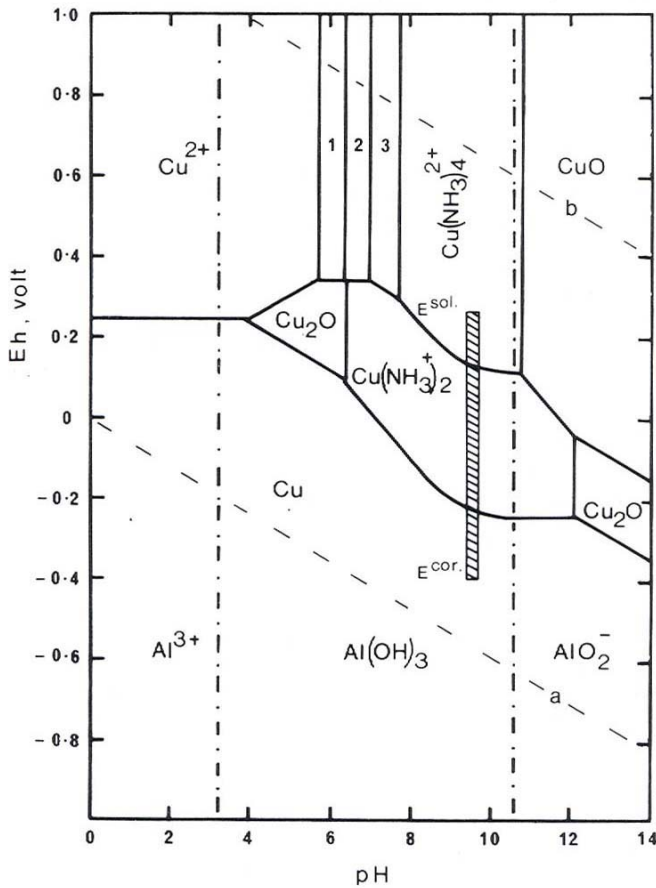
$$Cu \ + \ 4NH_3 \ + \ \tfrac{1}{2}O_2 \ + \ H_2O \ \longrightarrow \ Cu(NH_3)_4^{2+} + \ \ \ 2OH^- \ \ \ \ \ \ \ \ (1)$$
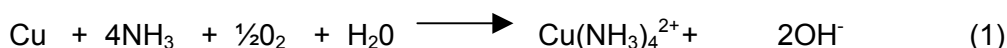
Figure 3

Potential –pH diagram for the system $Cu-NH_3-Cl-H_2O-Al$. The diagram is based on data from [6] and [7]. Region 1 is the stability domain for $Cu(NH_3)^{2+}$, region 2 for $Cu(NH_3)_2^{2+}$ and region 3 for $Cu(NH_3)_3^{2+}$. Solution conditions are $NH_3 = NH_4 = 0.25M$, $Cl = 2 \times 10^{-3}M$, $Al = 10^{-6}M$, $Cu = 1 \times 10^{-4}M$.

The copper (II) tetrammine ion can also act as an oxidant and can dissolve the surface copper metal,

$$Cu + Cu(NH_3)_4^{2+} \longrightarrow 2Cu(NH_3)_2^+ \qquad (2)$$
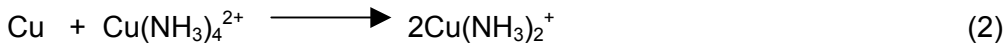
to form the copper (I) ammine complex which is rapidly oxidized by atmospheric oxygen to the $Cu(NH_3)_4^{2+}$ ion. The results of the solution monitoring of corrosion and redox potentials is shown in Figure 3 which is the combined Eh-pH diagram for copper and aluminium in ammonia, chloride ion ($2 \times 10^{-3}M$) and water.

The hatched area refers to the experimentally observed range of pH and Eh. The most positive voltages (0.28 volt) refer to the solution potential, measured at platinum electrode, and indicate that the copper tetrammine ion is the stable form of copper in the oxygenated wash solution. The most negative potentials, -0.4 volt, refer to the corrosion potential of the metal float; under the conditions found in the wash solution it is unlikely that any fresh pits can occur [4]. The potentials measured on the surface of the float –0.2 to + 0.1 volt, were in the stability range for the copper (I) diamine ion. According to the Pourbaix diagram (Figure 3) any copper ammine complexes could be reduced back to copper by aluminium metal if the oxygen (Eh) concentration was low. In practice this does not occur because of the combined effects of the pH of the wash solution which tends to 'repair' flaws in the oxide film, and the low chloride concentration and kinetic (energy) barriers associated with the cementation reaction. When there was no further increase in the chloride ion concentration and inspection of the float showed that the surface was free of redeposited copper and copper corrosion products the treatment was terminated.

Some sections of the float were riveted together with a layer of canvas between them prior to water-proofing with pitch. The material was bound into a solid mass of copper and aluminium corrosion products held together by pindan and general calcareous concretions. The fabric was cleaned by soaking in a solution containing 0.4 M-NH_3, 0.2 M-$(NH_4)_2SO_4$ and 0.5 wt% of the

disodium salt of EDTA at pH of 9.6 ± 0.1 for three months, with a wash in deionized water between layers of gauze to remove any loosened materials at the time of changing the washing solution. The release of chloride and copper was monitored and the copper release showed a dependence that fitted the kinetics of a chemically controlled semipassivated shrinking sphere [5]. Although the amount of chloride released was very small, only 30mg in three months, and the release data were not of sufficient quality to establish whether the release was a simple diffusion controlled process (t½) or the same process as the copper, it still amounted to 0.5% of the dry canvas weight. The copper release data were found to conform to the equation

$$t / T = 1 - (1-X_b)^{1/3} \tag{3}$$

where X_B is the concentration of copper at time t expressed as a fraction of the total released at time T. A plausible explanation of this behaviour is that ammonia has to diffuse into the grains of the distorted alumina and dissolve the copper corrosion products embedded in the Al_2O_3 matrix. As the reaction proceeds the diffusion path for the ammonia increases as the "copper containing sphere" shrinks. An obvious implication of such observations is that removal of stains/minerals from textiles is not necessarily a simple process and rarely will the release of undesired contaminants be a straight-forward once off immersion in a washing solution for a couple of hours.

REMOVAL OF IRON STAINS FROM BATAVIA LACE

A sample of lace from the wreck of the '**Batavia**' (1629) had been originally excavated from iron concretion and soaked in an EDTA solution before being mechanically cleaned of the softened massive iron stains. It was subsequently bleached (treatment details are not known) and put on display at the Geraldton Maritime Museum. After four years in the salty environment iron stains had reappeared and the lace required cosmetic treatment to return it to a "clean" state.

The iron stains were identified as akagenite (ß-FeOOH) [8] and monitoring of the iron concentration in a 5 wt% disodium EDTA solution was carried out using atomic absorption spectroscopy. The release data are shown in Figure 4 where the iron concentration is plotted against the square root of the treatment time. Since very little iron had been removed after one day it was decided to check the pH of the wash solution and it was found to be 10. After the pH was adjusted to 4.5 (where the H_2L^{2-} form of EDTA (H_4L) is the dominant species) the iron release rate increased from approximately 0.15 ppm hr$^{-½}$ to 0.81 ppm hr$^{-½}$. Further tests showed that the chemical suppliers had put the tetrasodium salt in a container labelled as the disodium salt of EDTA! After a total of 48 hours at pH 4.5 it was considered that a more rapid method of removing the iron minerals was needed since the effect of prolonged immersion on the textile fibres in such solution was not known. Spot tests on similar materials had shown that a mixture of 0.15 wt% Na_2EDTA, 0.5 wt% oxalic acid and 1 wt% NaCl was very efficient at removing old iron stains. Although the above formulation had a pH of 2.5 it was considered that an immersion period of an hour at such a pH followed by extensive washing would not unduly harm the object. The iron stains were removed in less than an hour but surface pH readings of the lace did not fall below 3 even after repeated washing in deionized water. However, one rinse in a 0.5 wt% sodium bicarbonate solution was sufficient to neutralize the surface acidity. The acid-base titration curve on the bicarbonate washings (Figure 5) showed up a series of inflexion points which roughly correspond to the pKa$_1$, pKa$_2$ and pKa$_3$ of EDTA and to the pKa$_1$ and pKa$_2$ of oxalic acid. Although the chloride / oxalic acid / EDTA mixture efficiently removed the iron stain the EDTA and oxalic acid were apparently chemisorbed on the cotton fibres and could only be removed by neutralization. Since chloride ions do not appear to have any marked effect on the strength of natural textile fibres the benefits of the addition of sodium chloride to the EDTA / oxalic acid mixture are considerable since it causes a marked increase in the rate of iron stain removal.
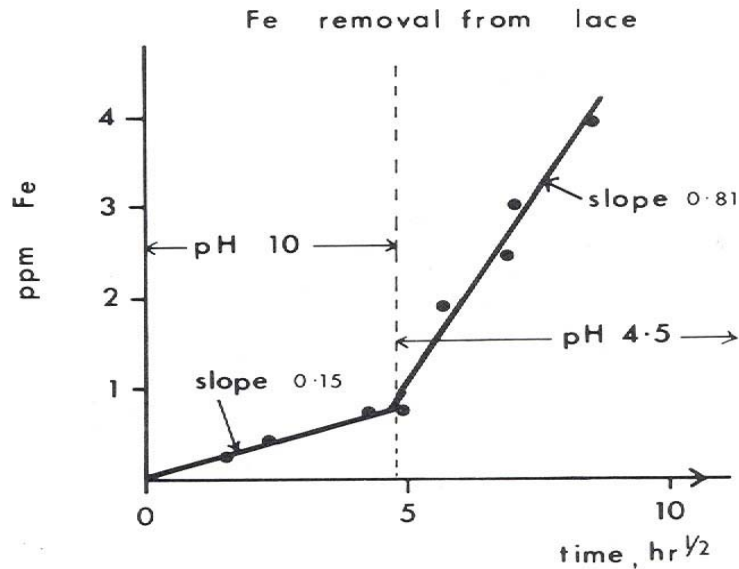
Fe removal from lace

Figure 4   Plot of iron concentration vs the square root of elapsed time ($t^{-\frac{1}{2}}$) for washing iron stained 'Batavia' lace (1629 in solutions of 5 wt% EDTA.
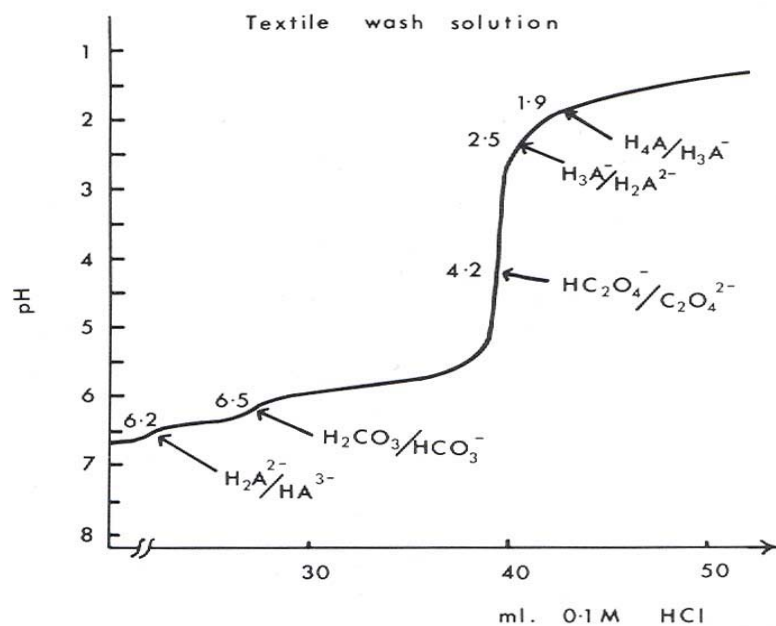
Textile wash solution

Figure 5   Acid-base titration curve for the bicarbonate rinse used to neutralise the acid residues on lace after iron stain removal using 0.15 wt% Na_2EDTA, 0.5 wt% oxalic acid and 1 wt% NaC1.

A COMPOSITE CANNON FROM THE 'BATAVIA'

The sectioned cannon was found to be actively corroding and the composite nature of the metals precluded all of the standard treatments since the tin-lead filler would dissolve in the caustic solutions needed to stabilize iron and the iron would corrode in the sesquicarbonate washes needed to stabilize the copper and the solder. Details of the composition and analysis of the treatment method have been reported [9]. The initial treatment of the smaller section involving washing in a 4 wt% sodium sesquicarbonate solution with monitoring of the concentration of chloride, copper, lead and iron in solution. A plot of the chloride release data against the square root of treatment time is shown in Figure 6.

During the first 324 hours ($0 < t^{1/2} < 18$) the chloride concentration in solution was linearly dependent on $t^{1/2}$ which indicated that the release was diffusion controlled while measurement of the corrosion potential, E_{corr}, showed that at a voltage of –0.325 V vs SHE (Standard Hydrogen Eletrode) and a pH of 9.95 the cannon was corroding. The Pourbaix diagrams for iron lead and copper showed that under these conditions copper was stable but that iron and lead were not. A red-brown material had deposited on the cut iron surfaces and it analysed as 63% lead and 37% copper. Presumably the material resulted from the reaction of lead and copper ions (copper from dissolution of corrosion products and lead coming from active corrosion) with iron in cementation reactions:
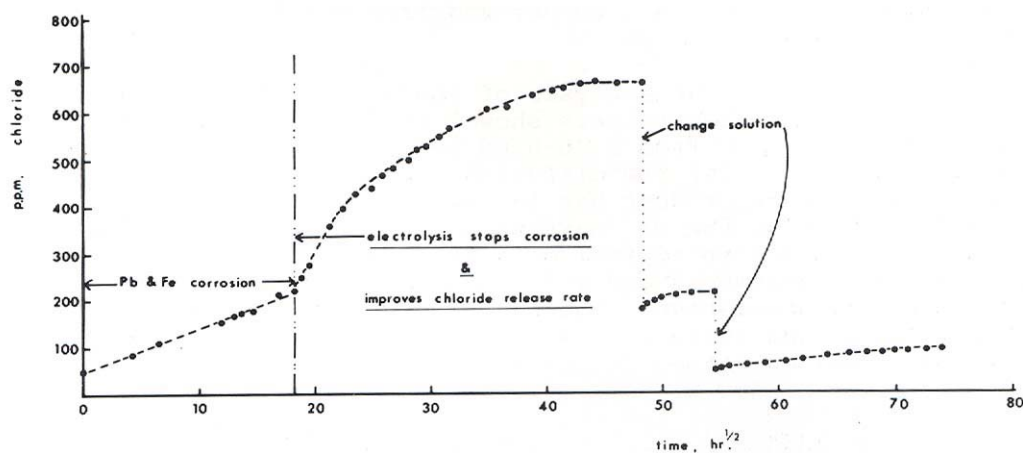
$$Fe \quad + \quad Cu^{2+} \quad \longrightarrow \quad Fe^{2+} \quad + \quad Cu \qquad (4)$$

$$Fe \quad + \quad Pb^{2+} \quad \longrightarrow \quad Fe^{2+} \quad + \quad Pb \qquad (5)$$

Figure 6   Plot of chloride concentration in a 300 1 wash solution during treatment of a section of a composite cannon **Batavia** (1629)) in 4 wt% sodium sesquicarbonate plotted against the square root of treatment time (hour½).

To improve the chloride release rate and to suppress the iron and lead corrosion, electrolysis (artefact negative) was commenced on the cannon section after 358 h using sheets of mild steel as the anodes. The applied voltage was 2.25 V; this voltage produced a small but steady evolution of hydrogen from the cannon section. Measurement of the cannon section voltage against a standard reference electrode showed it now had a potential of –1.018 V vs SHE. From the Pourbaix diagrams at pH 9.9 lead, copper and iron should be immune at this potential and pH.

Regular chloride analysis of the wash solution after commencement of electrolysis showed that the Cl⁻ extraction rate had increased from 2.80 ± 0.08 to 13.3 ± 0.5 g Cl⁻/h$^{1/2}$, which indicated that the diffusion coefficient for Cl⁻ ions in the corrosion product has increased by a factor of 22 [10]. The reduction in the Cl⁻ extraction rate after approximately 1000 h ($t^{1/2} = 31$) is typical of diffusion controlled Cl⁻ extraction treatments and indicted that Cl⁻ extraction was nearing completion. The solution was changed at 2450 h ($t^{1/2} = 49.5$) and again at 3000 h ($t^{1/2} = 54.8$). Very little chloride was extracted in the last wash and treatment was terminated at 5500 h ($t^{1/2} = 74$). Electrolysis was continued throughout treatment and the cannon section was rotated at 1500 h to ensure that areas in contact with supports were treated – as is standard practice in electrolysis [11]. The current density was approximately 0.8mA/cm^2 and total electricity consumption was 29 kWh. After electrolysis the cannon was cleaned of surface deposits by brushing with a soft wire brush, washed briefly in deionized water, and protective clear coatings were applied before the cannon was put on display.

The features of this treatment are that metal corrosion can be detected through an understanding of the voltage of the cannon in the treatment solution and what such data means in terms of the appropriate Pourbaix diagrams. Not only was corrosion eliminated by electrolysis but also the chloride release rate was subsequently increased thereby shortening the treatment time. Since the chloride release data showed only two plateau regions a total of three solution changes were necessary over the entire 229 days of washing. If the method of monthly solution changes had been used this would have consumed an extra 1.5 tonnes of deionized water and 60 kg of sodium sesquicarbonate!

SECONDARY MINERALISATION – EFFECTS ON CHLORIDE RELEASE RATES

When corroded copper bearing objects are being washed under aerobic conditions the chloride ions normally diffuse through a Cu_2O or $Cu_2O/Cu_2(OH_3)Cl$ duplex layer to reach the solution. Since there are cracks and other defects in the films the chloride ions can also report to solution via the routes. After conventional citric acid stripping of concretion any bare metal will become repatinated with a Cu_2O film over a few days and the chloride ions will have to diffuse through it. In sodium sesquicarbonate solutions some of the copper (II) corrosion products go into solution as the copper carbonate complex $Cu(CO_3)_2^{2-}$ [12]. If the object has been previously treated in a thiourea inhibited citric acid bath the wash develops an intense blue colour due to a copper (II) citrate complex [13].
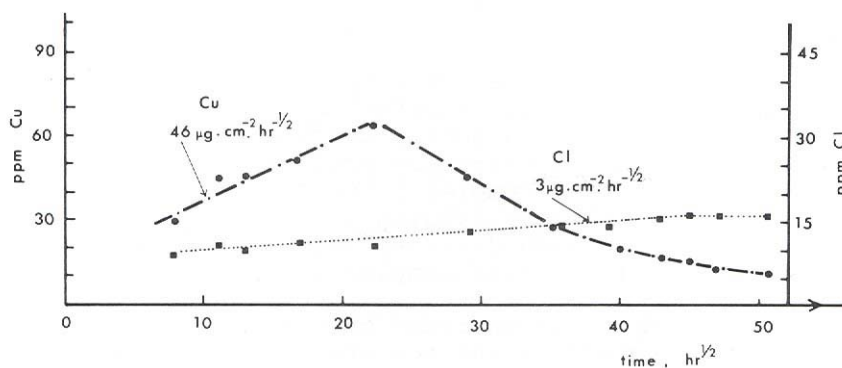

Figure 7   Treatment graph of copper and chloride concentrations vs the square root of treatment time ($t^{1/2}$) for the stabilization of an 1805 USA 1 cent piece recovered from the **Rapid** (1811). The washing medium was a 1 wt% solution of sodium sesquicarbonate.

During treatment of corroded objects made of coper and its alloys the wash solutions are routinely monitored for chloride, copper, lead, tin and zinc concentrations to check on the effectiveness of the treatment with regard to chloride removal and prevention of corrosion.

Inspection of the plots of chloride and copper release against $t^{1/2}$ show that the chloride release rate is normally linearly dependent on $t^{1/2}$ until it reaches a plateau. After changing the wash solution the chloride release continues to show a linear dependence on $t^{1/2}$ but the slope of the second wash is less than that of the first wash. As copper goes into solution the copper concentration shows a linear $t^{1/2}$ response but it will often reach a plateau before the chloride does. In some cases the amount of copper in solution can decrease; the most common cause of falling copper concentrations is precipitation as an insoluble copper compound. An example of such changes is shown in Figure 7 where a film of $Cu_2(OH)_3Cl$ precipitated on the surface of the USA 1cent 1805 piece recovered from the **Rapid** (1811). It should be noted that this precipitate did not reduce the chloride release rate.

Figure 8

Crystals of chalconatronite,
$Na_2Cu(CO_3)_2.3H_2O$ on a bronze
rudder gudgeon from the **Rapid**
(1811).
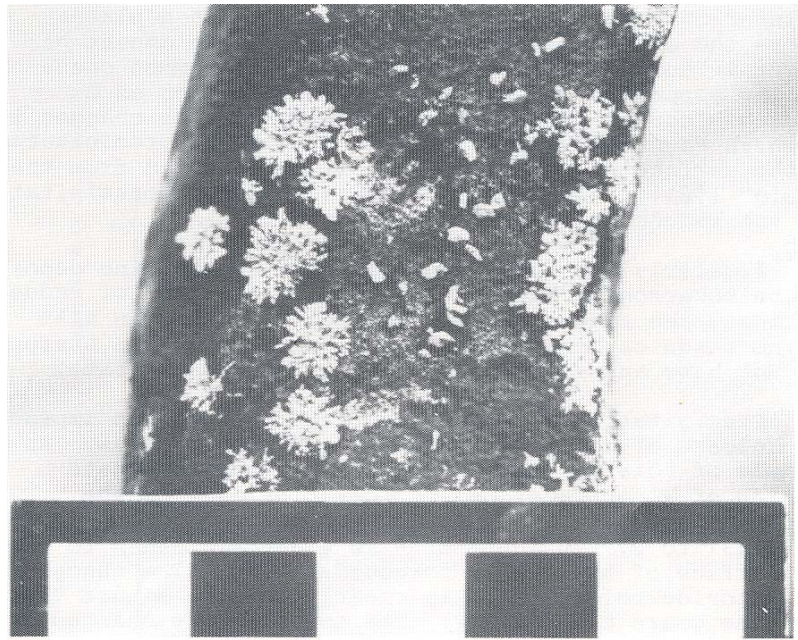
Similarly the formation of a blue crystalline deposit of chalconatronite $Na_2Cu(CO_3)_2.3H_2O$ on a series of rudder fittings, see Figure 8, that were being washed in a 1% sodium sesquicarbonate solution after citric acid stripping did not have any effect on the chloride release rate.

Precipitation of some secondary minerals can impede the release of chloride ions from corroded bronzes. An example of this was found during the sesquicarbonate washing of a series of bronze door pintles from the **Batavia** (1629). The chloride rate changed from 1.63 ± 0.31 to 0.76 ± 0.10ppm hr$^{-1/2}$ as a deposit began to cover the surface of the highly corroded bronze. The change in the chloride release rate is clearly seen in Figure 9 at the time where $t^{1/2}$ = 18 hr$^{1/2}$. The solution was changed at $t^{1/2}$ = 44 even though the chloride level had not plateaued since the changed patina was adversely affecting the treatment time. After being cleaned in an inhibited 2 wt% citric acid solution and scrubbed down with a brass wire brush the chloride release rate in the sesquicarbonate solution increased from 0.76 to 3.64 ppm hr$^{-1/2}$. The reason why the chloride release rate was higher in the second wash than on the first is because the pintles were stripped back to the metal during the cleaning process.
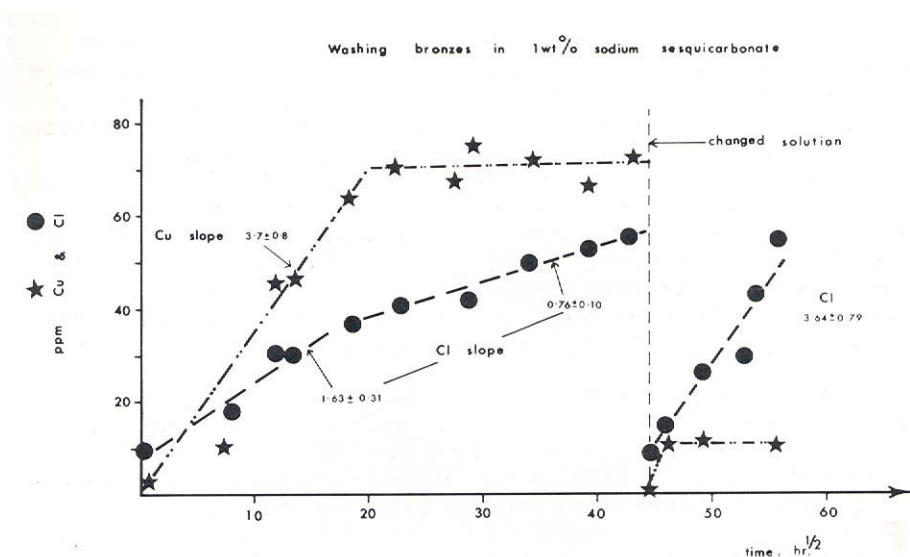

Figure 9   Plot of copper and chloride concentrations in a 1 wt% sodium sesquicarbonate solution vs the square root of time. The artefacts were a set of three bronze door pintles recovered from the **Batavia** (1629).
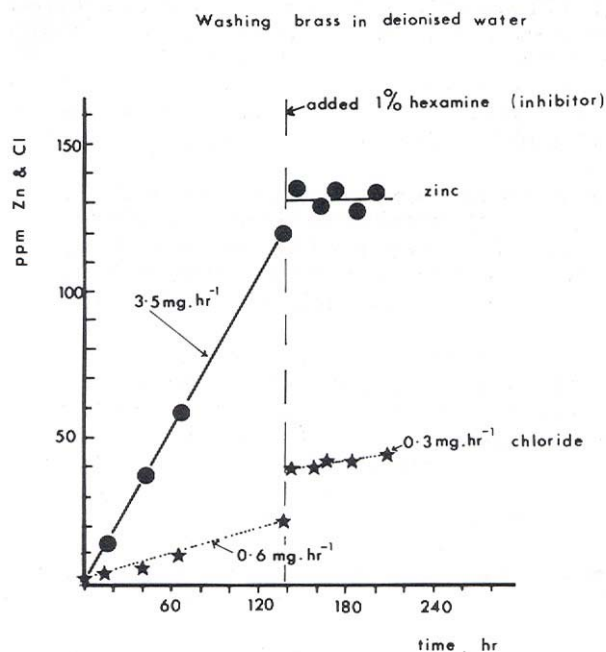
Figure 10   Plot of zinc and chloride concentrations in deionized water vs time (hr) during washing of brass candlesticks from the **Vergulde Draeck** (1656).

Analysis of the precipitate by X-ray diffraction showed that it was a mixture of cuprite (Cu_2O) and sodium bismuth oxide Na_3BiO_4. The bismuth is present in small amounts as an impurity in many seventeenth century bronzes. Since previous experience with bronzes of similar composition to the door pintles (92.7% Cu, 1.10% Pb, 0.45% Zn, 1.40% Sn, 2.13% Fe, 0.14% As and 0.075% Sb) had shown that a further eight months of washing would be needed to stabilize the fittings the 1% sesquicarbonate wash was discontinued and the alkaline dithionite treatment effected stabilization after six weeks [13].

CORROSION OF METALS IN DEIONIZED WATER

One method commonly employed to remove chloride ions from maritime archaeological artefacts is to simply immerse them in deionized (distilled) water and monitor the release of chloride salts by conductivity or by titration techniques. This works very well for materials such as wood, glass, ceramics, bone, ivory and copper but great care needs to be taken with objects made of pewter, brass and bronze.

A prime example of the type of corrosion problems that are often not noticed is found in the re-treatment of some brass candlesticks from the wreck of the **Gilt Dragon** (1656). The previous treatment had involved stripping the corrosion products in an uninhibited citric acid solution followed by a wash of a few hours in deionized water. After seven years in storage *Bronze Disease* had broken out in several areas. Since curatorial constraints require little or no change in patination a simple wash in deionized water was chosen as the most appropriate technique. After a few days it was apparent that a large amount of zinc was reporting to the wash solution. A plot of zinc and chloride concentrations against time (Figure 10) showed a linear increase with time which reflects film-free corrosion of the metal – the zinc and chloride ions were going into solution at a pH of 7.5 ± 0.3 as a result of a chemical reaction and not as a diffusion controlled dissolution of corrosion products. Despite the loss of 830mg of zinc in six days there was no apparent change in the surface of the candlesticks. During the initial wash copper was being released at a diffusion controlled rate of 1.1 ppm $hr^{-\frac{1}{2}}$. Addition of 1wt% hexamine (a zinc corrosion inhibitor) stopped further release of zinc. The chloride ions continued to be released but the rate of 0.3 mg per hour was considered too low so that candlesticks were treated by the alkaline dithionite method which stabilized the brass by removing a further 2500 mg of chloride [13, 14] after four weeks treatment.

When pewter objects are recovered from a wreck site they should not be placed in fresh water since this often results in whiskers of the basic lead carbonate, hydrocerussite $Pb_3(CO_3)_2(OH)_2$, growing out from the parent metal. Addition of a small amount of sodium sulphate (approx. 100 ppm) normally prevents such corrosion. Washing of brass and bronze fittings in deionized water normally presents few problems but if the material is a high leaded brass or a duplex brass secondary mineralization can occur (Figure 11). Examples of these problems are listed in Table 1 along with the composition of the parent materials. All the compounds listed were identified by X-ray diffraction or infra-red spectroscopy. With leaded bronzes the corrosion in deionized water is localized and occurs at tin-lead rich area of the cast metal. If the metal casting has resulted in a homogeneous distribution of the components then secondary mineralization is not a problem. If washing in deionized water is chosen as the method for removing chlorides then it is wise to keep a close check on the system to see if there is active corrosion. Access to an atomic absorption spectrophotometer is a decided advantage since analysis of copper, lead, tin and zinc in the 0-100 ppm range is a routine procedure with such instruments.
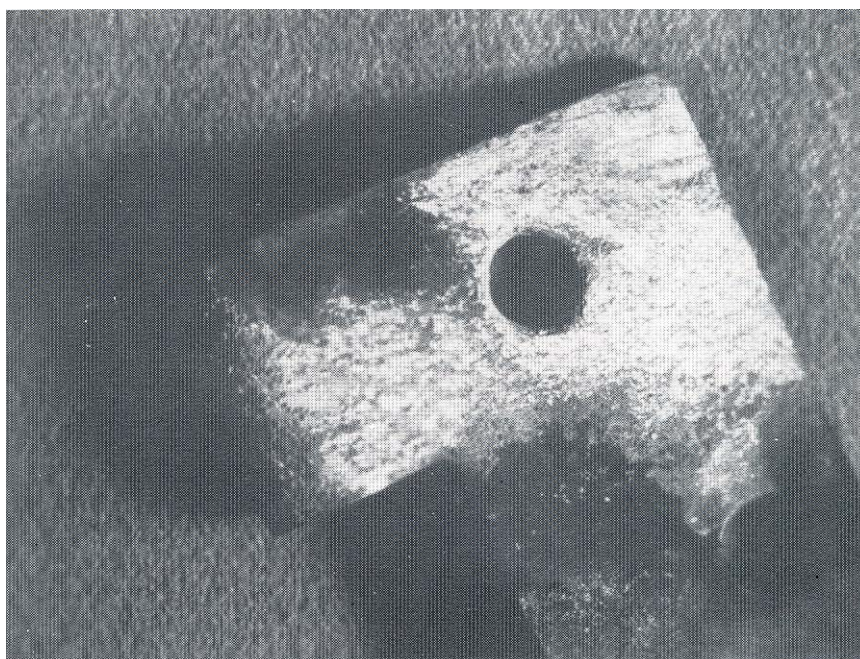

Figure 11   A leaded brass hinge from the *Rapid* (1811) showing secondary mineralization after washing in air saturated deionized water. The minerals were identified by X-ray diffraction as hydrocerussite, $Pb_3(CO_3)_2(OH)_2$ and lead oxide chloride hydrate $3PbOPbC1_2 H_2O$.

CONCLUSION

The importance of a thorough understanding of the nature of the materials with which a conservator is working has been shown to be of primary importance when decisions on alternative treatments are being appraised. Once the nature of the problem has been ascertained it is often necessary to develop a new technique or modify existing procedures to meet the demands of stabilizing an artefact. By monitoring the concentrations of chloride and metal ions in the wash solutions it is possible to determine when it is necessary to change conditions and to see what factors are controlling the release rates. Regular inspection of objects during treatment is essential if the effects of corrosion during conservation are to be minimized.

The adoption of such procedures not only serves to benefit the artefact but leads to considerable savings in time and cost of chemicals. Although the work described in the case studies above deals principally with shipwreck material we have found that the same mechanisms control chloride release rates from land based material recovered from Middle Eastern archaeological sites.

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APPENDIX – CHLORIDE ANALYSIS

The analysis of solutions and artefacts for their chloride content is by far the most frequently carried out analysis in marine archaeological conservation. It is the major monitoring technique used for the treatment of iron, copper and copper alloy artefacts. For this reason it is essential that the conservator be capable of obtaining accurate chloride analyses and know those factors which can interfere with the same. Full details of methods such as the Mohr, Volhard and mercuric nitrate titrations can be found in standard analytical chemistry text books [15]. The nature of the analytical problem will often dictate the choice of method but in our laboratories the Mohr titration and the chloridometer are most commonly used.

Mohr titration – For routine monitoring of caustic wash solutions from iron artefacts the Mohr titration is normally used since the fairly high chloride concentrations, typically 200-2000 ppm during early stages of washing, are suited to this method which has an accuracy of ± 20 ppm. For wash solutions with lower chloride levels the use of the chloridometer (see below) is preferable. Many metal ions interfere with the Mohr titration by forming precipitates with chromate ion, CrO_4^{2-}. Such metal ions can often be removed by filtering the solution after addition of NaOH (see standard texts, e.g., Vogel). Any reducing agents present in the solution also interfere by either reducing the AgCl to Ag metal and freeing Cl^- ions or by reducing the AgCl to Ag metal and freeing Cl^- ions or by reducing the CrO_4^{2-}. All reducing agents must be removed before addition of the CrO_4^{2-}. Fresh AgCl is white, CrO_4^{2-} is yellow and Ag_2CrO_4 is red (or red-brown). If any other colours appear this is a good indication that something has gone wrong.

Chloridometer analysis – Semi-automatic chloride analysis instruments are commercially available. Typically they require small volumes (1 to 2ml) and supply Ag^+ into the solution by anodically dissolving a silver wire at a fixed rate. When all the Cl^- is precipitated as AgCl the increase is free Ag^+ ions in solution is detected electrically by the increase in the d.c. current flowing between tow auxillary silver electrodes. The operating details vary for different machines and the manufacturers (Buchler, Corning & others) should be consulted for further information.

If used correctly these instruments can give rapid and very accurate Cl^- analysis on quite small sample volumes. Under routine use the accuracy is approximately ± 0.5ppm and higher accuracy can be obtained with care and practice. This is the best routine system currently available for low chloride measurements. Most of these machines have multiple operating ranges and with these they can be used for Cl^- levels up to several hundred ppm Cl^- if required – although with a corresponding loss in accuracy. In general, both oxidising and reducing agents interfere with although small quantities of these can sometimes be compensated for, they should be removed before analysis. Iron and copper ions may also interfere and should be removed.

Sample preparation – In maritime archaeological conservation the substances most commonly analysed for Cl^- ion content are marine iron wash solution and copper alloy wash solutions. As each of these require different sample preparation they will be covered separately.

(i) Marine iron wash solutions have a high pH, typically 12-14, and any metal ions such as Fe^{3+} which might be present will form insoluble hydroxides and generally settle to the bottom of the wash container. This leaves a clear solution which can be directly used in the Cl^- analysis as described above. If the solution contains any suspended matter it should be filtered before analysis.

The most common interfering ions found in these solutions are S^{2-} and SO_3^{2-}. The S^{2-} ion may be present in all artefact wash solutions. Its presence is usually first suspected with the Cl^- analysis gives unexpected and non-concordant results, e.g., in the Mohr titration a grey-black precipitate, loss of CrO_4^{2-} indicator, and vague or absent endpoints.

Both S^{2-} and SO_3^{2-} can be removed by acidification and heating or by oxidation and heating. In the former case A.R. H_2SO_4 is added dropwise to 25 ml of the solution until the pH drops below 10 (phenolphthalein indicator becomes colourless). The number of drops of H_2SO_4 used is noted and then twice this volume is added to each of the 25 ml aliquots for analysis. The samples are then

heated on a water bath until they have evaporated to one quarter of their original volume. They are then made up to the original volume with pure distilled water and the evaporation is repeated. At this point the samples are again made up to their original volume and are then ready for analysis. S^{2-} and SO_3^{2-} ions can also be converted into harmless SO_4^{2-} ions by addition of 2-4 mls of 30 volumes H_2O_2 to the caustic solution and then gently heating on a water bath to promote oxidation and to decompose the excess H_2O_2. This latter method works best when S^{2-} and SO_3^{2-} concentrations are small.

(ii) In copper and copper alloy wash solutions the main interference with the chloride analysis arises from soluble copper species. In the deionized water washes these can be soluble copper salts or copper citrate complexes. In the $NaHCO_3/Na_2CO_3$ washings the copper species are either copper carbonate or copper citrate complexes. The extent to which these species will interfere with the chloride analysis depends on the type of determination used and the concentration of the copper species. If lead containing alloys re being washed, soluble lead species may also interfere.

If the copper concentration is required it is first determined by atomic absorption spectroscopy then a piece of aluminium foil (Comalco etc.) approx. 50 cm^2 is placed in 25 ml of the wash solution. If the pH is in the 10-11 range copper will cement out on the aluminium foil in approximately one hour at room temperature. Aliquots of the solution are then removed for analysis

.

<center>**Table 1**</center>

Object	Composition									Compound	Formula
	Cu	Pb	Zn	Sn	Fe	Ag	Ni	As	Sb		
Brass hinge "Rapid' (1811)	69.6	4.16	24.3	0.13	0.7	0.01	0.06	0.05	0.03	Hydrocerussite Lead oxide Chloride hydrate	$Pb_3(CO_3)_2(OH)_2$ $3PbO \cdot PbC1_2 \cdot H_2O$
Brass gudgeon 'Chalmers' (1874)	63.0	13.6	20.5	2.37	0.82	-	-	n.d.	0.10	Hydrozincite	$Zn_5(CO_3)_2(OH)_6$
Bronze pall trace 'Rapid' (1811)	90.6	3.10	1.06	5.03	0.08	-	-	n.d.	n.d.	Hydroromarchite	$Sn_6O_4(OH)_4$
Bronze roller 'Rapid' (1811)	77.4	12.65	3.96	4.31	0.36	.014	0.21	0.019	0.96	Hydrocerussite Cassiterite	$Pb_3(CO_3)_2(OH)_2$ SnO_2
Muntz metal c.1852	59.9	-	40.0	-	-	-	-	-	-	Aurichalcite	$(Cu,Zn)_5(OH)_6(CO_3)_2$

n.d. – not detected.

Secondary corrosion products found on shipwreck brass and bronze artefacts after washing in deionized water that contained no corrosion inhibitors.