

## SUMMARY

This work reports several years of observations on the desalination of non-metallic artefacts recovered from historic shipwrecks off the Western Australian Coast. The washing of glass, stone and ceramics for periods of up to three years was monitored through regular measurements of wash solution conductivity and chlorinity. Periodic determinations of the concentrations of  $\text{SO}_4^{2-}$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  ions were also made in an attempt to understand the differences in behaviour. Three distinct types of desalination behaviour in static solutions have been observed and the results have been shown to be partly material specific. The diffusion-controlled release rates for removal of chloride ions from glass, stone and ceramics have been determined and the average treatment times are also reported. The results are discussed in terms of the nature of the wreck sites and the length of immersion in sea water.

## DESALINATION OF GLASS, STONE AND CERAMICS RECOVERED FROM SHIPWRECK SITES

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Introduction

The problems of salt efflorescence causing loss of surface detail on archaeological materials is well known and a plethora of data exists in reports that describe its nature, composition and cure. Less extensive are the reports that relate primarily to materials recovered from historic shipwrecks and to the problem of desalination of glass, stone and ceramics.<sup>1,2</sup> Since regular monitoring of the treatment solutions has proved to be a useful aid in understanding the stabilization of metallic maritime archaeological objects,<sup>3,4,5,6</sup> it was decided to monitor the desalination of non-metallic materials that included leather, amber, ivory, glass, stone and ceramics. Previous treatments given to wreck material recovered off the Western Australian coast had sometimes resulted in post treatment efflorescence on the surface of salt-glazed stoneware and lead-glazed earthenware objects.<sup>7</sup> The extended washing periods used in this work will hopefully avoid future problems.

Although there are advantages in speeding up desalination through the use of cascade systems,<sup>8</sup> the work reported here relates to static washing primarily because of the problems associated with treating over fifty different sets of objects at the same time and because of curatorial and financial constraints. For example, the supply of reticulated deionized water in the W.A. Museum's conservation laboratories costs approximately \$60 per thousand litres.

The artefacts used in this work were recovered from a number of historic shipwrecks off the Western Australian coast, which date from the *Batavia* (1629) through the *Vergulde Draeck* (1656) to colonial period wrecks such as the *Cumberland* (1830) and the locally built *Star* (1880). The glass plate, sheet and bottles that were examined probably vary in composition quite markedly, given that they span a period of nearly four hundred years in their production, and a knowledge of their composition would be of inestimable value in rationalizing apparent differences in behaviour. Elemental analyses for the artefacts are not available and so the data can only be assessed in terms of the nature of the wreck sites and the gross compositional form of the objects. Because of the often turbulent nature of the warm, and well oxygenated wreck sites<sup>9</sup> the extent of material degradation will be more marked than for objects of the same age that are recovered from less hostile locations. A range of glass and ceramic objects were recovered from a relatively sheltered site some 400m from the conservation laboratories in 1983 during a rescue operation. A new marina development for the America's Cup Challenge was to permanently cover part of the site of the old 'Long Jetty' and thousands of bottles dating from the 1850's to the 1920's were recovered from several metres of closely packed sand. Apart from the 'Long Jetty' material, all the other objects have firmly established chronology and provenance which facilitates further studies. Analysis of marine concretions on associated non-ferrous metal objects also provides useful data on the past microenvironment.<sup>10,11</sup>

Experimental

The wash solutions were analysed at intervals that varied from weekly to monthly as the treatments progressed. The containers were made of moulded high density polyethylene with nominal capacities of 20, 40 and 80 litres. The analysis samples were stored in plastic bottles that were shown not to release significant amounts of chloride, sulphate, sodium, potassium, calcium and magnesium ions into deionized water after standing for seven days. Chloride ions were determined coulometrically using a Buchler-Cotlove chloridometer. Sulphate was determined by analysis of excess barium after precipitation and digestion of barium sulphate following the addition of standardized barium chloride. Metal ion concentrations were determined by atomic absorption using standard additives to suppress interference which would otherwise result in variations of up to 20% in the analyses. Objects from the same site were normally separated into collections of like materials in an attempt to see if there were characteristic desalination responses that were material specific. Stabilization of the objects was initially assessed by monitoring the chlorinity of the wash solutions. Since chloride is the most abundant anion in sea water, the overall desalination process would be expected to mimic the removal of chloride. The other advantage of using chloride ions to "monitor the treatment" is that their analysis is much more straightforward than the procedures for sulphate ions. In order to gauge when non-chloride-containing salts were being released, the conductivity of the wash solutions was determined at the same time as samples were taken for chloride analysis. Periodic determinations of the concentrations of  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  and  $\text{SO}_4^{2-}$  ions were also made.

Results and Discussion

During the course of analysing the data from more than fifty washing experiments some patterns of characteristic behaviour began to emerge. For convenience

of discussion they are presented in the form of three different responses.

#### Type 1 - Rapid removal of chloride ions

The mass of data obtained during washing treatments that can last up to thirty months is most conveniently displayed in graphical form with plots of conductivity and chlorinity against some function of time. Most commonly, the data is plotted as a function of the square root of the treatment time since the most frequent "diffusion-controlled" response is that of a linear increase in chloride ion concentration with  $t^{1/2}$ .<sup>12</sup> After some time the rate of release of chloride ions 'tapers off' until a plateau is reached after which the solution is normally changed and the washing process continues until a second plateau of chlorinity is reached; the procedure is then repeated until the chloride level falls to that of the background deionized water ( $2 \pm 1$  ppm chloride).

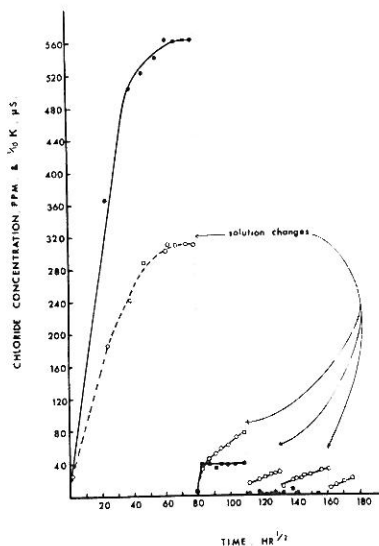


Fig. 1: Plot of chloride ion concentration ● and  $\frac{1}{10}$  conductivity ○ against the square root of treatment time ( $t^{1/2}$ ) for desalination of tryworks bricks from the *Lively* (c.1810), in deionized water. The wash volume was 9 litres.

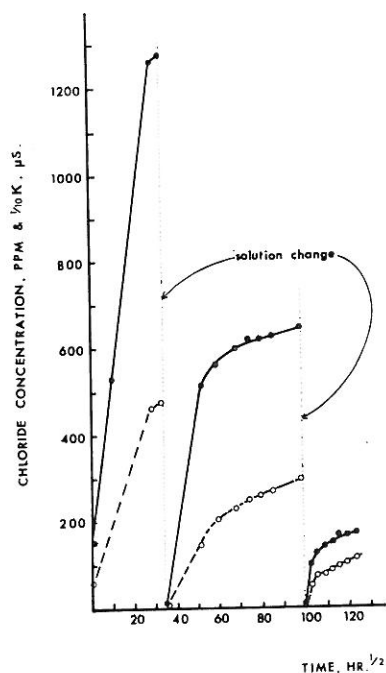


Fig. 2: Plot of chloride ion concentration ● and  $\frac{1}{10}$  conductivity ○ against the square root of treatment time ( $t^{1/2}$ ) for desalination of fire bricks from the steamship *Xantho* (1872) in deionized water. The wash volume was 32 litres.

A typical treatment graph is shown in Figure 1 for the desalination of low fired clay bricks for tryworks from the wreck of the *Lively* (c.1810). After the first change of wash solution the chloride release rate falls to zero, but the conductivity continues to increase as a function of the square root of treatment time ( $t^{1/2}$ ), i.e., the conductivity response is no longer mimicked by the chlorinity data. For conservators who rely on "the silver nitrate test" to ascertain whether or not desalination has been completed, the lack of conductance data could lead to premature cessation of treatment. The bulk of chloride ions are removed by the end of the second wash but sulphate (and possibly carbonate) salts continue to be released at a steady rate that does not vary significantly with subsequent solution changes. For example the mean rate of increase in conductivity for the last four wash solutions was  $8.09 \pm 2.8 \mu\text{S} \cdot \text{hr}^{-1/2}$ .

Analysis of the wash solutions for  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  supports the observation that  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$  are the principle anions being released into the wash solutions since the total anionic charge is balanced by the total cationic charge on the assumption that the above-mentioned ions account for 95-98% of the soluble species. A total of eighteen different desalination treatments showed very similar characteristics to that displayed by the tryworks bricks from the *Lively*. During the first wash, the mean value of the ratio of sodium to potassium (expressed as ppm) was  $21.7 \pm 5.4$  which is essentially the same as that for 'normal' sea water which has a value of 28.3.<sup>13</sup> For the third and fourth washes the Na/K ratios were much lower with typical values ranging from 4.8 down to 1.2. We do not believe that hydrolysis of glass is a major source of sodium and potassium ions in the wash solutions since similar concentrations and ratios were found in treatment solutions that covered a wide range of materials from sandstone, bricks, stoneware, bone china and earthenware to glass. It is essential that analysis of the surface characteristics of the wreck materials at all stages of the desalination process be undertaken in the future since it is only through such work that details of the mechanisms controlling release of salts can be elucidated.

For objects that conform to the type 1 behaviour (see Figure 1) the ratios of the concentrations (ppm) of calcium to magnesium found in the early and late stages of the desalination process are apparently sensitive to the type of material. For porous materials such as sandstone water purifiers from the *Cumberland* (1830) the Ca/Mg ratio does not change significantly during the course of desalination and remains at  $3.7 \pm 1.0$ . The mean value of the Ca/Mg ratio for desalination of earthenware is much the same as that found for stone, viz.,  $3.2 \pm 1.8$  whereas the situation with glass objects is markedly different. During the early stages of glass desalination the Ca/Mg ratio is  $13.2 \pm 1.5$  while in the later washes, when the bulk of the chloride ions have been leached out, the ratio falls to a mean value of  $6.3 \pm 1.1$ . The differences in behaviour probably lie in ion-exchange processes at the corroded glass-wash solution interface.<sup>14</sup>

#### Type 2 - 'Slow' removal of chloride

The desalination of some fire bricks from the engine room of the SS *Xantho* (1872) is an example of the second type of desalination response. A plot of the data obtained during the first twenty-one months of treatment is shown in Figure 2, where the chloride ions are seen to report to solution at roughly the same rate during the initial stages of each wash until the rate becomes much slower as a plateau is approached. Solution changes were made prior to the establishment of a more definite plateau since it was readily apparent that the rate at which the salts were dissolving was diminishing. The conductivity data mimics that of the chlorinity profile (or vice versa) for the three stages of the treatment. This behaviour may be contrasted with that shown in type 1 where there appeared to be a more rapid removal of chloride ions than sulphate ions. Effects such as ion pairing of sulphate and magnesium/calcium ions in the cracks and micro-fissures of type 1 materials could account for the differences in behaviour. The ratios of Na/K and Ca/Mg found at various stages of desalination for glass and stone/fire bricks objects that showed type 2 behaviour were not significantly different from those found for type 1.

#### Type 3 - Steady removal of chloride

A third type of response was shown by two sets of glass bottles from the site of the Long Jetty, some 50m from the shoreline of Bathers Bay, Fremantle. A plot

of the conductivity and chlorinity data is shown in Figure 3, where it can be seen that the sea water salts are still coming out at the same rate as they were some 700 days prior to the time of writing this report! Apart from an inadvertent solution change at 74 days ( $42.14 \text{ hr}^2$ ) when the objects were needed for a media release, the chloride ions are still being released at the rate of  $33 \text{ ppm}\cdot\text{hr}^{-1/2}$  or  $37 \mu\text{g}\cdot\text{cm}^{-2}\cdot\text{hr}^{-1/2}$  after the data has been corrected for the solution volume of 50 litres and an apparent geometric surface area of  $44,100 \text{ cm}^2$ .

#### Prediction of treatment times and release rates

A question of major importance to those concerned with managing a conservation facility or running an excavation is, how long will the desalination process take? There are advantages in the allocation of resources if one could simply look up a table of treatment times for different types of materials and begin to desalinate without having to devote time to proper monitoring. The first two types of desalination behaviour release characteristic amounts of chloride at each stage of the treatment and these are summarised in table I. For type 1 materials it may be sufficient to use only two washes since this would remove roughly 98±7% of the available chloride whereas a similar approach for type 2 materials would only remove 86±8% of the chloride.

One important variable in the desalination process is the time it takes to reach the first and subsequent plateaus, since it is only after the chloride release rate falls to zero that the solution needs to be changed. The mean values of the time taken to reach the first and second plateaus for both type 1 and type 2 are listed in table I. Although type 1 takes an average of twenty more days to reach its first plateau than type 2, the difference is not significant because of the large scatter in the data. Similar comments about the large variations in the mean values can be made for the data relating to the times taken to attain the second plateau. As far as chloride removal is concerned, the type 1 objects will be 'stabilized' in approximately one third the time taken for type 2. Although chloride removal is a major consideration in the stabilization of the wreck material the problems associated with insufficient removal of soluble sulphates are well known<sup>15</sup>, since cycling of relative humidity will cause stress in the object as the chemical composition of the residual salts changes.

In an attempt to rationalize the observed chloride release rates, the raw data was 'normalized' to correct for surface area and solution volume according to the formula  $R_N = R_{\text{ppm}} \cdot x/y$  where  $x$  is the wash volume in litres and  $y$  is the geometric surface area in square centimetres. With such a wide range of materials being examined, there is only a remote chance that any systematic trends will be observed since the real surface area of the objects could easily be an order of magnitude greater than the geometric value. When all the data is collated without regard to the physical nature of the object there are no discernible differences in chloride release rates. However, when materials are grouped some general trends emerge (see table II). The differences in the mean values of the rates for chloride removal from glass, stone, fire bricks and clay bricks are not statistically significant. However, the differences are significant for the earthenware group.

One of the main driving forces associated with the outward diffusion of salts will be the concentration gradient across the boundary between the object and the wash solution.<sup>16</sup> The mean values of the total amount of chloride removed during desalination can be conveniently expressed as the wt% chloride, and as such can be used as a measure of the driving force in the desalination process. For type 2 earthenware the mean chloride content was  $0.17 \pm 0.05 \text{ wt}\%$  while for type 1 the value was  $0.10 \pm 0.08 \text{ wt}\%$  (see table III). Whilst it is realised that total salt content will be only one of the parameters controlling the overall rate of desalination, the above does provide a ready rationalization of the observed differences. By way of comparison there is roughly the same amount of chloride released from stone and bricks as with earthenware and glass recovered from aerobic sites. The somewhat lower value of chlorides found in glass from anaerobic sites may be a reflection of the fact that the extent of 'corrosion' will be less for materials that are not being subjected to fully oxygenated conditions and strong surge (see table III).<sup>17</sup>

Various proposals have been made concerning the use of 'corrosion layers' on glass as a means of dating.<sup>18</sup> It was therefore of interest to look at the amount of chloride in the objects as a function of the years of immersion. The results show a remarkably uniform set in that the mean values of chloride (ppm per year of immersion) are the same for anaerobic and aerobic glass as for stone and bricks. The major difference occurs for ceramics and this is probably due to their composition.

The removal of soluble sulphates is less well documented because of the analytical procedures involved in the quantitative determination of sulphate ions. However, once the chloride ions have stopped reporting to solution the conductivity will be mainly due to sulphates. For type 1 materials, the conductivity increases at a steady rate for the third and fourth washes regardless of the solution being changed (see Figure 1). The conductivity data can be rationalized using the same type of procedure as outlined for normalizing the chloride release data. For type 1 glass the normalized 'sulphate' release rates are  $8.4 \pm 5.9 \mu\text{S}\cdot\text{cm}\cdot\text{hr}^{-1/2}$  while for sandstone, bricks, etc., the rate is

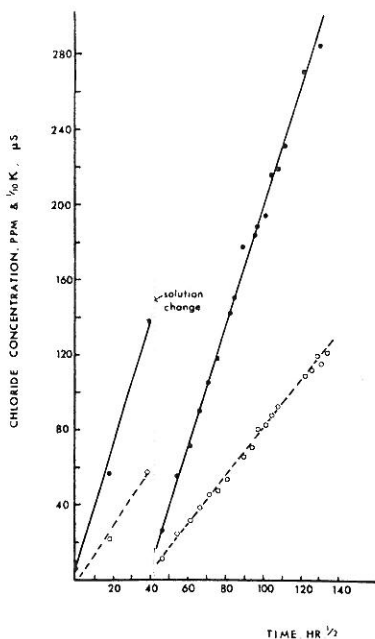


Fig. 3: Plot of chloride ion concentration ● and  $1/10$  conductivity ○ against the square root of treatment time ( $t^{1/2}$ ) for desalination of glass bottles from the Long Jetty site, in deionized water. The wash volume was 50 litres.

$48 \pm 16 \mu\text{S.cm.hr}^{-\frac{1}{2}}$ . Washings are not continued beyond 40 months as the amount of soluble salts reporting to solution is very small and the risk of damage to the object by prolonged immersion in deionized water is greatly increased.

#### Conclusion

The monitoring during extended washing of glass, ceramic and stone artefacts from shipwreck sites has shown that the release of salts is diffusion controlled. Analysis of the conductivity and chlorinity data has shown that there are three types of responses and that it is now possible to predict the extent of removal of chloride ions at each stage of the desalination process. The chloride release rates have been rationalized in terms of the nature of the materials and their porosity. The total amounts of chloride removed from glass, ceramics and stone are very similar and the results indicate that a major factor in the incorporation of salts is the length of immersion in the sea.

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Table I: Kinetic parameters for the desalination of glass, stone and ceramic objects recovered from shipwreck sites.

	Type 1	Type 2
% chloride extracted 1st wash	90.4±4.7	49.8±5.1
% chloride extracted 2nd wash	8.1±3.8	36.5±3.2
% chloride extracted 3rd wash	1.9±1.6	15.1±2.2
Time to reach first plateau (days)	64±28	44±10
Time to reach second plateau (days)	138±51	229±95
Time to reach third plateau (days)	n.a.	268±175

Table II: Normalized chloride release rates for desalination of glass, stone and earthenware in deionized water.

	Type 1	Type 2
Glass*	3.7±1.2	9.5±6.5
Stone, bricks*	97±58	78±13
Earthenware*	2.3±1.8	24±10

\*The units for the release rates are  $\mu\text{g}\cdot\text{cm}^{-2}\cdot\text{hr}^{-1/2}$

Table III: Chloride extraction characteristics for desalination of shipwreck materials.

	Wt% Cl <sup>-</sup> extracted	Cl <sup>-</sup> extracted per year of immersion as ppm of object wt.
Glass - aerobic	0.12±0.06	10.0±5.9
Glass - anaerobic	0.06±0.02	9.4±5.4
Stone	0.12±0.07	8.9±4.8
Ceramics	0.12±0.08	3.5±2.7