Section 1

Preventive Conservation

Some recent trends in corrosion science and their application to conservation

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Abstract

Conservators and corrosion scientists face many of the same issues, and thus it is reasonable to assume that recent advances in corrosion science may also be of use in conservation. Of course, there are also significant differences – while quite active interventions are permissible in conserving infrastructure or industrial plant, they may not be permitted for cultural artefacts. Further, while the conservator must deal with a limited number of normally stationary objects, the corrosion scientist may have to deal with distributed infrastructure (pipelines, powerlines) or mobile infrastructure (fleets of aircraft).

In this paper, some recent trends in research (predominately carried out at CSIRO) are highlighted and, where possible, implications for conservation are discussed. Areas covered include meta-methodology, models of degradation and new sensors.

Résumé

Les conservateurs et les spécialistes de la corrosion rencontrent des problèmes identiques. Il est ainsi raisonnable de penser que les avancées récentes dans le cadre des recherches menées sur la corrosion peuvent également être utiles pour la conservation. Il y a bien sur des différences notables. Ainsi des interventions actives sont permises pour les infrastructures conservées ou pour les sites industriels mais elles ne peuvent être autorisées pour les artefacts. De plus, alors que les conservateurs s'intéressent à un nombre d'objets limités normalement stationnaires, les scientifiques du domaine de la corrosion doivent prendre en compte des infrastructures distribuées (canalisations, lignes électriques) ou mobiles (flottes d'avions).

Cet article présente quelques unes des pistes de recherches récentes dans le domaine de la corrosion (et plus particulièrement les recherches menées au CSIRO). Les domaines abordés concernent la méta-méthodologie, les modèles de dégradation et les nouveaux capteurs.

Keywords: corrosion, degradation, sensors , aerosol, deposition , transport

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1. Introduction

One could regard corrosion science and conservation as sister sciences, or at least close cousins. Both disciplines are concerned with maintaining metal objects in as close to their original state as possible with minimum intervention. Further, both disciplines would agree that the intervention should not alter the function of the object. It is in the definition of "functions" that the fields tend to diverge – to the corrosion scientist "function" is purely utilitarian, while to the conservator many other values, often intangible, are associated with function.

Given this similarity of purpose of these fields, this paper will outline some recent trends in corrosion science and highlight areas that may be of relevance to conservators. However, the paper will not attempt to be exhaustive in mapping applications from corrosion science to conservation, rather it will provide examples that it is hoped can be expanded on by conservators. In discussing advances in corrosion science, one should not be restricted to the purely physical, for advances have occurred in our philosophical approach to the discipline. Advances that will be discussed in this paper include those relating to

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- Meta-methodology.
- Models of degradation.
- Sensors.

2. Meta-methodology

In this context, meta-methodology refers to the overall approach to a field. Until the 1990s, corrosion science was approached in a narrow reductionist manner. Two schools existed – one based on developing an electrochemical understanding of corrosion processes (Mansfeld, 1982; Fiaud, 1982; Stratmann, 1990; Stratmann & Streckel, 1990; Neufeld et al., 2002), and the other on empirical relationships between environmental parameters and corrosion rate (generally for atmospheric corrosion) (Guttman & Sereda, 1968; Atteraas & Haagenrud, 1982; Benarie & Lipfert, 1986). Although both made considerable progress, dialogue between the two groups was limited. By the late 1980s fundamental issues were constraining the application of either methodology.

Within the empirical approach to atmospheric corrosion, a number of very large research programs (Guttman & Sereda, 1968; Atteraas & Haagenrud, 1982; Benarie & Lipfert, 1986) had developed "dose" functions defining statistical relationships between climatic parameters and corrosion damage. Although these relationships were soundly based on large data sets, they suffered from a number of limitations. Firstly, as they defined statistical relationships between predefined variables, a relationship would not be identified if the variable was either constant or not included in the predefined variables. Further, these models defined statistical rather than causal relationships, and thus the statistical variable selected as significant may only have a correlation with the actual causal variable. This correlation may be determined by the environment and thus database specific. It is thus, perhaps not surprisingly, that dose functions derived in different countries or regions vary significantly (Jernberg et al 2004), and no consensus has been reached as to the "correct" dose function.

The electrochemical approach has developed accurate models to define the electrochemical processes occurring in immersed solutions (Mansfeld, 1982; Fiaud, 1982; Stratmann, 1990; Stratmann & Streckel, 1990). More recent work has allowed the development of an understanding of processes under thin moisture films (Neufeld et al., in press). However, these electrochemical models did not take account of the complex factors that control the formation of moisture films. Further, there is some uncertainty as to how the processes occurring under bulk solutions or thin films relate to processes that occur under cycles of micro-drop formation and evaporation that represent real service conditions.

In response to these limitations, a number of authors developed process-based models (Cole et al., 1999; Lyon et al., 1995; Graedel, 1998) that attempted to describe, on a more fundamental basis, the fundamental processes that control atmospheric corrosion. Graedel (1998) proposed the first model to systematically look at the chemical interactions across the range of interfaces that occur in the metal/oxide/solution/environment system. Graedel refers to his model as the "Gildes" model, where Gildes is an acronym for **G**as, **i**nterface, **l**iquid, **d**eposition layer, **e**lectrodic regime and **s**olid. Graedel applies the model to corrosion under moisture films on metal surfaces. However, while the Gildes model is a significant advance on previous models, at present its applications focus primarily on the liquid and the deposition regime. The current authors (Cole et al., 2003a; 2003b) considered it necessary to model more complex external environments than the Gildes model. In fact, processes controlling atmospheric corrosion on a range of scales, from macro through meso to local, micro and lastly micron, needed to be modelled. These scales are defined in line with EOTA (1997), so that macro refers to gross meteorological conditions (polar, subtropical etc.), meso refers to regions with dimensions up to 100 km, local is in the immediate vicinity of a building, while micro refers to the absolute proximity of a material surface. A diagram of such a model is given in Fig. 1.

This framework has been developed into a full model, as describe in a number of papers by Cole and co-authors (Cole et al., 2003a; 2003b; 2002c; 2004a; Cole & Paterson, 2004; Cole et al., in press, a). Specific results of the model are relevant to the conservation of metallic objects and will be discussed later in the paper.

The holistic model has proved very successful in providing information where there is limited uncertainty in the failure path that leads to corrosion. By and large this is the case for buildings (or for exterior sculpture), but it is not for well-built and complex structures such as aircraft. In such cases, failure occurs as a result of a long and hard to predict fault tree. Under these circumstances, any deterministic models (including process-based models) are not meaningful. In these circumstances, most researchers will use sensor-based data, which has the advantage that it relates directly to the actual situation.

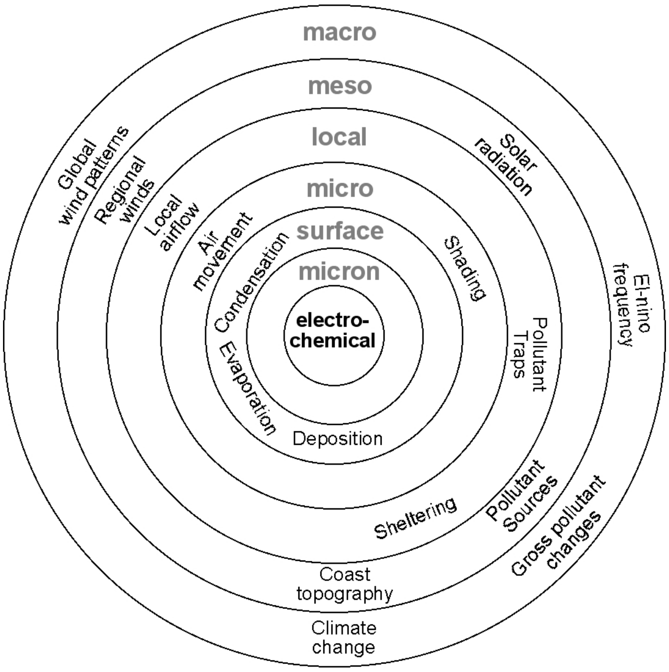

Fig. 1 Framework for a holistic model of corrosion.

The disadvantage is that standard statistical processing algorithms do not allow the inclusion of process understanding. Recently work at CSIRO is aimed at introducing into the statistical processing, operators that embed process knowledge and can be used to determine relationships between factors promoting damage (wetness, salinity etc.) and to measure damage. The same studies are also considering how arrays of agents (microchips linked to an array of climate and damage sensors) can be distributed throughout a complex object. This allows the agents to learn from each other and, in particular, it allows the relationships established from the most advanced damage zone to be used to predict damage progression at other points.

Thus, the recent history of corrosion science indicates a progression from reductionist models with a precise but limited technical focus, to holistic models that attempt to unite models across scales and disciplines, and then finally to a multi-agent approach that attempts to use learning to allow models to be developed directly from sensor data. A critical question is whether this experience is transferable into the field of conservation. The experience indicates that a reductionist approach at too fine a level can lead to misleading conclusions. The corollary in the context of conservation is that studies of the degradation of metallic objects need to extend past simple exposure analysis to a fuller understanding of pollutant sources, transport, deposition, and moisture layer formation and chemistry. In the example of black spots on brasses, discussed later in this paper, this implies an understanding of sources of sulfur species, the effect of indoor climatic conditions on their transport, and the chemistry that develops on surfaces as a response to deposition of sulfur species.

Sensors have frequently been used in the conservation of metallic cultural objects. The principal that progression of damage of an individual object can be assessed by reference to like objects (as in the CSIRO approach) has possibilities, but may be restricted by the requirement to minimise all damage to cultural objects.

3. Models of Degradation

The holistic model discussed above has deepened our understanding on a number of fronts, including:

- Deposition, retention and cleaning of pollutants from objects and, in particular, how the shape of objects influences these processes.
- The effect of marine aerosols on surfaces and different damage forms associated with sea salt relative to NaCl.
- Factors promoting wetness on metal surfaces.

3.1 Deposition, retention and cleaning of pollutants

In Australia, the main atmospheric pollutant is marine aerosols and thus an understanding of aerosol production is paramount. Marine aerosols are produced both in the open ocean and by breaking surf. Cole et al. (2003a) outlined the factors controlling aerosol production in both cases. In the open ocean, aerosols are produced by whitecaps of ocean waves. Whitecap production varies systematically with longitude and season, being at a maximum in low latitudes in July and at a maximum in high latitudes in December, and low all year round in tropical seas. Thus, tropical seas produce a relatively low volume of marine aerosol, resulting in decreased marine corrosion in near-equatorial regions. Salt production is also controlled by ocean effects such as local wind speed , beach slope, and fetch.

Factors controlling aerosol transport are also outlined in Cole et al. (2003a). Aerosol residence times are controlled by convection, gravity and aerosol scavenging by cloud drops, raindrops and physical objects on the ground (trees, buildings etc.). Thus, marine aerosol transport is likely to be higher in dry climates with low rainfall and low ground coverage, while it will be restricted in humid and high rainfall climates with forest cover. Aerosols produced by surf tend to be coarse (5–20 µm) and those produced by whitecaps are generally smaller (0.5–3 µm). Thus, surf-produced aerosol rapidly deposits (due to gravity), while ocean-produced aerosol may be transported considerable distances.

A GIS system has been developed (Cole et al., 2004a) to both define the concentration of marine aerosol at the shoreline arising from both surf- and ocean-produced aerosol, and then to estimate the transport of this aerosol to a given point inland. An Australia-wide map of airborne salinity has been derived and is presented in Fig. 2. The salinity map highlights the pronounced effect of both ocean state (as defined by whitecap activity) and climate factors in controlling airborne salinity in Australia. For instance, southern Australian coastal zones, where whitecap activity is high, have appreciably higher airborne salinity levels than Australia's northern coast, where whitecap activity is low.

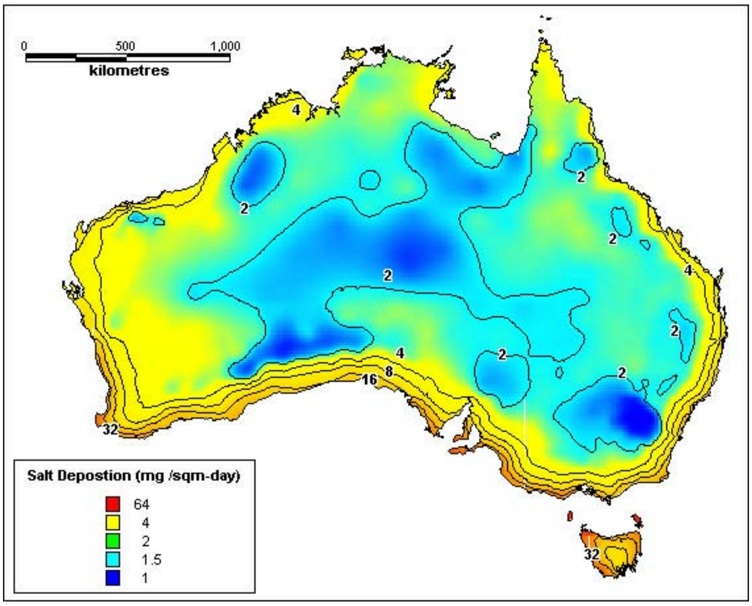

Fig. 2 Salinity map of Australia.

Marine aerosol deposition onto objects is primarily controlled by wind turbulence, and deposition onto an object is a function of turbulence intensity, wind speed, object shape and, to a lesser extent, aerosol size (Cole & Paterson, 2004). For marine aerosols of 0.1–10 µm, the deposition efficiency (as a function of size) is relatively constant, while the efficiency increases rapidly for aerosol sizes above 20 µm, so that the efficiency of 100 µm aerosol is roughly four times that of the 20 µm aerosol. The size and shape of objects are also important. The deposition on an exposed plate (at 45°) is likely to be more than that on an equivalently exposed salt candle. For complex forms such as dwellings, deposition efficiency will vary across a structure, with deposition being highest at the edges of a structure where turbulence is highest. Figure 3 presents the results of a computational fluid dynamics simulation in which particles impact on a simplified building of dimensions 10 m high and 20 m by 20 m in plan. In Fig. 3 the units are particles per square metre, given that 225 particles are released each square metre upstream of the building.

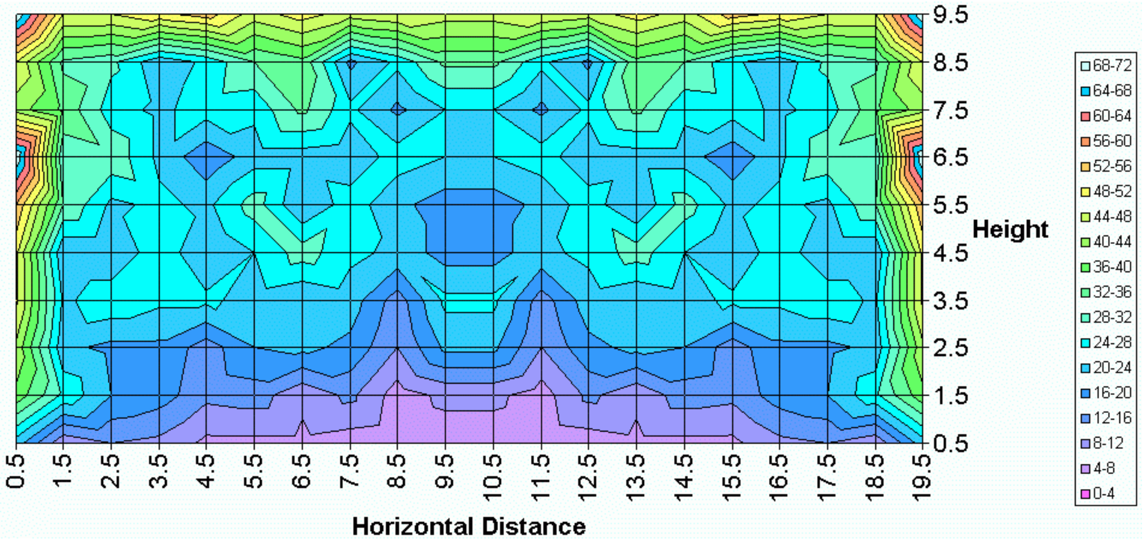

Fig. 3 Aerosol deposition on the front face of a high building (scale total (sum of all sizes) particles per m^2).

A knowledge of airborne salinity and its deposition is of course relevant to the preservation of metal objects exposed in the open. The mapping work defined in Fig. 2 provides an indication of environmental severity in a given geographical location. For example, where salinity is greater than 8 mg/m^2.day, moderate atmospheric corrosion (of course the extent of the corrosion rate depends on the material) is probable. However, preventative maintenance, primarily regular washing, would be sufficient to protect most metal work (with the exception of uncoated iron or steel). Where salinity is greater than 32 mg/m^2.day, severe corrosion is possible for some metals and more active protective measures such as coatings may be required.

Local effects may, however, change these effects. Key effects relate to roughness and turbulence. Surface features, trees, buildings etc., scavenge salt from the atmosphere, depleting aerosol concentration to roughly the height of the object. Thus, a structure in a landscape with significant features of greater height than itself will have a reduced salt load compared to the same structure in an open area. This can of course be used to advantage in landscaping, as trees may be planted to reduce salt loads on structures that are upwind from marine breezes. Structures that rise above the surrounding landscape may show a maximum in salt deposition (and thus possibly corrosion) just above the height of surrounding objects. The second major effect is that of turbulence. This can, of course, lead to differential deposition on an object (as in Fig. 2) and thus additional attention during maintenance should be given to edges on objects. However, turbulence may also affect objects placed on structures. For example, “gargoyles” placed on medieval churches are at a position of high turbulence and thus will suffer from increased pollutant and aerosol deposition. In a more modern context, care should be taken when placing structures near or around sculptures or other openly exposed pieces, to ensure that they do not produce heightened turbulence on the cultural object. This may be negated to some extent due to moisture effects, where increased turbulence will promote drying and lead to decreased corrosion rates, which is especially important when hygroscopic salts are present on a surface.

3.2 Modes of deposition and resulting oxide products

Previously, we discussed the fact that aerosol size depended on its source (surf or whitecaps), but as marine aerosols are hygroscopic, their size also depends on ambient relative humidity (RH). Further, when an aerosol first breaks free of a wave it has seawater composition and then gradually equilibrates (and thus decreases in size). Thus, marine aerosols may take four forms (Cole et al., 2004b) – non-equilibrium near-ocean aerosol (size range 6–300 µm), wet aerosol (3–150 µm), partially wet aerosol (1–60 µm) and dry aerosol (<1–20 µm) – depending on time of flight and ambient RH. These size ranges are based on aerosol mass or volume; mean sizes based on the number or the surface area of aerosols are much smaller. When these aerosols are deposited on a metal surface, a number of characteristic surface "forms" result from the surface aerosol reaction (Cole et al., in press, a). These forms differ in the extent of retained salts, degree of surface alteration and in the formation of corrosion nodules. For example, when a wet aerosol impacts on an aluminium surface (limited initial reactivity), a cluster of deposited salt crystals are formed. These crystals have compositions of either NaCl, MgCl or $CaSO_4$, indicating that the original seawater solutions have segregated. In contrast, if the same aerosol impacts on a galvanised steel surface, there will be strong oxide growth on the surface (predominately simonkolleite and gordaite), with the retention of a NaCl crystal on this oxide layer. Interestingly, rather than the clean crystal edges that are observed for the NaCl crystal formation on aluminium, the NaCl crystal on galvanised steel appears to blend into the underlying oxide. Further oxide formation tends to be favoured at the grain boundaries and triple points on the galvanised surface (see Fig. 4).

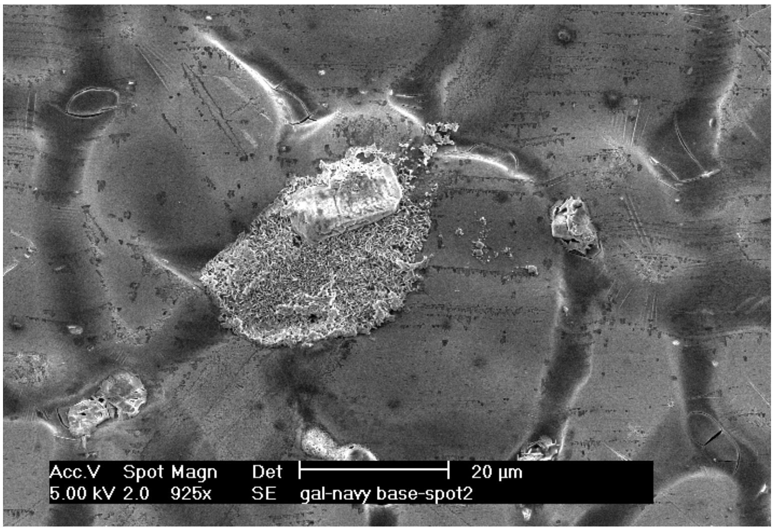

Fig. 4 SEM micrograph showing increased activity between salts and a galvanised steel surface at grain boundaries and triple points.

Recent work by Cole et al. (submitted) investigated the phases that form when microlitre saline drops were placed on zinc. This study demonstrated the variety of corrosion products that may form, and highlighted the importance of mixed cation products in a situation where Na and Mg concentrations are orders of magnitude higher than the Zn concentration generated by anodic activity. The study also highlighted that when dealing with microlitre droplets, processes within the droplet (anodic and cathodic activity, mass transport and diffusion) can dramatically alter droplet chemistry and lead to corrosion products that would not be expected from the initial conditions.

The implications of these observations to the conservation of metallic objects are both direct and indirect. The study of course provides direct evidence for mechanisms of zinc corrosion in marine environments. It also reinforces that when considering objects exposed to marine conditions, consideration must be given to the size range of aerosols and to the chemistry of marine aerosol. Misleading results can be made if marine exposures are approximated with immersion or NaCl only exposure. The unique dynamics of droplets are relevant not only to marine locations, but to all cases were corrosion is promoted by localised wetting or deposition of rain aerosol or hygroscopic particulates. Droplets with volumes in submicrolitres can undergo significant changes in chemistry unlike corrosion in immersed situations, and the chemical changes can either enhance or restrict corrosion.

3.3 Wetting and surface temperature

The presence of a moisture layer is a prime requirement in the corrosion of metals in almost all circumstances. As a first approximation, a surface will wet when the surface relative humidity (RH_s) is greater than the deliquescence RH of any contaminating salts. RH_s can be calculated from the ambient air RH and the surface temperature of the metal. Work by Cole et al. (in press, b) has validated this approach. The surface temperature of an exposed metal can be derived by considering both undercooling to the night sky and daytime solar heating. For undercooling, the rate of heat transfer between the surface of any object and the sky through radiation is given by:

$$Q/A = \varepsilon\sigma(T_{sky}^4 - T^4) = h_r(T_a - T)$$

where Q is the heat flow rate (in watts), A is the surface area facing the sky, ε is emissivity, σ is the Stefan–Boltzmann constant (= 5.6697×10^{-8} W m^{-2} K^{-4}), T_{sky} is the mean temperature of the sky, T is the temperature of the surface of the object, h_r is radiation heat transfer coefficient, and T_a is the local air temperature.

However, estimation of surface temperatures also needs to take into account the effect of convection (air above object) and conduction (within the object), and thus wind speed becomes an important limiting factor. Clouds also tend to reduce undercooling (due to reflection of radiation from the earth). Change in the surface temperature of an object in the morning depends on the change in local air temperature, direct and diffuse solar radiation on the object, and heat loss from evaporation. Further, if the surface is wet (e.g. from condensation) a number of other factors apply. Firstly, the effect of evaporation and condensation on heat transfer to the surface must be considered. Secondly, emissivity of water ($\varepsilon = 0.96$) rather than of galvanised metal ($\varepsilon = 0.12$) is used in calculating the radiative heat losses. Thus, undercooling will be significantly reduced by the presence of a condensation layer. After sunrise, the rise in the plate temperature will also be significantly reduced by the cooling effects of evaporation from the surface. Taking all these factors into account, an accurate estimation of surface temperature can be derived (Cole et al., 2004b, p.22). The implications of these results will be considered along with that of moisture layer formation and chemistry in the next section.

3.4 Moisture layer chemistry and pollutants

In considering the effect of pollutants on surfaces, as with marine aerosols, it is vital to consider transport and deposition processes (Seinfeld & Pandis, 1997). Deposition onto a surface may, in principle, be wet deposition (facilitated by rain) or dry deposition (deposition by gases or by particles). A number of transport processes are common to both gases and particles – aerodynamic transport through the atmospheric surface layer to a thin layer of stagnant air adjacent to the surface, molecular or Brownian transport across this thin layer, and finally uptake by the surface. The uptake by the surface is very significantly affected by any surface moisture. The surface absorption of gaseous species is controlled by the normalised reactivity. Gaseous species can also be absorbed in moisture droplets, either in the air or on surfaces:

$$A(g) \Leftrightarrow A(aq) \qquad [1]$$

$$\text{where } [A(aq)] = H_A\, p_A \qquad [2]$$

where p_A is the partial pressure of A in the gas phase (atm), $[A(aq)]$ is the aqueous phase concentration of A (mol L^{-1}), and H_A is Henry's law coefficient. Table 1 presents the effective H_A and normalised reactivity values for various gas species. The effective H_A in Table 1 differs from that represented in Eq. [2], in that it takes into account reactions of the aqueous species.

Where H_A is high and the normalised reactivity is low (e.g. sulfur dioxide), then deposition will be primarily through absorption into a moisture droplet (be it a wet aerosol or a surface moisture film). Where H_A is low and the normalised reactivity is high (ozone), direct gaseous absorption will dominate.

As indicated above, the uptake of gaseous species into moisture layers may be significantly affected by aqueous reactions. For example, the uptake of SO_2 in aqueous solutions is governed by the following equations (Seinfeld & Pandis, 1997):

Table 1. Relevant properties of gases for dry deposition calculations (extracted from Seinfeld & Pandis (1997)).

Species	H_A* (M atm^{-1}) at 298 K	Normalised reactivity
Ozone	1×10^{-2}	1
Nitrogen dioxide	1×10^{-2}	0.1
H_2S	0.12	—
Ammonia	2×10^{4}	0
Sulfur dioxide	1×10^{5}	0
Hydrogen peroxide	1×10^{5}	1
NO_3	2.1×10^{5}	—
Hydrochloric acid	2.05×10^{6}	0

* Effective H_A assuming a pH of 6.5.

$SO_2.H_2O \leftrightarrow H^+ + HSO_3^-$ [3]

while $HSO_3^- \leftrightarrow H^+ + SO_3^{2-}$ [4]

The balance of HSO_3^- versus SO_3^{2-} depends on pH, with the former dominating at pH values of 2.5–7, and the latter above this. A major aqueous reaction of importance is the oxidation of SO_3^{2-} or other forms of S(IV) to SO_4^{2-} or other forms of S(VI). This may occur via a variety of mechanisms, including reactions with O_3, H_2O_2 and O_2 (catalysed by Mn (II), Fe (III) and NO_2):

$$S(IV) + 0.5\ O_2 \overset{Mn^{2+},Fe^{3+}}{\Rightarrow} S(VI) \quad [5]$$

for example, where S(IV) may be HSO_3^- or SO_3^{2-} and S(VI) is HSO_4^{2-} or SO_4^{2-}.

According to Hoffman and Calvert (1985), the reaction rate is given by:

1.2×10^6 [Fe(III)][S(IV)] [6]

The sulfate that forms from the oxidation of S(IV) may exist as SO_4^{2-} or HSO_4^- (H_2SO_4 dissociates to HSO_4^- under pH ranges likely for droplets in the atmosphere or on surfaces). The balance is governed by:

$HSO_4^- \Leftrightarrow H^+ + SO_4^{2-}$ [7]

However, the absorption of ammonia into moisture films will tend to reduce the acidity produced by SO_2 absorption through the following equations.):

$NH_3 + H_2O \Leftrightarrow NH_3.H_2O$ [8]

$NH_3.H_2O \Leftrightarrow NH_4^+ + OH^-$ [9]

In Fig. 5, the ion concentration in a droplet exposed to conditions of CO_2 at 400 ppm, SO_2 from 20, 40, 75, 150 and 300 ppb, and NH_3 at 20 ppb, is given (Cole, 2000). This examination of pollutant deposition and aqueous chemistry has a number of implications to the conservation of metallic objects. Clearly in the case of metallic objects located in the open, the implications are direct. In this case the major implication is that a knowledge of the gaseous SO_x may not give a reliable measure of corrosivity. Deposition rates, which will depend highly on both rain and RH, and oxidants and catalysts (such as O_3, H_2O_2 and Mn (II), Fe (III) and NO_2), and any alkali precursors (e.g. ammonia), will control the pH of resulting moisture films or drops.

In an interior environment, the possible deposition pathways for pollutants will be highly dependent on RH and on any hygroscopic particulates or aerosols. If RH is low and in the absence of hygroscopic species then only direct gaseous deposition is possible. However, if the RH exceeds the deliquescent RH (DRH) of particulates in the air or on metal surfaces, then pollutant deposition will be enhanced by the absorption of gaseous species into the aqueous phases that form when the particulates wet. The DRH of some common salts is given in Table 2.

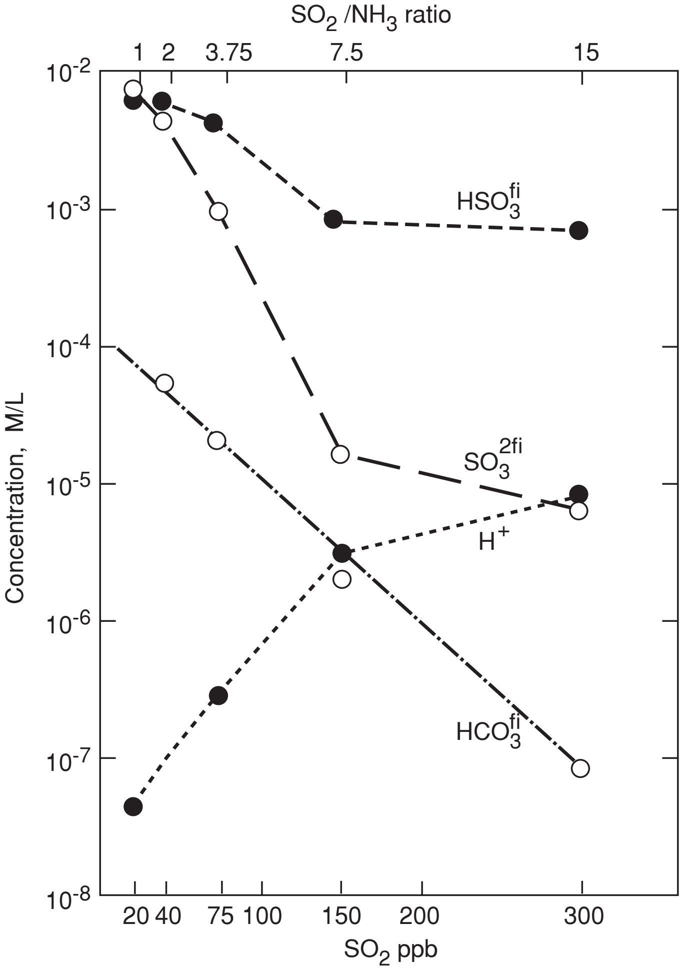

Fig. 5. Ion concentration as a function of gaseous SO_2 concentration and SO_2/NH_3 ratio (from Cole (2000)).

Table 2. DRH for common aerosols (at 20°C) (from Seinfeld & Pandis (1997)).

Salt	DRH (%)
Na_2SO4	84.2
NH_4Cl	80.0
$(NH_4)_2SO_4$	79.9
NaCl	75.3
$NaNO_3$	74.3
$(NH_4)_3H(SO_4)_2$	69.0
NH_4NO_3	61.8
NaHSO4	52.0
$(NH_4)HSO_4$	40.0
MgCl	35.0

An example where these factors may be in play is in the black spots on brass. It is observed that such black spots are favoured by the presence of high RH and hygroscopic dust particles (Weichert et al., 2004). Further,

SO_2 is readily absorbed into the aqueous phase (as indicated by its high H_A). Thus, under these condition, acidic sulfide and sulfate containing moisture phases are likely to form. The reaction of moist aerosols or surface droplets of such a composition with bronzes could well lead to spotting, although the corrosion products likely to form would be chalcanthite $CuSO_45H_2O$, antlerite $Cu_3SO_4(OH)_4$ and brochantite $Cu_4SO_4(OH)_6$, rather than covellite (CuS).

3.5 Surface cleaning

Experimental studies have indicated that surface cleaning of deposited salts by wind and condensation drip-off is of limited efficiency, and that surface cleaning by rain is the predominate mechanism of surface cleaning (Cole et al., 2004c). Surface cleaning occurs when raindrops run off the surface, collecting surface salts that are in their path. Run-off occurs when a raindrop on a surface has grown through coalescence to a critical size. When the slope of the surface is θ (0° for horizontal and 90° for vertical) and the maximum contact angle between the water and the surface is ϕ (the minimum contact angle is here assumed to be zero), then the maximum volume of a drop that can be retained on the surface V_{max} is calculated from (all dimensions are in mm):

$$A_{\max} = 7.49\,(1-\cos(\phi))/\sin(\theta)$$
$$h_{\max} = 1.2(1-\cos(\phi))^{0.8}(1+0.5/\sin(1.06\theta))$$
$$V_{\max} = \frac{8}{3\pi}\frac{A_{\max}^2}{h_{\max}}$$

Figure 6 presents the volume of a raindrop required for run-off against the contact angle. Figure 6 indicates that the more wettable a surface (the lower the maximum contact angle ϕ), the lower the drop volume before instability. Thus, more wettable surfaces will clean in lighter rain than less wettable surfaces.

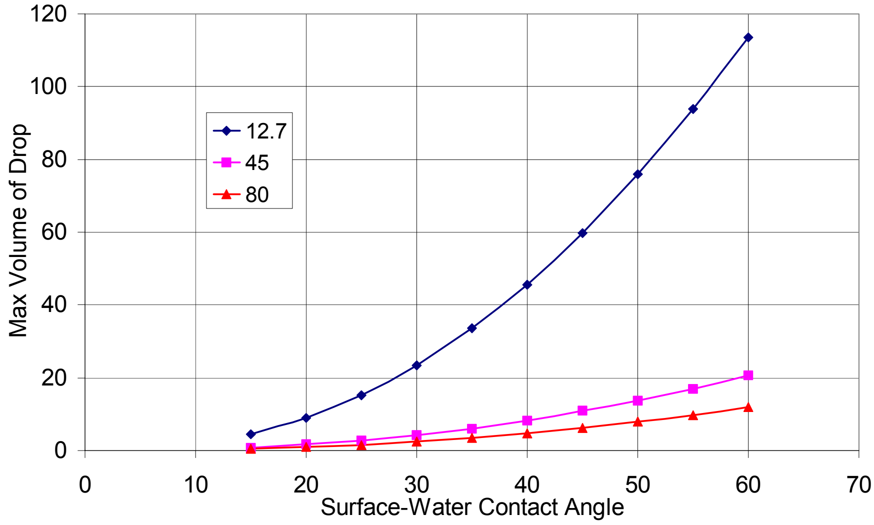

Fig. 6. Droplet run-off from a surface as a function of the surface-water contact angle ϕ for three surface slopes of θ = 12.7, 45 and 80.

The results of these studies are most relevant to cultural objects exposed in the open. The results indicated that below a given amount of rain, the rain will be retained on the surface and may promote salt concentration rather than cleaning. If rain is in excess of this critical value, wash-off will occur and the surface will be cleaned. The volume of rain deposited in a "shower" shows a relationship to latitude, and thus the average volume of rain per shower is significantly lower in Hobart relative to Cairns. Thus, maintenance practices in Hobart should not rely on cleaning by rain, despite the relatively high rainfall is this city. A second effect relates to the wettability of a surface. As indicated in Fig. 5, the higher the surface contact angle, the greater the maximum volume of a drop before run-off, and thus the greater the volume of rain before wash-off. Thus, surface treatments that reduce wettability will also reduce the effectiveness of rain washing.

3.6 Oxide properties

The ability of passivation films of varying chemistry to protect zinc was investigated by Muster and Cole (2004) and Muster et al. (2004). Passivation films replicating those produced during atmospheric corrosion (zinc oxide, zinc hydroxychloride, zinc hydroxysulfate and zinc hydroxycarbonate) were formed as precipitates from aqueous solution, and as surface films on zinc metal powder and rolled zinc sheet. The protective nature of oxides was evaluated in terms of stability (solubility) in chloride environments, surface charge and porosity. Microelectrophoresis measurements performed on precipitated oxides as a function of pH showed that oxides containing a majority of zinc hydroxycarbonate and zinc hydroxysulfate compounds possessed a negative surface charge below pH 6, whilst zinc oxide-hydroxide and zinc hydroxychloride surface films possessed iso-electric points higher than pH 8. The ability of chloride species to pass through a bed of 3 μm diameter zinc powder was found to increase for surfaces possessing hydroxycarbonate and hydroxysulfate surface species, suggesting that negatively charged surfaces can aid in the repulsion of chloride ions. Electrochemical analysis of the open-circuit potential as a function of time at a fixed pH of 6.5 showed that the chemical composition of passive films on zinc plates influenced the ability of chloride ions to access anodic sites for periods of approximately one hour. The ability of metals to wet was also shown to vary with the chemistry of its surface oxide. Contact angle determinations using liquid penetration and Wilhelmy balance techniques were able to systematically rank the oxides in order of their wetting properties. In addition, data from wet perimeter measurements on passivated zinc plates suggested that zinc hydroxychloride and zinc hydroxysulfate films possess a greater porosity than zinc oxide-hydroxide and zinc hydroxycarbonate films.

These results have direct implications to cultural objects coated with or composed of zinc or zinc alloys. However, the work also demonstrates the relationship between iso-electric points and chloride diffusion in controlling corrosion, which will affect a wider range of materials and may indicate methods of developing protective coatings or films.

4. Sensors

There are several electrochemical approaches used to sense corrosion processes, including linear polarisation resistance (LPR), electrical resistance (ER), electrochemical impedance spectroscopy (EIS) and electrochemical noise (EN). In addition, corrosive processes are dependent upon environmental conditions and can therefore be monitored using microclimate probes to measure such things as temperature, pH, gas concentrations, RH, time of wetness (TOW), solution conductivity and chloride concentration. Other methods fall into the domain of non-destructive testing and include techniques based upon optical (i.e. CCD and optical fibre), ultrasound/acoustic, electromagnetic (i.e. eddy current) and electromechanical effects (Agarwala & Ahmed, 2000).

LPR and ER are well-developed approaches for corrosion sensing, and have the ability to provide an estimate of the actual corrosion rate of the sensing element, therefore making it somewhat simpler to create "sensed-to-actual" damage relationships. In addition, both LPR and ER sensing devices utilise degrading electrodes that replicate the material of interest. Another approach is the use of galvanic couples (i.e. Zn-Cu, Zn-Cd or Al-Cu) to detect the bridging of electrodes by moisture/electrolyte. Galvanic approaches require calibration to enable the detected current fluxes to be related to degradation rates of the material of interest. Galvanic sensors are often used merely as TOW sensors (ASTM, 1989). ER methods appear to be the most suitable electrochemical probes for in-service monitoring where the presence of electrolyte films is infrequent. In addition, the accuracy of LPR sensors also requires a continuous evaluation of the ionic exchange properties at the metal–solution interface. Solution resistances in thin electrolyte films must also be characterised for LPR (Klassen & Roberge, 2003). EIS is particularly useful for studying the degradation of organic films. One EIS approach utilises a conductive paint electrode to test for changes in the performance of painted metals (Davis & Dacres, 1999). EN is a technique that measures temporal fluctuations of current or potential to sense changes in the kinetics of electrochemical processes. EN measurements are non-destructive, however data is often difficult to interpret. Wain et al. (1996) have reported on the use of EN for the evaluation of coatings on museum artefacts.

In terms of corrosion sensors, the most exciting progressions are likely to be made in the areas of semiconductor devices, fibre-optic sensors and microelectromechanical sensors (MEMS). Semiconductor devices based on Silicon technology are already developed to detect changes in electromagnetic radiation, mechanical damage, magnetic fields, temperature and humidity (Middelhoek & Hoogerwerf, 1990). Some advancement in the area of chemical sensing has been made based upon field-effect transistor (FET) devices. Ion-sensitive FET (ISFET) devices exist for gases (CO, O_2, CO_2, NH_3), and simple ions such as protons (pH), sodium, potassium and chloride have been constructed. FET devices are also well developed as temperature and RH sensors (Kelly & Owen, 1990). Both *intrinsic* and *extrinsic* fibre-optic sensors show promise to detect physical strains in materials through deformation of the fibre. However, extrinsic fibre-optic sensors have the ability to detect the concentrations of chemical species in solution volumes too small for traditional ion-selective electrodes. A typical set-up for such a system would involve an optical fibre in contact with an electrolyte containing ionophores enclosed by an ion-selective membrane. A system has been developed to sense Cu ion concentrations down to 10^{-7} M using a cell volume of 200 nl. One of the main advantages of fibre-optic sensors is their immunity to corrosive processes. Their small size also allows them to be incorporated into or onto structures with minimal side effects (Lee, 2003). MEMS devices are generally based upon the piezoelectric effect, thus converting mechanical to electrical energy and vice versa. There are several MEMS systems developed to detect physical changes such as pressure, strain or acceleration (Galea et al., 2001). One particularly exciting adaptation of MEMS is to utilise piezoelectric materials to emit and detect ultrasound waves. Ultrasound wave techniques have the ability to detect localised defects based upon variations in wave propagation. One of the key advantages of MEMS is their small size and their ability to be incorporated into arrays on surfaces. MEMS devices may also be designed to function as gas sensors. Also, it is possible to utilise SAW devices that exhibit chemically selective thin films. The adsorption of chemical species onto SAW devices alters the transmission of acoustic waves.

Each of the techniques above is applicable to monitoring the condition of cultural objects. The selection of the particular system will depend on practical considerations, cost and the exact need. For example, if very early indication of conditions that may give rise to damage is required, FET or ISFET devices may be appropriate, or if a small amount of damage can be tolerated, LPR, ER or galvanic sensors would provide a more direct reading.

5. Conclusions

This paper has reviewed progress in corrosion science in the areas of meta-methodology, models of degradation and sensors for studying corrosion. It has been highlighted that the following advances have been made in the last decade:

- Meta-methodology – the modelling of corrosion has moved from a narrow reductionist process to a holistic approach, and then onto a sensor-based learning approach.
- Models of degradation – the new holistic models of degradation include an understanding of pollutant sources, transport and deposition, the nature and chemistry of any moisture layers formed on the surfaces, and the properties of oxides that develop on a surface.
- Sensors – a wide range of sensors, including linear polarisation resistance, electrical resistance, electrochemical impedance spectroscopy, electrochemical noise and galvanic couples, have been developed. Others including field-effect transistor devices, ion-sensitive devices, fibre-optic sensors and microelectromechanical sensors are in the late stages of development.

The implications of these developments for the conservation of metallic objects and structures are indicated.

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Monitoring of archaeological and experimental iron at Fiskerton, England

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Abstract

The Iron Age site at Fiskerton is under threat of desiccation. In order to understand the present condition of the wooden structure and the metal and other artefacts, a project has been set up to monitor the ground water levels and quality, and the changes in condition of experimental modern materials placed in the vicinity of the causeway. This paper describes those aspects of the project which relate to the iron samples, including characterization of the corrosion products of three archaeological artefacts from recent excavations using XRD and SEM-EDS.

Abstract (Spanish)

Fiskerton, un yacimiento de la edad del hierro, está en peligro de deshidratación. Para comprender mejor el estado actual de la estructura de madera, de los objetos metálicos y otros hallazgos, se ha iniciado un proyecto para controlar los niveles freáticos, la calidad del agua y unas estructuras realizadas con materiales modernos situadas cerca del yacimiento. Este trabajo se centra en los aspectos relacionados con las muestras de hierro e incluye la caracterización, por medio de XRD y SEM-EDS, de los productos de corrosión de tres objetos arqueológicos recuperados recientemente.

Keywords: iron, corrosion, monitoring, XRD, SEM

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1. Introduction

The pre-Roman Iron Age wooden causeway at Fiskerton was excavated in part in 1981 (Field and Parker Pearson 2003). Associated with the causeway are ferrous weapons, tools and other artefacts, and finds of bronze, pottery, stone, bone, jet and amber. The causeway appears to run from the site of the modern village of Fiskerton (five miles east of the city of Lincoln), down to the now canalised River Witham. Dendrochronology has dated the causeway to have been in use from at least 457 to 321 BC, although its precise function has not yet been established

The causeway has been under a fairly intensive arable farming and drainage regime for a number of years, and concern has been raised that this may have led to the desiccation of this internationally important site. Recent changes to land management with reversion to grassland will reduce plough impact, and a further planned land-use change will reduce the drainage of the site, allowing water-tables to rise. Whilst this recent initiative (which will see the creation of a natural wildlife habitat under a local Countryside Stewardship Scheme) would at first appear beneficial for the site, the effects of raising the water levels on the already desiccated soil and archaeological structures and artefacts are not known. It is possible that this may be detrimental due to the introduction of different water chemistry and oxygen regimes on site.

In 2001, a research committee was established to assess the survival and threats to the archaeology in the immediate vicinity of the causeway and in the wider area of the River Witham Valley (Catney and Start 2003).

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Through its direction, and under the initiative and project management of English Heritage (the government's advisor on the historic environment in England), a number of surveys of the site at Fiskerton have now been completed including geophysical, auger and field walking surveys. The purpose of these surveys was to provide as much information about the site at the point of this significant land-use change. In addition to those projects aimed at characterising the archaeological and palaeoenvironmental aspects of the site, a conservation management project was also set up with the following aims:

- To assess the current state of preservation at the site
- To determine the impact of re-watering on the preservation of archaeological materials at Fiskerton
- To test methodologies for assessing conditions of a variety of archaeological materials so that these methodologies could be used in the future at other sites in the Witham Valley and elsewhere.
- To provide guidance on future management of archaeological material at Fiskerton.

The project involves the assessment of the condition of previously excavated archaeological materials and also the deterioration of a range of modern experimental samples buried in the vicinity of the causeway. Additionally, the groundwater levels and quality are being monitored through sampling at a number of points at the causeway site. Research and monitoring will be on-going for a period of at least three years. The results of this work will help inform decisions about the precise nature of future land-use change, as well as provide a proxy measure for the preservation of the site.

This paper describes the project and presents the initial results to date which relate to the archaeological and the experimental iron. The first samples of the buried experimental materials were removed from the ground in June 2004 and the preliminary results are included and briefly commented on. The three main components of the project are the analysis of previously excavated (archaeological) iron artefacts, analysis of experimental iron samples, and the monitoring of the groundwater.

1.1 Analysis of archaeological iron artefacts

The metal artefacts from the 1981 excavation were examined and recorded during the programme of investigative conservation in 1982 (White 2003). In subsequent years, selected ferrous artefacts were analysed by metallography to investigate their metal structure (Fell 2003), and corrosion layers were analysed by x-ray diffraction (XRD) together with comparative samples from other waterlogged sites (Fell & Ward 1998). The presence of iron sulphides was concluded to be one factor in the unusual preservation of some of the ferrous artefacts at Fiskerton, although clearly the corrosion processes which cause the different corrosion types in the ironwork assemblage are complex. A separate study on a single artefact concluded that the presence of ferrous carbonate and complex calcium iron silicates was significant in the preservation of the artefact (Biek et al. 2003).

Subsequently, there have been a few small-scale excavations and casual finds of metalwork close to the causeway in response to dredging work in the dykes. In particular, an excavation in 2001 yielded ten iron artefacts of which three were selected for study of corrosion products and for metallographic examination (Figure 1). Selection was based on their robust condition and because they seemed to have been waterlogged probably continuously since burial. The three artefacts analysed were a currency bar (10), a shafthole axehead (11) and a socketed axehead (131), each of which provided:

- Five samples of surface corrosion products for XRD analysis
- One metallographic sample comprising a continuous corrosion layer from metal outwards, for the technological study of the metal (to be reported elsewhere) and for the study of corrosion products by scanning electron microscopy with energy-dispersive x-ray analysis (SEM-EDS).

1.2 Burial of experimental iron samples

To assist our understanding of the corrosion processes, modern test pieces of iron, serving as analogues for the archaeological artefacts, were inserted in the ground at two locations adjacent to the causeway. Samples will be extracted from both locations at intervals over three years. The installations also included materials being studied by other researchers (copper, bone, antler and horn), mounted separately and according to schemes devised for previous burial experiments elsewhere (e.g. Simpson et al. 2004). Analyses of the iron will include:

- Corrosion rate, as a measure of the weight of corrosion products generated per sample over time (cf. Matthiesen et al. 2004).
- Corrosion products to be analysed by XRD with any heterogeneous regions in the metal samples examined by SEM.
- Characterization of corrosion type and comparison with archaeological samples from Fiskerton analysed previously (cf. Fell and Ward 1998).

Figure 1. Axeheads 11 (upper) and 131 from Fiskerton excavations 2001. The lower axehead (131) is socketed and lugged. The 'V' notches from the cutting edges (left) are where the metallographic samples have been removed.

1.3 Monitoring of groundwater

The groundwater was monitored via peizometers (dipwells), which are tubes with finely perforated tips to permit the ingress of water. Clusters of peizometers were placed at five locations in the vicinity of the wooden causeway, with the following aims:

- To establish base-line data for groundwater levels at monthly intervals
- To measure on-site pH, redox potential, temperature and conductivity at monthly intervals
- To provide samples for detailed chemical composition of the groundwater at one monitoring point at monthly intervals
- To measure changes in these data over time.

In each of the five peizometer clusters, water levels have been recorded monthly since August 2003, whilst pH, redox potential, temperature and conductivity have been measured since October 2003. The chemical composition of the water is measured in the laboratory by the Environment Agency, the government body responsible for water use in England, with results available from February 2004.

The relationship between the water levels in the peizometers and the archaeology on site is less than clear. Crude estimates suggest that most of the archaeological material recovered from excavations came from the level or above the level of the highest peizometers. However, the base of any vertical timbers of the causeway would be likely to be much lower than the lowest peizometer. During the 1981 excavations only one vertical timber was excavated (due to the difficulty of such an operation), which was five metres long (Field and Parker Pearson 2003, 41). Given that the depth of "soft" sediment in some areas of the causeway is as deep as six metres, the potential for the survival of at least some of these vertical wooden structures is highly likely. This is important as it is often the working of the points of such timbers that is of most interest to wood and tool specialists (*ibid*). In the course of the next year, it is likely that small excavations will take place on site to investigate the condition of the preservation of unexcavated sections of the causeway.

Aside from the information that the monitoring programme will provide for understanding the conservation of the site, it also provides essential data for the experimental iron samples described previously.

2. Methods

2.1 Archaeological iron

Since excavation in 2001, the artefacts have been stored under desiccated conditions at the conservation laboratories of Lincolnshire County Council Heritage Service. The three artefacts selected for analysis were each sampled in 2004 to provide surface corrosion products for XRD analysis and a metallographic sample for the study of the corrosion layers by SEM-EDS.

The corrosion products for XRD analysis, chosen at random but biased towards black or darker coloured products, were selected as those that could be readily detached from the surface of the artefacts. Samples in the order of 1mg were ground in an agate mortar and mounted on a flat single-crystal silicon sample holder, designed to reduce background scatter. X-ray diffraction data were collected on a Philips PW 1840 diffractometer using cobalt K_α radiation (wavelength 0.179026 nm) incorporating a solid-state silicon detector. A search-match computer programme (Philips, based on JCPDS files) was used to identify unknown components in the diffraction patterns by comparison with standards in the powder diffraction file.

The samples for metallography and investigation of the corrosion layers were removed from the cutting edges of the two axeheads and through the end of the currency bar, using a jeweller's piercing saw. The samples were mounted in Buehler epoxy resin and ground and polished to 0.25 μm fineness in diamond slurry according to standard metallographic techniques. The mounted samples were examined firstly under a metallurgical microscope at magnifications up to x400, and then by SEM-EDS in a Leo 4401 Stereoscan electron microscope with Isis EDS software at 25 kV accelerating voltage and probe current of 2.0 nA with a germanium detector. Back-scattered electron images were obtained from unetched carbon-coated surfaces.

2.2 Experimental iron samples

The iron test pieces for burial at Fiskerton were mounted on rods of inert material and installed as two groups of six rods each and placed adjacent to the two clusters of groundwater monitoring peizometers nearest to the River Witham (clusters 1 and 2). One sample rod will be extracted from both locations at intervals of six months, 12 months and then probably yearly thereafter depending on initial results and changes to water levels and chemistry.

The installation system was similar to that devised for the experimental work at Nydam Mose, Denmark, for which we are very grateful to David Gregory for advice. Our system is rather simpler however, comprising core rods of glass fibre reinforced polyester, spacers of polypropylene, and the samples attached with nylon cable ties in recesses along the rods. Each two metre rod was fitted with eight samples of iron spaced over a length of 1.2 m. Different soil conditions and depths were factors in the positioning of the experimental samples on the rods. In total, 96 test pieces were required and these were made as strips of annealed ferritic wrought iron each measuring approximately 50 mm long, 10 mm wide and 4 mm thick. Each strip of iron was marked with a punch before accurately recording the weight and dimensions.

The rods were installed on 22 December 2003 and the first (6 month) extraction was made on 22 June 2004. Samples were initially stored wet at 4°C but were later transferred to desiccated storage at ambient temperature. Because the site is 400 km away from our laboratories, it is not possible to analyse samples immediately and these difficulties must of course be allowed for in our conclusions.

2.3 Groundwater monitoring

Clusters of either three or four Casagrande porous plastic peizometers, with a modified tip length of 130mm were installed at each of the five selected locations. Using results from an auger transect adjacent to the line of the causeway, the peizometers were installed at various depths, ranging from 0.6 m below the surface, to a maximum of 1.9 m below the surface depending on the depth and complexity of the deposits.

In almost all of these clusters the deepest sample was deliberately placed much lower than the known archaeological horizons to ensure that water would be available even in the driest months. The uppermost peizometers were installed just below the bottom of the plough soil and most degraded peat horizons, but still within deposits that were for the most part in a less than optimal state of preservation. The general state of preservation of organic material within the deposits was found to improve with depth, with well preserved peat occurring somewhere between 1m and 1.3m below the ground surface. Three additional peizometers measure the water levels at positions east of the causeway, to provide a non-linear picture of groundwater levels.

Water levels are measured using an electronic dip-meter with audible depth indication and the other data recorded from water samples recovered in the field using samples drawn from the peizometers using a bailer. Water chemistry data were monitored using a Pro-Sys portable multi meter for pH/mV, TDS, conductivity and temperature, with individual probes for each test.

Further determination of the chemical composition of the groundwater is provided from a 1.5 litre water sample drawn from one peizometer at cluster 2, the only sample point which has shown slightly faster rates of recharge, with water availability throughout most of the year. The analysis of these samples is funded and measured off-site by the Environment Agency. Measurements include lead, ammonia, nitrate, sulphide, chloride ion, orthophosphate, silicate, sulphate, calcium, tin, manganese, iron and copper.

3. Results

The XRD results from the samples of corrosion products from the three archaeological artefacts are summarised in Table 1. The dominant crystalline phases determined from each artefact were greigite (Fe_3S_4) and siderite ($FeCO_3$). Greigite formed a major component of the crystalline phases in nine of the 15 samples, often in conjunction with siderite, although the latter was only a major component in six samples. Other components detected were pyrite (FeS_2), mackinawite ($Fe_{1+x}S$), goethite (α-FeOOH), magnetite (Fe_3O_4), vivianite ($Fe_3(PO_4)_2{\cdot}8H_2O$) as well as small amounts of calcium carbonate and other soil constituents such as quartz.

Table 1. Summary of XRD results of archaeological samples

Sample	Object	Crystalline components
1	Bar 10	**greigite** (siderite calcite)
2	Bar 10	**greigite calcite**
3	Bar 10	**vivianite calcite** siderite (?goethite ?magnetite)
4	Bar 10	**calcite siderite** (greigite pyrite ?magnetite)
5	Bar 10	(greigite goethite siderite + other)
6	Axe 11	**greigite** (siderite) (calcite)
7	Axe 11	**greigite** magnetite
8	Axe 11	**greigite** (calcite)
9	Axe 11	**greigite siderite**
10	Axe 11	**siderite** greigite magnetite goethite
11	Axe 131	**greigite siderite pyrite**
12	Axe 131	**greigite siderite pyrite** (?mackinawite)
13	Axe 131	goethite magnetite calcite quartz
14	Axe 131	**greigite siderite** pyrite
15	Axe 131	**pyrite** vivianite calcite (goethite)

Major constituents shown bold; minor shown normal and trace levels are bracketed

The corrosion layers on the metallographic samples were very thin, a consequence presumably of little active corrosion of the artefacts in the waterlogged burial environment. Adjacent to the surviving metal (which in all three artefacts comprised ferrite with small amounts of pearlite or grain boundary cementite) there were occasional traces of remanent cementite. Remanent structures are not uncommonly preserved in less corroded iron artefacts such as those from anoxic environments at near neutral pH. Elemental mapping of part of the corrosion layer from axehead 11 distinguished in particular, concentrations of S in the outer corrosion layer including occasional circular forms, presumably framboidal sulphides (Figure 2).

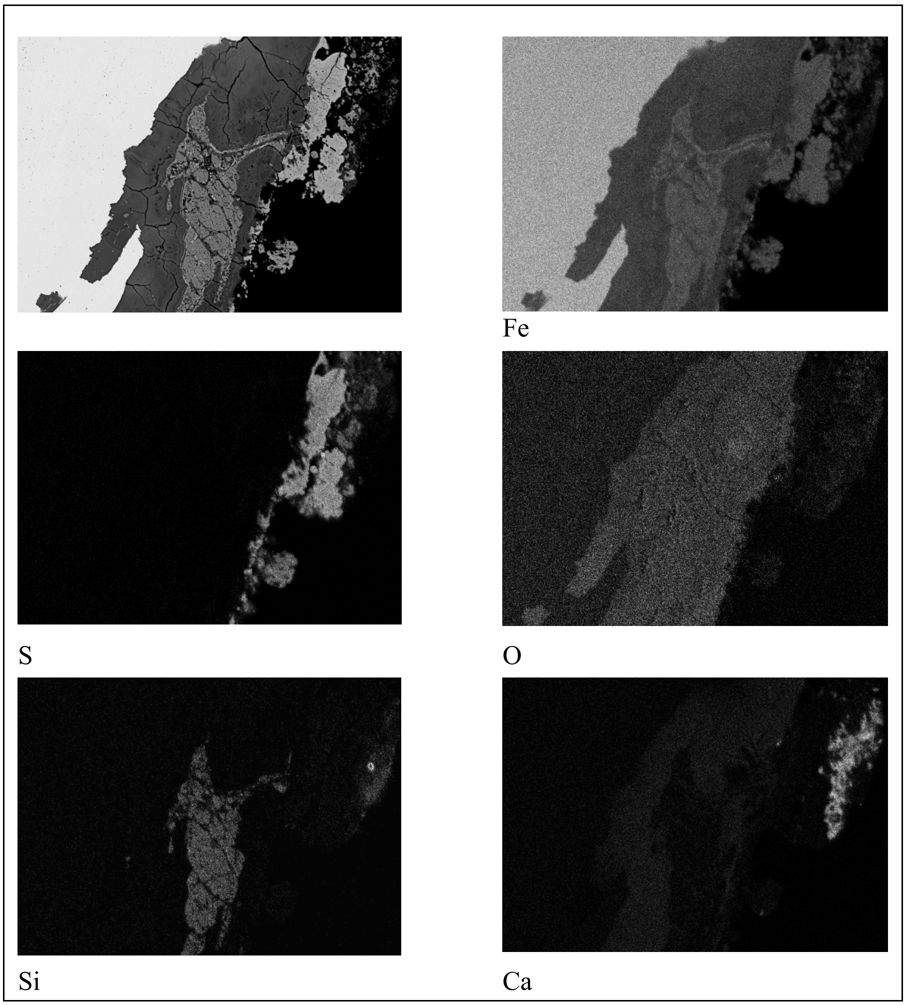

Figure 2. Scanning electron micrograph of metallographic sample from axehead 11, showing top left, that there are two corrosion layers, an outer layer (centre) in contact with the metallic iron (left), and an outer layer (right). The back-scattered electron images show element distributions for Fe, S, O, Si, P. Width of each image, 0.4 mm

In terms of the analysis of the modern experimental samples of iron and the ground water monitoring, only preliminary results can be presented at this stage.

Visual appearance of the iron samples extracted at six months suggests that there has been considerable oxidation of the upper samples from both groups and probably in all the samples from cluster 1. The latter are nearest the delph of the river, within clay deposits which seem to suffer from frequent changes in water levels. The cluster 2 samples, however, are buried in peaty layers and water levels are more consistent. The smell of hydrogen sulphide was very noticeable when these samples were removed. Pronounced orange staining was visible on the plastic installation rod at a position equal to 0.8 m below ground level. Because of the extensive oxidation, only the lower six of the eight samples on the rods removed from each cluster were analysed by XRD (Table 2). These were determined a few weeks after extraction from the ground and may therefore reflect some recent corrosion. There are two principal findings. Firstly, iron sulphides are present in samples from cluster 2 but not in the samples from cluster 1. Secondly, iron carbonate was not detected in any samples.

Table 2. Preliminary XRD results for 6 month experimental samples

Depth* (m)	Crystalline components # Cluster 1	Cluster 2
0.98	**quartz calcite** goethite	**goethite** quartz
1.19	**goethite** (magnetite)	**goethite calcite** (?akaganeite)
1.32	**goethite calcite**	**mackinawite calcite** goethite (magnetite)
1.45	**quartz calcite** goethite (magnetite)	**mackinawite** calcite
1.58	**quartz** calcite	**goethite mackinawite calcite** greigite
1.61	**quartz calcite** goethite (magnetite)	—

 # Major components shown bold, minor shown normal, trace levels are bracketed;
**Approximate depth below ground to mid sample; — Not analysed because of insufficient sample*

Water levels on site during the 10 months for which data are available are highly variable (Figure 3). For peizometer A in cluster 2, water levels were recorded between only 0.69 m below ground in January 2004, to as low as 1.62 m below ground two months earlier, a difference of nearly one metre. Similar results were recovered from the other monitoring positions, with the highest level recorded only 0.09 m higher, from peizometer C, cluster 3. Some of the shorter peizometers, and those towards the north end of the site have only recorded water during part of the year, even though every attempt was made to ensure that at least one peizometer would be long enough to sample water even in the driest conditions. For the months of October and November, water level data (and therefore samples for other analyses) was only recovered from 10 out a possible 34 peizometers, less than 30% of the number installed. Water levels in cluster 1 are in general slightly lower than those for cluster 2 reflecting the dewatering effect of the adjacent delph (drainage ditch).

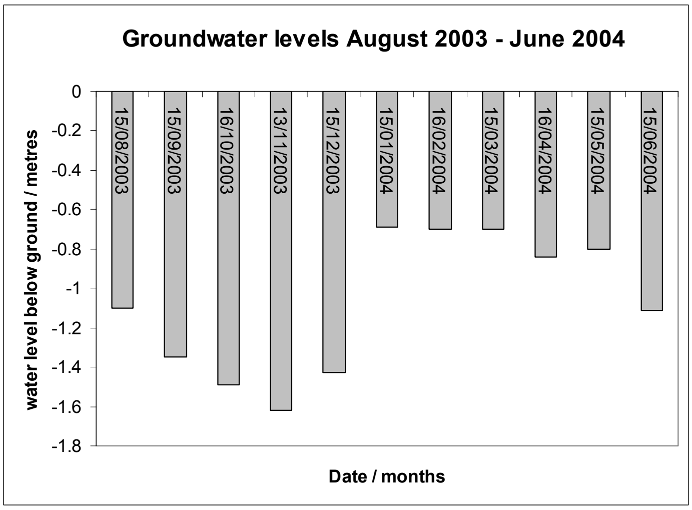

Figure 3. Water levels from peizometer A, cluster 2, from August 2003 to June 2004. The bars on the graph are a visual representation of the empty peizometers. The bottom of the bars mark the water level below ground level.

There is only a limited amount of data so far collected for pH, redox potential, conductivity, temperature and chemistry and these results require careful interpretation and may in time need to be calibrated. However, it is worth noting that, as far as can be established, the tests undertaken are providing a proxy measure of the state of preservation of the deposits. Where deposits are below the level of the groundwater year round, pH values vary between about 6 and 7. Redox values for these samples usual fall between +100 and -200 mV. In contrast to this, in deposits that have only recently been re-wetted, following a period of time where the groundwater level was below the depth of the peizometer, a different set of results are seen. In the first month that a sample is re-wetted, pH readings are usually as low as 3.5 – 4.5, and become less acidic with the increasing time that the deposits are below the level of the groundwater. In these samples, redox values are typically between +330 and +125 mV.

4. Discussion

The range of crystalline corrosion products detected on the archaeological artefacts, and in particular the preponderance of greigite and siderite, is very similar to the previous results for the analysis of artefacts from the 1981 excavation at Fiskerton (Fell and Ward 1998). In those analyses, made many years after excavation of the artefacts, pyrite and greigite were recorded as the major sulphide phases in equal numbers of artefacts, whereas in the present study, greigite dominated. Pyrite appeared on one artefact in particular (axehead 131), and this was the artefact which appeared to be most corroded of the three. This is probably in agreement with the generally accepted pathway for the conversion of the monosulphide, mackinawite, to other metastable phases including greigite, and finally to the disulphide phase, commonly pyrite (Morse et al. 1987; Vaughan and Lennie 1991; Walker 2001).

The second major constituent of the corrosion layers, siderite, was found in 10 samples. This is a similar ratio to the previous analyses where six of nine sampled artefacts from Fiskerton were found to have siderite in their corrosion layers. The formation process for siderite at Fiskerton may be related to sulphide production through the reduction of organic matter (Fell and Ward 1998, 114). Siderite is a major corrosion product on iron artefacts from Nydam Mose, Denmark, whereas sulphides are absent (Matthiesen et al. 2003). The authors suggest three possible mechanisms for the formation of siderite and that the layered appearance in the corrosion layers may indicate that it is not a simple formation process (Matthiesen et al. 2003, 190). They further discuss the possible protective nature of siderite on ironwork at Nydam. At Fiskerton, the presence and possible significance of siderite was noted by Biek et al. (2003). Clearly, however, the corrosion processes and siderite formation at these two sites are not the same and further research and monitoring of the site conditions at Fiskerton is necessary to better understand the corrosion mechanisms.

Elemental mapping for axehead 11 showed sulphur concentration in the outer corrosion layer and this result is similar that for axehead 131 from the 1981 excavations (Fell and Ward 1998, fig 3). This may explain why many of the corrosion products analysed by XRD showed high sulphide levels and it is worth reiterating that the sampling procedure for corrosion products was biased towards the darker deposits. Of the few artefacts examined by metallography, the layering in the corrosion mantle seems less complex than at Nydam. In our artefacts, the outer layer containing sulphides could result from changes in burial conditions, in particular pH, at some time in their history.

The preliminary results for the experimental iron samples show the sulphides mackinawite and greigite forming at cluster 2, but no siderite. Groundwater measurements at cluster 2 have indicated readings of pH 6.2 and of calcium carbonate 125mg/l – conditions which are not too favourable for the formation of siderite. However, it is clearly premature to attempt elaborate interpretation of the data at this early stage. The presence of goethite and other iron oxides in most of the samples is probably due principally to post-excavation corrosion .

Of the site monitoring data available from Fiskerton, the current indication from the water level results suggest that much of the archaeological site is likely to be above the level of the groundwater. This is very much seasonally affected, with the driest months in October and November and the wettest (or months where the water levels were highest) occurring during January, February and March. This is not likely to provide a particularly beneficial environment for the preservation of organic deposits, nor inhibit the corrosion of any surviving archaeological metals, or the recently introduced experimental samples. When water levels are low, the potential for oxygen diffusion to previously anoxic deposits increases, which would in turn encourage activity of aerobic bacteria, and also further advance the corrosion of metals. At Fiskerton, this potential was certainly exacerbated during the driest months, when much of the upper 0.5 m of soil on site was completely dried out, and in many places deep cracks to a similar depth were visible. Given that the recent land-use change is from arable to grassland, there should be fewer periods when the field is fallow with no crop cover. Whilst this should reduce the amount of direct moisture loss through evaporation from the bare soil, the results from June 2004 would suggest that other mechanisms, such as evapo-transpiration are likely to be contributing to the reduction in water levels.

Redox data are the hardest to measure in any monitoring project, and the type of data collection method that we have employed on site has been suggested to be less reliable than other, non-water sample based methods of redox measurement (Smit 2002, 96). However, the same author also recognises that redox data from dipwells do bear some similarity to the results from other, ‘more accurate’ methods. The principal concern with redox results from groundwater is that oxidation/reduction reactions occur during the time that the water is in the borehole. This is similar to our experience, and early results indicate lower redox potential readings in peizometers before purging, and similar to Smit, particularly where water samples had collected in the dead-end of the peizometer and had not been effectively emptied. By purging the water the day before, changes in redox within the borehole will only relate to reactions occurring over a 24 hour period. In the near future we hope to also further calibrate our results, through comparison with results from *in situ* redox electrodes, or modelling the potential for oxygen (and other electron-acceptor species) transfer within the closed dipwells. The pattern of low pH and high redox potential in deposits where waterlogged conditions have recently been re-established, is similar to that recorded by Caple and Dungworth (1998) in laboratory experiments on the re-hydration on organic deposits. If nothing else, this would suggest that at least the basic trends identified in the redox data do replicate those from earlier work.

Since the burial of the experimental materials, water levels on site have been rising. Potentially this suggests that to begin with, samples would become exposed to water with high acidity and, as indicated by the high redox values, the presence of significant numbers of electron acceptors. This may also have been the scenario in antiquity – variations in water levels and chemistry, resulting in complex corrosion processes on the ironwork. Over the next three years, we will be monitoring site conditions and the deterioration effects on the experimental materials, as well as possibly recovering additional archaeological artefacts. This will provide data towards better understanding of the corrosion sequence as well as informing on the best system to preserve the site and the artefacts for the future.

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Saving archaeological iron using the Revolutionary Preservation System

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Abstract

Over the last few decades much research has been devoted to the removal of chlorides from and the stabilization of iron objects after excavation. Once this treatment is complete, iron artefacts are generally examined briefly by researchers and then passed to the collections manager. These materials represent structural hardware, tools, weaponry and, occasionally, decorative objects. They are sparsely represented in exhibit spaces and therefore usually occupy the "dead storage" areas of a museum or university laboratory. Often forgotten, iron objects generally turn to dust during their years of storage. For the past 12 years, researchers at Memorial University of Newfoundland have been uncovering the archaeological remains of one of Canada's earliest English settlements. George Calvert, later Lord Baltimore, established the Colony of Avalon in 1621. The site has been occupied almost continuously since then. More than one million artefacts have been excavated with approximately 20% of the assemblage made of iron. Realizing that treated iron in storage was re-corroding, fast intervention was needed to prevent further damage to the objects while preparing a re-treatment strategy. Our solution was to bag all re-corroding iron in RP/ESCAL enclosures. The Revolutionary Preservation (RP) System is an airtight packaging system. It was purchased to store items in an oxygen-free, low relative humidity (RH) environment thus preventing further corrosion until they could be re-treated. This paper outlines the authors' observations and experiences in bagging hundreds of fragile iron artefacts. In addition, preliminary results of an accompanying research project studying 150 building nails stored under a variety of conditions will be described.

Keywords: Archaeological iron, storage, corrosion prevention, Revolutionary Preservation/ESCAL

1. Introduction

The Ferryland archaeological site is located approximately 80km south of St. John's on the Avalon Peninsula of the Island of Newfoundland within Canada. Located on the Atlantic ocean this temperate zone provides a moist, acidic soil with a high salt content.

Historical documents indicate that Calvert's colonists constructed a mansion house, brew house, salt works, forge, hen house, kitchen, fishing stores and dwellings around the "Pool". Lord Baltimore visited his colony in the summer of 1627 and returned with his family in 1628. Sir David Kirke was granted the Island of Newfoundland in 1637 and took control of the colony in 1638. The Dutch attacked the area in 1673 inflicting significant damage on several plantations, especially Ferryland (Lovelace 1675). The colony recovered from this attack, but after the French captured and burned the settlement in 1696 activity at the site ceased until the 1700s.

The present Ferryland Project began excavations in 1992. The site itself is believed to cover an area of approximately 30,000 m^2. To date about 1,100 m^2 have been excavated and designated as Areas A through G. Briefly described, these areas represent the landward palisaded edge of the colony (Area A), the houses of middling planters (Areas B and D), a waterfront warehouse complex (Area C), defensive works (Area E), a high status house, possibly the Kirke residence (Area F), and another waterfront area with an early 18th century domestic structure (Area G). Artefact assemblages including textiles, glass, ceramics, ferrous and non-ferrous metals, brick and wood are concentrated in areas defined by structures. To date catalogued artefacts number about half a million with many numbers representing two or more objects. Of this group about 20% are made of iron. Each year of excavation uncovers about 7,000 iron nails and 1,000 to 2,000 iron objects. Though we are required by permit to document and retain the nails, conservation of these object types is not a requirement. We are required, however, to fully conserve and store all non-nail iron objects. The cost of conserving artefactual remains, for the Ferryland project, is equal to that of excavation. Table 1 presents the cost of conservation for a nine year period. The building facility is included here as this serves as the official repository for the collection.

Table 1. Total Cost for Conservation of Artifacts from 1991 to 1999

conservation supplies	$77,874
building facilities	$626,000
salaries	$1,289,840
analyses, treatment containers and collection storage containers	$323,000
TOTAL	$2,316,714

Table 2 shows the number of hours required to conserve artifacts. Note that objects made of iron require much more time to conserve because chloride removal is required to stabilize ferrous metal.

Table 2 . Hours Required to Care for an Historic Archaeological Collection

Hours required to process artifacts from 10 weeks of excavation				
Material	Number of Artifacts	Hours		
		Cataloguing	Stabilization	Conservation
glass ceramic pipe	18,000	1,500	1,500	1,000
bone	1,100	100		175
iron objects	544	200	500	5,000
iron nails	12,000	10,000	2,000	1,000
misc. inorganic + organic	78	48	30	800
copper	47	10		37
lead objects	105	15		38
lead shot	276	30	40	
wood	300	25		25

By the early modern period iron was used for a variety of objects from structural hardware, to blacksmith's tools, to snuff boxes (Figure 1). For this reason iron artifacts are numerous on any historic site and scattered through all areas of excavation. For the thousands of iron objects excavated each year at Ferryland condition varies greatly by object and area of excavation. Some are better preserved than others. Because the site's soils are coarse in texture and allow easy movement of water and dissolved salts objects appear to always be exposed to the corrosive environment of a maritime climate.

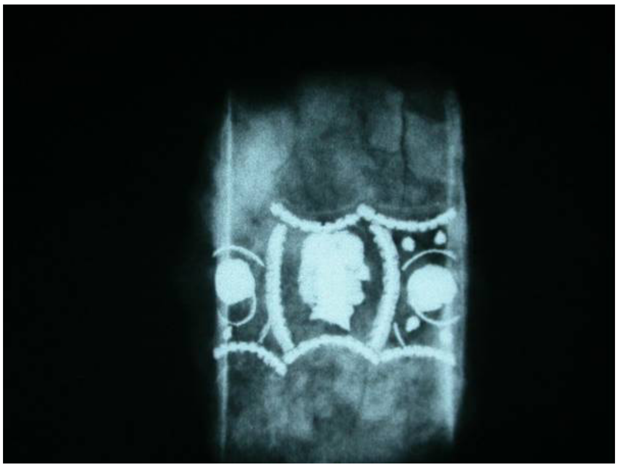

Figure 1 X-radiograph of iron snuff box with silver decoration

Geochemical analysis of the soil solution indicates a range of chloride concentrations from 635 ppb to 33,109 ppb. Soil pH ranges from 3.81 (H_20) to 5.74 (H_20). Corrosion rate measurements range from 0.02-0.22 millimetres per year. After some 350 years of burial this means that an object's corrosion layer could vary from 7 mm to 77 mm. Table 3 shows the optimal and mean values for the soil composition.

Table 3 Optimal Burial Environment

	Particle size distribution (%)			pH			SiO_2 wt%	Cl (ppb) for soil solution	Cl (ppm) for soil
				H_2O					
Optimal	43	53	4	5	30	0.09	55	3,858	417
Occupation/destruction events									
mean	45	50	4	5.03	22	0.08	55	3,169	399
Fill/building events									
mean	48	48	4	4.61	33	0.09	56	6,487	358

Table 4 provides a summary of soil texture for the site. The burial environment has been described by event to distinguish between areas of occupation and building construction. Fortunately most iron objects were excavated from soils with a lower rate of corrosion. The higher rate of corrosion corresponds with areas of high soil chloride concentrations where the seawater is in constant contact with soils. These are areas along the colony's waterfront where recovered metals were found to be in poor condition. Thick corrosion layers can be expected in areas with high chloride concentrations.

Table 4 Soil texture of the Ferryland Archaeological Site Matrix

	pH	Organic wt%	Colour	Mineral Composition
Range	3.81 to 5.74	2 to 30	dark yellow brown - dark grey	subsoil- quartz, albite, phlogopite
Occupation events				
mean	5.03	11.3	dark yellow brown - dark brown	quartz, albite, sepiolite, phlogopite, illite, muscovite
Fill/building events				
mean	4.61	10.8	Pale brown - brown	quartz, albite, phlogopite

We know that soaking iron in sodium hydroxide solutions removes most of the chlorides.

2. Treatment

At Memorial, iron artefacts have been treated with aqueous sodium hydroxide solutions of either 0.5 or 1.0% (w/v) through at least six changes of solution. Most treatment times average two years. This treatment method has been developed based on work by Scott and Seeley (1987),Costain (2000) and Mathias (1994). Mathias worked with Costain on the holding solution experiments while interning at the Canadian Conservation Institute (CCI). Realizing the ability of sodium hydroxide to remove chlorides, after monitoring solutions for chloride concentrations, Mathias felt this would be a suitable treatment for the bulk treatment of iron at Memorial University. This decision was made in consultation with Judy Logan, archaeological conservator working at CCI. After treatment some mechanical cleaning is conducted, but no such cleaning is performed during treatment because of the limited availability of personnel. In many instances it appears that chlorides remain within the pores of the artefacts and will not move into solution if a thick silica-rich corrosion layer is still present during and after chemical treatment. It is these artefacts for which the RP/ESCAL system is used. Because chlorides are potentially still trapped in the iron they will begin to re-corrode during the summer months when the relative humidity can exceed 65% in June, July or August and akaganeite will form. Figure 2 presents the change in RH for the collections storage area from 1993 to 2003.

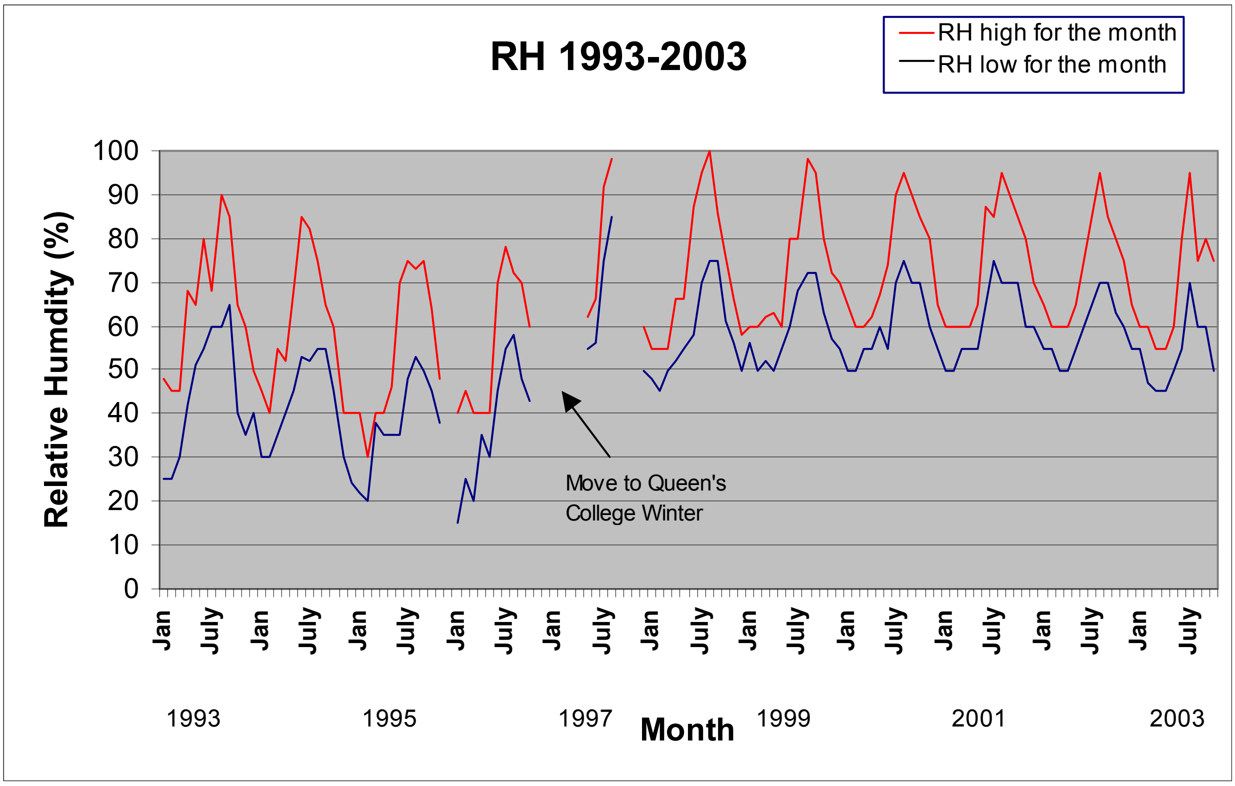

Figure 2 RH for collections storage area from 1993 to 2003.

During the winter of 1996/97, the conservation lab and collections storage were moved from the Ingstad building to the lower level of Queen's College, several city blocks away. Queen's College is located next to a large pond, which seems to have had an adverse effect on the ambient environment inside the building. Data collected over a ten year period at both buildings shows an average increase in relative humidity of over 10% at Queen's

College as compared to the Ingstad Building.

The archaeological iron collection is currently stored either in baked enamel, gasket sealed, metal cabinets, if a non-nail iron object, or in large plastic tubs, for nails. The cabinets are conditioned with silica gel sachets but given the limited availability of staff these are not well maintained. Individual items are wrapped in acid-free tissue and placed in hard plastic boxes or in polyethylene bags. Ethafoam supports are made for delicate items. Humidity is controlled only through the use of portable dehumidifiers. Figure 3 shows an area of "fuzzy" akaganeite which developed along a crack on an object stored under these conditions.

Figure 3 Akaganeite growing on iron substrate

A scanning electron microscopy image, (220 X magnification and 20 KV), of akaganeite growing perpendicular to the iron substrate, is shown as Figure 4.

Figure 4 SEM of akaganeite growing perpendicular to iron substrate

Overall it was found that the interesting iron objects stored in the larger collections storage area in the storage cabinets were at greater risk of physical breakage because of the appearance of akaganeite. To date we have not observed the akaganeite phase on freshly excavated iron (Mathias 1999 and Turgoose 1985). Akaganeite appears only after an object has been treated, dried and in storage for a period of at least one year. This observation may be specific to the burial environment from which the archaeological iron was excavated and the storage environment, in terms of both relative humidity and air pollutants (Turgoose 1982b and Jones 1992). As stated above, accelerated deterioration because of corrosive processes, occurs with an increase in relative humidity within the storage environment. Humidity is necessary for this type of atmospheric corrosion. Condensed water forming with an increase in relative humidity on the surface of the metal will provide the electrolyte needed for electrochemical corrosion (Jones 1992). Contaminants near the surface layer, such as chlorides, enhance the effectiveness of the electrolyte (Jones 1992). Thus uncontaminated iron would not corrode as the humidity increased, however, this is not the case for the Ferryland iron (Mathias 1999). The ESCAL/RP will slow the deteriorating effects of the environment by reducing humidity and oxygen until these objects can be re-treated. Therefore, to prevent corrosion from occurring, archaeological iron should be stored in an oxygen free environment with an RH of less than 15%

2.1 Revolutionary Preservation (RP) System

The RP agent is available in two different forms - RP-A, for use with metal artefacts, and RP-K, to be used with non-metal items. The use of RP-A will result in a microenvironment with an RH of less than 10% and an oxygen concentration of below 0.1%. RP-A is available in three sizes - 3A, 5A, and 20A. The numbers correspond to the volume of air each packet can condition - 3 = 300 ml, 5 = 500 ml, 20 = 2000 ml.
The RP-A packets contain mordenite, calcium oxide, polyethylene and activated carbon, along with unsaturated organic compounds, the makeup of which is proprietary information.

The heat-sealing layer of ESCAL film is linear low density polyethylene (LLDPE). In rolls of ESCAL that are pre-sealed on two sides, the LLDPE layers are already oriented to the inside, where they will melt together when heat of an appropriate temperature is applied. In ESCAL film, the plastic must be folded correctly or the heat will not seal the bag. Although heat-sealers are recommended for use with the ESCAL film and RP system, they can be quite expensive. Heat sealing using a tacking iron has also been suggested as a low-cost option to the more expensive heat sealers. As an alternative, the conservation lab at Memorial has used a conventional iron for heat-sealing the ESCAL bags. The strength of the seal created by the iron was tested by pulling on the film to try and separate the newly joined layers. It was impossible to tear the seal by hand, indicating that the iron creates a sufficiently strong seal.

The microenvironment created using ESCAL and the RP agent can last from four to six years assuming: a good seal has been obtained, that the film remains undamaged, and the proper amount of RP agent has been added. After this time, the RH will begin to rise, although the oxygen-free environment can last much longer (Conservation by Design 2003).

To determine how much and how long the RH drop takes in the microenvironment using the RP system, a datalogger was enclosed to chart the decline of the RH. A HOBO LCD Temperature/Relative Humidity datalogger was used, set at a sampling interval of two minutes. The logger has an operating range of 0-95% RH, but a measurement range of only 15-95%. The ambient RH at the time of placement in the enclosure was 42%. In just over two hours, the RH within the package dropped to 15% (lowest range for the logger).

Although the temperature in the enclosure is not directly affected by the RP agent, there was a temperature spike noted on the logger graph. It is possible that the oxygen-scavenging reaction caused by the RP agent is exothermic, resulting in small rise of 1ºC in temperature during the first two hours of enclosure.

2.2 Working with the RP System

The following points illustrate the method used in packaging the artefacts:

- The appropriate size ESCAL film is chosen (either 160 mm or 480 mm wide)
- The ESCAL is cut (with ordinary scissors) to fit the object, making sure to leave enough room for the RP packets and sufficient plastic to seal the enclosure on both ends
- One end of the bag is sealed with the iron set to the ‘nylon’ setting
- The object is protected if needed - delicate objects may be placed in small, hard plastic boxes with microfoam padding, and objects with sharp projections may be padded with microfoam to prevent the possibility of puncturing the bag
- The object is then placed inside the bag, along with its catalogue tag. If the objects are small, more than one may be placed in each enclosure. They can be placed in polyethylene bags within the ESCAL to separate them.
- The appropriate number of RP packets are placed in with object, then the end is sealed with the iron. This is determined by calculating the volume of the bag and subtracting the volume of the object. It is much easier to measure only the volume of the enclosure and disregard the volume of the object - this may result in adding slightly more RP agent than is necessary. This will not harm the object, and the manufacturer has suggested adding 25-50% more RP agent to each enclosure. Through trial and error we have found that for wrought iron one bag of the RP- 5A is needed per 100 gram of weight.
- The artefact’s catalogue number can be recorded on the white strip on the ESCAL film.

Previous studies of the RP system using archaeological metal indicate that there should be no change in the appearance of the objects. Research has been conducted in which excavated iron nails were used as samples to show that objects stored using the RP system do not corrode while in storage, and in fact have a slight decrease in weight, due likely to a loss of moisture (Lampel 2003). Nails stored only in polyethylene bags suffered an average weight gain of 7.4% after three years, due to the formation of corrosion products.

After working with the system, it was possible to determine easier methods of working, and several problems were also discovered. The bag of RP agent contains 25 packets, and these should be exposed to air for only 30 minutes before being resealed in their new enclosures. Because most artefacts are small and use only one packet per enclosure it is most efficient to design a working session where 20 artefacts will be bagged. In this way, the entire bag of RP agent could be used.

Heat sealing the ESCAL film with an iron is a fairly straightforward task, though several problems were encountered. If the object is large a bag formed from the large tube (480 mm in width) of ESCAL is difficult to seal. Because several passes have to be made with the iron to seal the end, it is difficult to seal without incorporating any air channels. Also the corrosion ‘dust’ created by the iron artefacts can actually prevent a complete seal.

When the oxygen is removed from the enclosure, the bag does suck down about 20%. In most cases, this is a visible change, and it indicates that the seal was successful and the correct number of RP packets was enclosed.

2.3 Why is the use of ESCAL/RP system advantageous to archaeologists?

From the perspective of field archaeology the use of the RP/ESCAL system is advantageous for a number of reasons including: its relatively low cost; its ease of use in the field; the accessibility of the artefacts following their enclosure; and the opportunity to stabilize artefacts while alternate conservation strategies are considered. Figure 5 shows stored iron objects in RP/ESCAL bags. These enclosures make access easy as they support the object and allow for close examination of the object while still providing a stable environment free from the contaminants of handling.

Figure 5 Storage of iron in RP/ESCAL bags

The relatively low cost of the RP/ESCAL enclosure system derives, on the one hand, from the low cost of the enclosing materials themselves, and on the other, from savings in terms of labour in a field laboratory. In our experience with the purchase of some $3,000 (Canadian dollars) worth of materials, which may at first glance seem overly expensive, we have managed to enclose more than 200 iron objects of various sizes and still have more than half of the original materials left for additional enclosures. Although other barrier films may be used with the RP agent, ESCAL is recommended for long-term storage as it has very low rates of migration for both water vapour and oxygen - it is 2,000 times more effective as a barrier than polypropylene bags, and it's transparent, so that objects can be viewed without opening the package (MGC 2003). A carefully planned strategy for the initial processing of the artefacts themselves (for example, a light cleaning followed by the documentation of the object and its condition post-excavation) combined with the careful and judicious use of the enclosing materials, makes a little go a long way. The labour savings in a field lab derive from the relatively "light" handling an artefact receives prior to its being enclosed in a relatively sturdy environmentally-appropriate enclosure. The light handling of the objects not only protects them, but reduces the number of laboratory staff required to process the objects themselves.

The ease with which enclosures can be created in the field is likewise advantageous in terms of time, effort, and materials. In our experience, it is more efficient to enclose a number of objects at once where attention can be focussed specifically on cutting ESCAL enclosing tubes to size, estimating the number of RP sachets to be included, placing the artefacts within the enclosure and then heat-sealing it. It doesn't take long to get the feel for estimating the size of tube to be cut and the number of sachets to be added. Once the iron is up to heat, sealing the enclosures is quick. A team of two can easily enclose some 20 objects an hour. Laboratory requirements for creating the enclosures are meagre: a clean work area; a flat surface upon which to iron the ends of the enclosures; and an electrical outlet for the iron.

Once enclosed in the RP/ESCAL system the artifacts can be easily visually examined not only for purposes of additional identification, but also to monitor their condition. For the purposes of transportation and storage, the semi-rigid nature of the enclosure allows the objects to be packed more readily, albeit carefully, for travel, while in storage the enclosure provides ongoing environmental protection for the object. If an artefact requires closer examination or additional stabilization, it is as easy as cutting the end of the ESCAL tube and removing the object. In this sense, the RP/ESCAL system is readily reversible, unlike most other chemical treatment strategies. Following examination or additional stabilization, a new enclosure can be made and the artefact returned to a stable storage environment.

Perhaps the most important advantage of the RP/ESCAL system for field archaeologists is that it provides us the opportunity to consider alternate stabilization strategies -in a real sense it buys us time. It is abundantly clear that a variety of conservation strategies have been undertaken in various circumstances and that some have been more successful than others. Depending on the degree and nature of the corrosion experienced by ferrous objects, different conservation strategies are appropriate. This system allows archaeologist to take the necessary first steps, in the field, to stabilize objects until the best long-term strategy is selected. Because the objects themselves have not been otherwise "treated", this system reduces the likelihood that inappropriate and irreversible treatments will be performed by archeologists who lack the specific knowledge that is the realm of the conservator.

3. Methods

A small research project was begun in December 2003 in an effort to determine the efficiency of the RP/ESCAL system in reducing the re-corrosion of iron nails recovered from the Ferryland archaeology site. The total sample included 150 nails, half of which had received 2.5 years of treatment in sodium hydroxide to remove chlorides, the other half had received no post-excavation conservation treatment. Each group of 75 nails was subdivided into three groups of 25 nails each. These three groups of treated and untreated nails were then stored differently. The first group of 50 nails (25 treated and 25 untreated) was stored in individual RP/ESCAL enclosures, the second group of 50 nails (25 treated and 25 untreated) in individual polypropylene bags, and the third group of 50 nails (25 treated and 25 untreated) stored without enclosure. The total sample of 150 nails has been stored in an ambient environment. Our intention is to visually monitor the condition of the three groups three times each year for the next five years.

Additionally it was decided to select a group of objects(not nails) from four areas of excavation, and make observations about the RP/ESCAL packaging technique over the course of the experiment. A total of 55 objects were sealed in the RP/ESCAL system, some with microfoam for support and protection against film puncture. Once bagged the initial weight was recorded. The quality of the bag seal was visually assessed as good, fair or poor. The initial bagging occurred March, 2004. Objects were monitored in April and June of 2004.

4. Results

The first monitoring interval for the nail experiment has revealed the following. All nails treated with sodium hydroxide appear stable regardless of method of enclosure. Some untreated nails show signs of continued deterioration and this varies by method of enclosure. After being bagged for 5 months:

12% of those nails in RP/ESCAL enclosures are visibly cracking;
60% of those nails in polypropylene bags are visibly cracking; and
56% of those nails with no enclosure are visibly cracking.

The nails were monitored again in June. Though the time interval between examinations, in this case, was short, we were entering the first period of increased humidity and felt we may see changes. The treated nails remained stable. However within the untreated nail group an additional nail in each of the polypropylene and RP/ESCAL groups appeared cracked. The results are presented in Table 5. The second group of objects being monitored showed that for three samples the protective microfoam had moved off the intended area of protection. This will probably result in bag damage. Overall, however, the seals were good.

Table 5 Total Nails Showing Signs of Deterioration

	Untreated Nails			Treated Nails		
Date	no enclosure	polypropylene	RP/ESCAL	no enclosure	polypropylene	RP/ESCAL
Dec. 15/03	0	0	0	0	0	0
May 20/04	14	15	3	0	0	0
June 11/04	14	16	4	0	0	0

*Samples for untreated nails were excavated in 2003

5. Discussion

It is too early to know yet how effective the bagging of corroding iron in the RP/ESCAL system will be but at this point it does look promising. Experiments, to date, do reveal that it is important to have a good seal and that for archaeological objects with sharp edges and irregular three dimensional shapes maintaining the seal will be the greatest challenge. I know that over the past 24 years that I have been involved in the preservation of our heritage that there has been a move away from bench conservation treatment to preventive conservation. Institutions can no longer afford a conservator who may spend one year on one object. To justify the conservation position they must have one conservator stabilizing hundreds or thousands of objects per year. This preservation system, if it proves successful, will help archaeological conservators meet their goal of stabilizing thousands of objects. However, I must emphasize that archaeological materials will require some form of chemical stabilization prior to storage and the use of the RP/ESCAL system. The ESCAL packaging system will, however, continue to protect these fragile objects once removed from chemical treatment and make them easily accessible to researchers.

Additionally the RP/ESCAL system can be used for fragile artefacts being excavated and as an emergency intervention. In the former case, objects excavated from a wet saline environment can be bagged and held in a stable state until aqueous treatment for chloride removal can begin. The Ferryland cross made of iron, brass and gold, provides an example for the latter. This 17th century artifact began re-corroding while on exhibit in 2003. Figures 6 and 7 show the extent of damage.

Figure 6 Ferryland iron cross with physical signs of damage

One of the orbs cracked off as a result of this damage. Figure 7 shows the cross-section image of the orb. Note that the corrosion has progressed from the metal surface inward to the core. This object is currently bagged in RP-5A/ESCAL awaiting further treatment.

Figure 7 Cross-section view of Ferryland cross orb

6. Conclusions

Collections storage issues are becoming more challenging for institutions worldwide. Within academic units, issues such as budget cuts and increasing numbers of students are forcing administrators to carefully monitor space usage. Archaeology departments with on-going research projects will require significant space for collections storage. Because the RP-5A/ESCAL system provides a constantly low RH and oxygen free environment it may be ideally suited for the metal artefacts in these collections. It is a relatively low cost solution compared to air-conditioning the larger collections storage space. Additionally these enclosures provide support to archaeological objects which may be moved many times in their post-excavation period.

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Suppliers

The RP Agent and Escal Barrier Film are manufactured by
Mitsubishi Gas Chemical Company
5-2, Marunouchi 2-chome, Chiyoda-ku, Tokyo 100-8324, Japan
www.mgc-a.com

The RP System is supplied to Canada and the USA by
Keepsafe Systems
570 King Street West
Suite 400
Toronto, Ontario
M5V 1M3
www.keepsafe.ca

and in the UK by
Conservation by Design Limited
Timecare Works, 5 Singer Way
Woburn Rd. Ind. Estate
Kempston, Bedford
MK42 7AW
www.conservation-by-design.co.uk

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Innovative conservation approaches for monitoring and protecting ancient and historic metals collections from the Mediterranean Basin

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Abstract

The paper outlines a three-year European funded project, acronym PROMET, under the auspices of Sixth Framework Programme, priority INCO. This will start in October 2004, and sets out to establish and promote a conservation strategy designed for the Mediterranean region by developing an approach to monitor and to protect metal artefact collections using state of the art portable analytical techniques and new corrosion inhibitors and/or coatings safe and effective to use. There are 23 partners involved from 13 different countries in Europe and in the Mediterranean Basin, with a total budget of around 4 million Euros.

Keywords: metal artefacts, Mediterranean Basin, Laser-induced breakdown spectroscopy, micro X-ray Fluorescence, corrosion inhibitors, coatings.

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1. Introduction

The European Commission under the Sixth Framework programme supports research in several priorities, one of which is specific measures in support of INCO International Cooperation (INCO,2003), and includes measures related to research in the protection and conservation of Cultural Heritage. Under these auspices, two projects related to the preservation of archaeological and historic metals collections were submitted in May 2003, acronyms PROMET and APHRODITE. Both projects passed the evaluation phase, and the experts recommended merging into one project. The project co-ordinators of PROMET and APHRODITE, Vasilike Argyropoulos and Emma Angelini respectively spent considerable time in merger negotiations, and were successful in unifying both projects under common objectives and deliverables.

In particular, the problems and needs of metal artefacts made of precious metal alloys (including gilded materials), iron and copper alloys from the Mediterranean Basin will be identified. New prototype portable techniques, Laser-induced breakdown spectroscopy and micro X-ray Fluorescence will be developed as complementary analytical tools for metals characterization. Also commonly applied analytical techniques will be used for quickly surveying large metals collections. These analytical tools together with statistical methods will be applied to survey collections in the different countries in the Mediterranean Basin specifically Egypt, Greece, Italy, Jordan, Malta, Morocco, Spain, Syrian Arab Republic, Tunisia, and Turkey, and pilot studies will be carried out to highlight the problems and needs of the collections. In parallel, safe corrosion inhibitors, derived from vegetable oils, mature tobacco, tannins from wood, Physical vapour deposition (PVD) and Plasma enhanced chemical vapour deposition (PECVD) barrier films, synthetic microcrystalline or polyethylene-based waxes will be developed and tested on artificially and naturally aged metal coupons. Finally, the most effective products that meet conservation standards will be tested on a selection of artefacts specifically for the environmental conditions of the Mediterranean Basin.

The paper outlines these objectives, activities, and expected deliverables of one of the highest funded projects under the INCO measures for Cultural Heritage, and highlights the importance of this research related to metals in the conservation field.

2. Main Objectives

The project aims to establish and to promote a conservation strategy to protect Mediterranean archaeological or historical metals collections exhibited or stored in buildings without the benefit of a controlled environment. The overall scientific and technological objectives of the project are categorized under the two main actions:

Monitoring

- To optimize existing portable scientific instruments and documentation methodologies for the characterization and classification of large numbers of metal artefacts.
- To develop new non-destructive or on-line micro-destructive analytical techniques for analysing in-*situ* the compositional variations of metal artefacts.
- To identify the conservation problems and needs of metals collections situated in the Mediterranean Basin.
- To develop a codified approach in establishing procedures for conservation and restoration of metallic artefacts.

Protecting

- To determine the long-term effectiveness of past treatments (coatings and/or corrosion inhibitors) used to preserve metals collections in the Mediterranean Basin in terms of their success in protecting the metal substrate, inertness and reversibility.
- To determine**,** by means of a systematic scientific approach**,** the most compatible, reversible, and environmentally-friendly corrosion inhibitors and/or coatings to protect objects made of precious metals, copper and iron alloys.

The main conservation problems that metal artefact collections face in the Mediterranean Basin may be attributed to the high relative humidity and to the presence of aggressive agents in the atmosphere. Conservation strategies have to be tailored to take into account the different environmental conditions and the degradation causes occurring in the countries of the Mediterranean Basin. To decrease the rate of the degradation phenomena, it is not possible to protect the metal collections by placing them in strict environmentally controlled areas or by treating them on a regular basis, due to the large number of objects and the heavily cost of repeated maintenance. Furthermore, many of these artefacts are contaminated with soluble salts, such as chlorides, and can only be saved by proper documentation/analyses, stabilization treatment, and protecting them with an appropriate corrosion inhibitor and/or coating. Our project aims to establish and promote a conservation strategy designed for the Mediterranean region by developing portable monitoring systems and protection methods, including the identification of degradation phenomena, for collections of precious metals, iron and copper alloys.

Portable techniques, as Laser-induced breakdown spectroscopy (LIBS) and micro X-ray Fluorescence (μ-XRF) will be optimized and proposed as analytical tools for characterizing metal artefacts and for identifying degradation phenomena. The technological development of non-destructive techniques for the characterization of metal artefacts of artistic and historical interest is of outstanding importance due to the difficulties in obtaining permissions for removing bulk material for destructive analyses. These advanced analytical methods will be applied to survey collections of archaeological or historical metal objects in different countries in the Mediterranean region, such as Egypt, Greece, Italy, Jordan, Malta, Morocco, Spain, Syrian Arab Republic, Tunisia, and Turkey**,** and to identify the conservation problems.

In parallel, safe corrosion inhibitors and chemical agents as well as Physical vapour deposition (PVD) and Plasma enhanced chemical vapour deposition (PECVD) barrier films and synthetic microcrystalline or polyethylene-based waxes will be either developed and/or validated for use on artificially and naturally aged metal reference alloys.

A maintenance policy for metals collections will be highlighted through dissemination-related activities, such as workshops, conference, an English-Arab web-site and the publication of a book.

3. The Consortium

The objectives of the proposed project could only be tackled by uniting the efforts of a Consortium made up of representative group of scientists, conservators, and archaeologists from across Europe and the Mediterranean Basin. Table 1 summarizes the participants involved in the project, which come from 13 different countries of Europe and of the Mediterranean Basin. The key element of this Consortium is the collaboration in innovative research between European and South Mediterranean Institutions. For example, the Institute of Electronic Structure & Laser (IESL), Foundation for Research & Technology, Heraklion, Greece and the National Institute of Laser Enhanced Sciences (NILES), Cairo University, Egypt will cooperate to produce a prototype portable LIBS for analyzing metal objects. Moreover, European Institutions as Malta Centre for Restoration, SVUOM Ltd, Czech Republic, Laboratory of Research on Historic Monuments, France, Politecnico di Torino, Dipartimento di Scienza dei Materiali ed Ingegneria Chimica, Italy, will cooperate with southern Mediterranean institutions as Laboratoire des Matériaux Minéraux et Composites, Université de Boumerdes, Algeria, and IBN TOFAIL University-Faculty of Science, Department of Chemistry, Morocco to develop new corrosion inhibitors and barrier films. In the consortium end-users, museums and conservation training institutions are also represented and will participate in the design and testing of the analytical techniques and restoration products.

Table 1. Participants involved in the project.

Role*	Partic. No.	Participant name	Partic. short name	Country	Participation in Workpackages (WP)
CO	1	Technological Educational Institution of Athens	TEI	Greece	WPL: WP1 and 4, WP 2, 3
CR	2	Foundation for Research & Technology- Hellas	FORTH-IESL	Greece	WP 1,2,3,4
WPL	3	Malta Centre for Restoration	MCR	Malta	WPL: WP3 WP 1,2,4
CR	4	Department of Metallurgy and Material Engineering, University of Malta	DMME	Malta	WP3
CR	5	Laboratoire des Matériaux Minéraux et Composites. Université de Boumerdes	LMMC	Algeria	WP1,3,4
CR	6	SVUOM Ltd	SVUOM	Czech Republic	WP1,3,4
CR	7	National Institute of Laser Enhanced Science	NILES	Egypt	WP1,2,3,4
CR	8	The Laboratory of Research on Historic Monuments	LRMH	France	WP1,3,4
CR	9	Laboratory for Material Analysis Institute of Nuclear Physics. NCSR Demokritos	Demokritos	Greece	WP1,2,3,4
CR	10	Institute of Archaeology and Anthropology	IAA	Jordan	WP1,2,3,4
CR	11	Royal Scientific Society	RSS	Jordan	WP1,2,3,4
WPL	12	Politecnico di Torino, Dipartimento di Scienza dei Materiali ed Ingegneria Chimica	POLITO-SMIC	Italy	WPL: WP2 WP 1,3,4
CR	13	Consiglio Nazionale delle Ricerche, Istituto per lo Studio dei Materiali Nanostrutturati	CNR-ISMN	Italy	WP1,2,3,4
CR	14	National Technical University of Athens, School of Chemical Engineering	NTUA	Greece	WP1,2,3,4
CR	15	Consejo Superior de Investigationes Cientificas, Centro National des Investigaciones Metalurgicas	CSIC-CENIM	Spain	WP1,2,3,4
CR	16	National Research Center, Physical Chemistry Department	NRC-EC	Egypt	WP1,2,3,4
CR	17	Egyptian Museum, Cairo	EM-MC	Egypt	WP1,2,3,4
CR	18	Jordan University of Science and Technology, Faculty of Computer and Information Technology	JUST	Jordan	WP1,2,3,4
CR	19	Institut*e* National du Patrimoine, Conservation Laboratory	INP-CL	Tunisia	WP1,2,3,4
CR	20	IBN TOFAIL University- Faculty of Science, Department of Chemistry	IBN-DC	Morocco	WP1,2,3,4
CR	21	EGE University, Department of Protohistory and Near Eastern Archaeology	EGE-PNEA	Turkey	WP1,2,3,4
CR	22	Ministry of Culture- Directorate General of Antiquities and Museums, Chemistry Laboratory	MC-DAM	Syrian Arab Republic	WP1,2,3,4
CR	23	University of Aleppo, Department of Materials Engineering	ALP-ME	Syrian Arab Republic	WP1,2,3,4

***CO** = Coordinator, **WPL**=Workpackage leader, **CR** = Contractor
WP1: Project Management, **WP2**: Documentation and monitoring of metals collections
WP3: Development of safe coatings and corrosion inhibitors for the protection of metals
WP4: Preventive Strategies for saving metals collections

4. The Impact of the Project

The significance of this project is not only the size of the research group, amount of funds, deliverables, but also the extent of the experimental studies to be carried out for developing tailored strategies for the conservation of metal artefacts collections. A noticeable amount of funds in Europe is mainly devoted to 'hot' topics such as stone/ marble, mosaics, or wall-paintings degradation and conservation. Thus, the conservation knowledge for metal artefacts is underdeveloped in the Mediterranean region, including southern Europe. As a result, conservators from this region hesitate or delay to properly care for these types of artefacts, because of a supposed lack of knowledge and know-how to take measures to prevent against the artefacts unwanted damages. This is understandable, since the conservation problems and needs for metals collections are complex and can vary, e.g., the original surface of a metal artefact varies greatly depending on the technology of the object, the burial conditions, and its care after excavation. Furthermore, most archaeologists in the region are more interested in the information that ancient coins can provide, and care for these metal objects first, leaving in most cases other metal finds stored away and uncared for many decades.

The pilot studies for surveying metals collections in the Mediterranean Basin will be adopted as a strategy as well as a cost model for implementing maintenance programs for similar collections owned by museums, or historical sites in the Mediterranean region. The portable techniques, LIBS, and micro-XRF will be optimized within the project for monitoring large collections in a reproducible, reliable, and non-destructive way in order to implement maintenance programs for museums and historical sites.

The development and optimization of the most effective and environmentally-friendly corrosion inhibitor(s) and/or coating(s) to protect metals collections in the Mediterranean region will promote viable solutions when conservators cannot house their collections in strict environmentally controlled areas or retreat objects on a regular basis. The Consortium will consider the different environmental effects on the metal artefacts collections specific to the Mediterranean region, such as less rain but higher humidity containing sea salt than in other European countries; the new corrosion inhibitors and/or coatings studied for the proposed project will be tailored for use against these environmental conditions. These coatings and/or corrosion inhibitors, which can withstand the effects of soluble salts and high relative humidity will provide an improvement to the conservation field, since these are the most detrimental causes for corrosion of metal artefacts. A test site will be set-up also in the Czech Republic to compare the results with the ones obtained in the test sites in the Mediterranean Basin.

In summary, developing and testing environmentally friendly corrosion inhibitors and coatings will produce a noticeable advancement for the international conservation community, because it provides alternative choices to already existing practices of using toxic corrosion inhibitors and/or coatings.

5. Project Design

The workpackages (WP) involved in the project design, and the participation of each partners in the associated WP, along with the project leader for each WP are also given in Table 1. The approach taken in the project is described below:

5.1 The approach for the study of metallic artefacts collections

Precious alloys artefacts: The activities will be focused on the systematic identification of the degradation causes of Ag, Ag-Cu, Au, Au-Ag-Cu based artefacts, including Ag and Au coated or joint metal objects from pre-Roman to Medieval periods, selected on the basis of cultural, artistic or economical consideration and also taking into account the nature of the archaeological context of their finding. Advanced laboratory analytical techniques (XPS, FEG-SEM-EDS, XRD, GDOES, XRF, DTA-TG, EIS and OM and also in situ XRD, XRF and electrochemical portable instruments) will be used for the microchemical and microstructural characterisation of the corrosion products and of the bulk nature of the artefacts and for evaluating the protectiveness of restoration materials.

Copper and iron based artefacts: Three types of collections made of copper and/or iron alloys will be studied for the project:
In Greece, a collection of about 3000 classical archaeological artefacts made up of copper and iron alloys (not including coins) from the archaeological site of Messene near Kalamata in Greece will be studied. In Jordan, a collection of ancient artefacts made of copper alloys will be studied. Finally in Malta, a collection of steel metal armours from the Palace Armoury in Valletta will be studied.

A conservation survey will be conducted for each of these collections. The approach designed for the project will be used to select a representative sample for further non-destructive analyses. This approach will begin with the design and distribution of a questionnaire to all partners for the classification of the surveying collection. This classification will be based on the chemical and microstructural characteristics of the artefacts and on their conservation conditions. The aim of this step is to produce an overview of the identified collection and to select a representative sample of artefacts for further analyses. The statistical analysis will allow a classification of the artefacts, same frequencies (based on the characteristics that have been collected from the questionnaire), probabilities, and other measures of summary statistics. If our data provides information about different methods of conservation (for example occurrence, effectiveness of the method) it will be possible for a statistical comparison of these methods using statistical “tools”, as “Factor Analysis” or “Regressions” or “ANOVA tables”. This approach will provide for systematic determination of the characteristics that make up a metals collection in order to determine the ‘actual’ problems and needs.

5.2 The Technological Developments

5.2.1 The Techniques

A major technological advancement for this project will be the development of LIBS (by FORTH-IESL and NILES groups) and µ-XRF (by Demokritos group) into prototype transportable analytical techniques and thus the improvement of the quality and the speed of the information taken when these techniques are applied to metals collections *in-situ.* The potential use of Mass Spectroscopy techniques (e.g. Time Of Flight- Mass Spectroscopy, **TOF-MS**) in combination with LIBS analysis will also be considered in order to enhance the information obtained. The need for such development is due to the existing limitations of portable analytical techniques in determining compositional variations for metal artefacts with different mineralised layers that make up the original surface, and the different shapes or intricate surface details that define the artefact. Thus, our research will have an impact in this field as to the analytical information that can be obtained from metal artefacts in-*situ* by upgrading the following criteria:

- *Fast*, so that a large number of artefacts may be analysed or a single artifact investigated at various locations.
- *Versatile,* allowing to obtain average compositional information but also permitting local analysis of small microscopic areas
- *Sensitive and multi-elemental on-line analysis,* making possible the use of trace-element fingerprints.

LIBS and µ-XRF will be developed as complementary analytical tools. The former provides on-line in-depth analysis of the various layers of the studied surface by laser ablation of a minute amount of material (1-10µm in depth and ~100µm in diameter). On the other hand, µ-XRF offers non-destructively compositional information of the superficial surface layer. The combination of these techniques will allow an integrated analytical study of both the outer surface as well as the stratigraphy of the corrosion layers, with minimum material loss. This innovation will improve the in-*situ* analytical characterisation of metal collections.

5.2.2 The Corrosion Inhibitors and Coatings

In parallel with artefact analyses, new environmentally friendly corrosion inhibitors and barrier coatings will be tested for use in protecting metals collections in the Mediterranean Basin. These products exist on the market, but were developed for protection in industrial environments, and are usually tested and applied on non-corroded metal surfaces for short-term protection (less than three years). By contrast, archaeological or historical metal artefacts are generally covered by corrosion layers of different composition and thickness, and due to the lack of funding in the conservation field, the restoration treatments must be able to protect the artefacts as long as possible (5-10 years). Few data are available on the protective effectiveness of these products on corroded metals over the long-term in the Mediterranean region.

The following types of corrosion inhibitors will be studied in this project:

- For copper and iron alloys: salts of linear aliphatic organic acids, which are derived from vegetable oils such as olive, colza, sunflower oils, products extracted from mature tobacco, and new products found from our market survey.
- For iron alloys: products extracted from wood as tannins.

- For silver alloys: nitrogen-based and sulphur–based innovative inhibitors.

Many of these patented corrosion inhibitors, are widely employed for industrial purposes. For example, aliphatic organic acids are applied with zinc coatings in the car industry (e.g., ATOFINA, ARCELOR, TUBEUROP). Tobacco extracts as inhibitors of metallic corrosion have already been patented (INHIBITEX). Tannins are commonly used in industry for tannin-based rust converters.

However, in the conservation field, only tannin-based products are commonly used for iron-based artefacts. Aliphatic organic acids or extracts from mature tobacco have not been tested for protecting copper or iron-based artefacts. In this project, short-term and long-term testing of the above-mentioned corrosion inhibitors both on naturally and artificially aged copper, iron, and silver alloy coupons and real artefacts will be performed. A major advance in the conservation field will be the replacement of toxic inhibitors currently used by conservators, which often need special care in application or for disposal, (e.g., benzotriazole, ethylenediamine).

The following types of coatings will be studied in this project:

- PVD coatings.
- Organosilicon coatings by PECVD or by sol-gel technique.
- Synthetic microcrystalline or polyethylene based waxes; and
- New products found from our market survey.

The thin film technology concerning a large variety of non-equilibrium processes for leading-edge surface modifications of materials is gaining popularity, because it allows the design of substrate by means of the deposition or modification of thin films in an extremely versatile and environmentally friendly way, i.e. by employing low pressure plasmas, also called cold plasmas or glow discharges.

Environmental considerations are becoming more and more important as a consequence of the Kyoto Earth Summit. World-wide initiatives such as EU IPPC Directive (Integrated Pollution Prevention and Control – 96/61/CE), has identified targets for different industrial sectors, including corrosion protection, the development of ‘best available techniques’ (BAT).

A wide variety of void-free, high-adherence thin films (100-10.000 angstrom) deposited by PECVD are one of the most important technological results of thin film technology.

Two other important aspects of the research are the application of technology for the modification of the very top surface layers of solid materials by grafting chemical functionalities, so called Plasma Treatments (PT), and the ablation of materials by reactions with active species generated in the plasma to form volatile products, so called ‘Plasma Etching’ (PE).

Among the various applications, PECVD deposition of silicon containing organic compounds (i.e. organosilicons) appears particularly promising for corrosion protection of metallic materials. Since, PECVD a highly versatile technique in that the production of a variety of coatings with a wide range of properties simply by means of a proper selection of the experimental conditions is easily achieved. For example, the SiO_2-like coatings are characterized by high chemical and thermal stability, good dielectric properties, low gas permeability, etc.

The experimental apparatus employed for PECVD allows various operations to be carried out in the same reactor, before the deposition step, including the possibility of removing surface contaminants or performing surface modifications, like oxidation, reduction, etc. The deposition of complex multi-layers of different chemical composition and properties may also be carried out. Recent literature shows more and more studies devoted to this PECVD using organosilicon precursors for various substrates, mainly steels, light alloys and to a lesser extent artistic alloys and this also appears particularly promising for corrosion protection of metallic artefacts.

Although the PVD technique is often considered to be irreversible, the challenge of our project is to apply it to metal plates covered with corrosion layers and for which a compromise has to be found between a good protection and lower adherence performance. The technique has been in existence for 10 years, with a multitude of applications for industry. The main goal of our research is to adapt the technique for the production of a coating with very low permeability to oxygen and water, which is easily deposited onto a metal surface at low temperatures and which could be removed to some extent. Thus, a low melting point ceramic would be chosen for both short-term and long-term testing to provide a dense but 'soft' coating to the metal surface. The coating process will be plasma assisted (magnetron sputtering) in order to further lower the deposition temperature. Initial short-term tests, such as mechanical and electrochemical assessment will be used to determine the optimal coating conditions. Then long-term testing of this type of coating will be required on aged coupons, and finally real artefacts, to determine its overall effectiveness to the conservation field.

Many types or combinations of synthetic microcrystalline or polyethylene waxes are used for the protection of both outdoor monuments and indoor metal artefacts, although not specific for use in the Mediterranean Basin. Few data may be found on the effectiveness of these coatings on artefacts situated in environments that usually have higher temperatures, and/or humidity containing sea salt than in northern Europe, and North America. This research will provide tailored new coatings for application to metal artefacts in the Mediterranean Basin.

A three-year project is needed due to the requirements for field tests of metal coupons with corrosion inhibitors and coatings based on international standards (e.g., EN ISO 8565 *General requirements for field tests),* and can be justified by summarising the design as follows:

1st Year:
-Survey of treated collections in the Mediterranean Basin
-Selection of metal coupons for testing based on the characterization of real artefacts
-Preparation of test metal coupons by accelerated ageing
-Market survey of corrosion inhibitors and coatings commonly employed in industry and selection of protective coatings and corrosion inhibitors for study
-Development of innovative coatings and corrosion inhibitors
-Development methods of application of coatings and corrosion inhibitors for the pre-weathered coupons (by accelerated ageing)
-Short-term testing of corrosion inhibitors and coatings
-Preparation of test coupons by natural ageing at test sites in the Mediterranean Basin.

2nd, 3rd Years:
-Removal schedule of naturally-aged test coupons after 3, 6 and 12 months of exposure at selected test sites in the Mediterranean Basin
-Application of coatings and corrosion inhibitors to pre-weathered coupons and scientific analysis prior to exposure in order to determine their adhesion properties
-Exposure of coupons with coatings and corrosion inhibitors for natural weathering at selected test sites in the Mediterranean Basin
-Monitoring of coupons during the 12 months exposure
-Scientific analyses of coupons with corrosion inhibitors or coatings after removal from natural weathering
-Testing of highly rated corrosion inhibitors and coatings (determined after short-term testing and results from batch 1 of outdoor testing) on a selection of real artefacts with a 6-month exposure
-Ratings for all the coatings and corrosion inhibitors.

6. Expected results and outcomes

The project will deliver two prototype portable equipments: LIBS and µ-XRF to the market, which will be able to carry out non-destructive or micro-destructive analyses of ancient metal artefacts.
The surveys conducted will provide an accurate description of the different degradation phenomena occurring on metallic artefacts in the Mediterranean basin.
The project will formulate new products, i.e., corrosion inhibitors and barrier coatings for the protection of metal artefacts. On the basis of the project results, it will be possible to provide effective tools for the protection of culture heritage by offering reliable solutions that are easily used and environmentally friendly. Furthermore, this project will investigate the legislative policy for conservation of metallic artefacts collections in each participating country.

In addition, PhD theses, scientific publications, conservation guidelines, and new environmentally-friendly conservation products for metal artefacts will be the expected outcomes of this project.

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Corrosion monitoring and the environmental impact of decommissioned naval vessels as artificial reefs

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Abstract

The former Australian Naval vessels, HMAS Swan and HMAS Perth were scuttled as artificial reefs off the Western Australian coast in 1997 and 2001, respectively. In addition, the former HMAS Hobart was sunk in Gulf St Vincent, South Australia in 2002. During the preparation of the ships prior to sinking, significant quantities of metals, such as copper, copper alloys, aluminium, lead and steel, petroleum hydrocarbons and other potential pollutants were removed. Since it is possible that corrosion products and residual hydrocarbons may impact on the local marine environment, corrosion and sediment monitoring programmes were implemented on each of the three vessels. The concentrations of heavy metals, total petroleum hydrocarbons and butyl tins in the surrounding sediments were periodically monitored. The results demonstrate synergistic interactions between modern shipwreck materials, sediments, biota and the marine environment and the long-term stability of the vessels.

Keywords: artificial reef, marine environment, naval vessel, corrosion, environmental impact, sediment, butyl tin compounds

1. Introduction

Artificial reefs are not a new concept. For centuries Japanese fishermen have attempted to increase the fishing productivity of their local waters by dumping rocks into the sea (Russel, 1975). By 1970 artificial reefs had been placed at more than 3500 sites around Japan. During the 1960's and 1970's over 100 artificial reefs had been constructed in the coastal waters of the USA and many other countries including Australia. In the 1970's, several tyre reefs were constructed in Gulf St Vincent and Spencer Gulf, SA and derelict ships and barges were sunk in the Pacific Ocean off the coast of Sydney, NSW. In the early 1970's artificial reefs were established in the lagoon at One Tree Island Reef in the Capricorn Group of the southern Great Barrier Reef. Similarly, three vessels were scuttled and three artificial tyre reefs were established off the Western Australian (WA) coast in an attempt to enhance recreational fishing and diving (Morrison, 2003a). The colonisation and/or corrosion of these artificial reefs were not monitored rigorously and there is little, if any data published for comparative studies.

The scuttling of decommissioned Royal Australian Navy (RAN) vessels as artificial reefs, the *Swan* in 1997, the *Perth* in 2001 and the *Hobart* in 2002, has provided the opportunity to study the environmental impact of these enormous contemporary ships on the local marine environment and obtain biological, physico-chemical and corrosion data from the time of 'wrecking'. The results provide important information on the synergistic interactions between modern shipwreck materials, sediments, biota and the marine environment and the long-term stability of the vessels. This knowledge is becoming more important as it is apparent that more of these decommissioned naval vessels and confiscated illegal fishing boats will be sunk as artificial reefs in the near future. Perhaps more importantly, the information can be used to better understand the deterioration of historic shipwreck sites and ultimately assist in the development of appropriate *in-situ* management strategies for underwater cultural heritage sites.

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1.1 The Vessels

The *Swan* (DE50) was an Australian built River class destroyer escort, laid down in the Naval Dockyard, Williamstown, Victoria in 1965 and first commissioned in 1970. It was 113m in length and 24m tall from keel to the tower, with a beam of 12.5m and a 5.3m draught. The *Perth* (DDG38) and the *Hobart* (DDG39) were American built Charles F. Adams class guided-missile destroyers, laid down in 1962 by the Defoe Shipbuilding Co., Bay City, Michigan, USA and commissioned in 1965. They were approximately 134m in length and 38m tall from keel to tower, with a beam of 14.2m and a draught of 6.1m (Chant, 1984; Gillet, 1986, 1988; Gillet & Graham, 1977; Odgers, 1989). The vessels' hulls were primarily mild steel plate and possibly small quantities of a carbon-manganese steel. The superstructure was aluminium alloy, probably 5083 (4.5% magnesium) primarily used for welded plate structures but thin material, such as furniture, ductwork, panel linings, awnings and general sheet metal work could have been 5052 (2.2% magnesium). In the late 1980's and 1990's the RAN had been using organotin self-polishing paint so the paint system below the waterline on the vessels would be a vinyl anti-corrosive plus antifouling International Intersmooth Self Polishing Co-polymer, which contains tributyl tin and cuprous oxide. The *Swan* was last painted with the anti-foul in 1994. The original paint above the waterline was probably zinc chromate primer with alkyd enamel undercoat and topcoat. Some or all of this may have been replaced in the 1980s and 1990s with zinc rich epoxy primer, epoxy intermediate coats and alkyd topcoat.

All hydrocarbons, harzardous material and liquids, debris and as far as was practicable, all metals of environmental concern were removed prior to scuttling in accordance with the Environmental Management Plans (EMPs). This was undertaken to minimise the environmental impact as a result of heavy metal and petroleum hydrocarbon contamination. During the preparation process, a number of measuring points were attached to predetermined positions on the hull and superstructure of the vessels to facilitate the corrosion monitoring programmes. After the preparations were completed and the vessels had passed rigorous inspections by Environment Australia, the *Swan* was scuttled on 14 December 1997 in Geographe Bay, Dunsborough, Western Australia, the *Perth* on 24 November 2001 in King George Sound, Albany, Western Australia and the *Hobart* was scuttled in Yankalilla Bay, Gulf St Vincent, South Australia on 5 November 2002. Post scuttling monitoring of the wrecks and surrounding sediments is required to provide information relating to the long-term stability of the vessels and establish the impact they have on the local marine environment. The monitoring regimes for each vessel varied however, they include a combination of sediment sampling for detection of heavy metals, total petroleum hydrocarbons and butyl tin, ecotoxicological assessments, recording the rate of colonization by fishes and encrusting marine life and corrosion surveys. The biological and sediment surveys were a requirement of the EMPs as prescribed by the Commonwealth or State environmental departments. However, the corrosion surveys were a proactive idea of the authors.

2. Experimental

2.1 Monitoring Programmes

The monitoring programme for the *Swan* required biological and sediment surveys in accordance with the Sea Dumping Act (1981) (Environment Australia, 1984; Morrison, 2003a). A baseline study of the fish community and the encrusting biota of the proposed wreck site and reference site was undertaken prior to sinking. The wreck was then monitored one month after scuttling, three times a year for the first two years and then annually for the next three years. The detailed results of these surveys will be reported separately. The sediment at the proposed wreck site and the selected reference site was analysed for a suite of heavy metals [aluminium (Al), iron (Fe), cadmium (Cd), chromium (Cr), copper (Cu), lead (Pb) and zinc (Zn)] and total petroleum hydrocarbons (TPH) prior to scuttling and repeated at 5 and 12 months after sinking. Baseline corrosion data was collected a few hours after scuttling, then again 12 months and 4 years after sinking.

The sediment sampling programme for the *Perth* involved baseline monitoring of the proposed wreck site and the selected reference sites followed by post scuttling monitoring after 6 and 12 months in accordance with the EMP governed by the Western Australian Environmental Protection Act under the supervision of the Department of Environmental Protection (DEP) (Morrison, 2003b). The sediment was analysed for nickel (Ni), tin (Sn) and mercury (Hg) in addition to the aforementioned heavy metals, TPH, total organic carbon (TOC) and tributyltin (TBT). Ecotoxicological assessment of the sediment during the baseline sediment survey was also performed in order to separate the ecological effects of the vessel from any existing contaminants. However, because the levels of TBT and metals in the sediments did not exceed ANZECC/ARMCANZ (2000) guidelines the toxicity testing was not carried out after the initial baseline assessment and hence, the ecotoxicological results will not be presented in this paper. The rate of colonisation of the *Perth* by fishes and encrusting marine organisms was not recorded. The results of the five-year biological survey of the *Swan* could be extrapolated to this site so it was deemed unnecessary. The baseline corrosion survey was undertaken shortly after sinking then further monitoring occurred after 6 and 16 months.

A baseline benthic survey of the proposed wreck site for the *Hobart* prescribed by the Environmental Protection Authority (Morrison, 2002) was conducted to determine the existing assemblage and sediment quality. Unfortunately, no further sediment or biological monitoring has been undertaken due to monetary constraints, therefore the results of this survey will not be presented. The corrosion monitoring programme involved measurements at 3 and 6 months post-scuttling. The corrosion surveys will continue for five years after which time the programmes will be reviewed and continued if deemed necessary.

2.2 Corrosion Monitoring

The corrosion monitoring programmes of the scuttled vessels involved measuring the corrosion parameters (E_{corr} and surface pH of the metal surface) of a number of stainless steel (316) bolts attached to various positions on the steel hull and the aluminium superstructure of the *Swan*, *Perth* and *Hobart* prior to scuttling. The attachment and documentation procedure is outlined in Richards (2003a). The corrosion potentials (E_{corr}) of the various positions on the vessel were measured on a high impedance digital multimeter, sealed in a custom-built plexiglass waterproof housing, set to read at 2V direct current. The measured voltage refers to the difference in electrical potential between a platinum working electrode and a silver/silver chloride/seawater electrode. The E_{corr} of the point was measured by firmly pressing the platinum electrode onto the head of the stainless steel bolt. Good electrical contact was made when the voltage reading was very stable, changing only ±1mV. Measurements of surface pH were effected by a BDH GelPlas flat surface pH electrode connected to a Cyberscan 200 pH meter sealed inside the custom-built plexiglass waterproof housing. The surface pH was measured by mechanically removing a small area (~2cm^2) of paint directly adjacent to the stainless steel measuring point then quickly placing the tip of the flat surface pH electrode onto the bare metal surface. The minimum pH reading was recorded. The water depth at each position was measured with a digital dive computer. The temperature, salinity and dissolved oxygen concentration of the seawater column was measured on-site at 0.5-1m intervals to a maximum depth of 24m with the appropriate sensors connected to a TPS 90DC Microprocessor Dissolved Oxygen and Conductivity meter.

2.3 Sediment Monitoring

2.3.1 Sampling Procedure

Replicate sediment samples from the *Swan* (Morrison, 1998) scuttling and reference sites (3km north west of the wreck site) were collected by divers from random locations along a 100m north-east transect using a polycarbonate hand corer inserted to a depth of 2cm. Replicate sediment samples from the *Perth* scuttling and reference sites were obtained at the prescribed locations using a Van Veen grab. Samples from the wreck site were collected at distance intervals of 10m, 50m 125m and 500m away from the vessel, along two perpendicular axes (south and west). The reference area is approximately 1.7km north of the scuttling site. The sampling and reference sites were located using a GPS. A sub-sample of the surface sediment (top 2cm) was obtained for analysis. All sediment samples were frozen prior to analysis.

2.3.2 Analysis

A representative sample of sediment was acid digested and the metals in solution (Al, Cd, Cr, Cu, Fe, Ni, Pb, Sn and Zn) measured by atomic absorption spectroscopy (AAS). Mercury ions were reduced by stannous chloride reagent in acidic solution to elemental mercury. This mercury vapour was then purged by nitrogen into a cold cell in an atomic absorption spectrometer or mercury analyser. The concentrations of TPH in the sediment samples were determined by gas chromatography using a flame ionisation detector (GC/FID) after solvent extraction with dichloromethane (DCM). TBT analyses were performed using quartz furnace atomic absorption spectrophotometry and TOC was determined on a dried and pulverised sub-sample by LECO induction furnace. The TBT results were normalised to 1% TOC. The detailed sediment sampling and analytical procedures used on the *Swan* are described fully in Morrison (1998), for the *Perth* in Morrison (2003b) and for the *Hobart* in Morrison (2002).

3. Results

3.1 Corrosion Monitoring Programme

The baseline corrosion survey of the *Swan* was performed on 14 December 1997, four hours after sinking then repeated after 1 year (351 days) and 4.25 years (1562 days) post-scuttling. The surface pH of the metal surfaces were not measured until the 4.25 year survey to allow the vessel to attain some form of 'steady state' with the local environment. The measuring point positions are shown diagrammatically on the general arrangement plan of the former HMAS *Swan* in Figure 1 and their positional descriptions outlined in Table 1. The corrosion potential and surface pH of each point measured on the *Swan* at the specified time intervals are shown in Table 2.

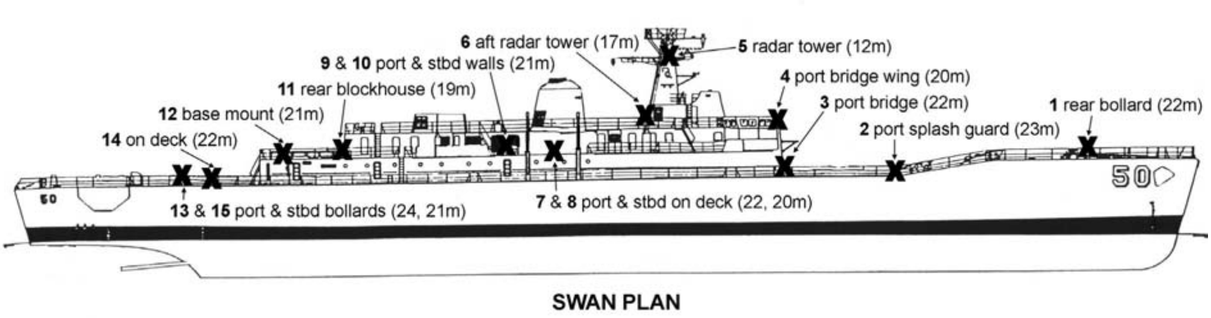

Figure 1. General arrangement plan of the HMAS *Swan* indicating the position of the 15 measuring points on the vessel.

Table 1. Positional descriptions of the measuring points on the *Swan.*

POSITION NO.	POSITIONAL DESCRIPTION
1	Bow, main deck, rear bollard
2	Bow, main deck, aft spray guard (B), port end facing bow
3	Superstructure below bridge, 1.4m above lower main deck, midway towards port side
4	Upper deck, open wing bridge, port side, directly above door on upper deck
5	Radar tower, main mast, first stage down from top, on deck, left of ladder, starboard side
6	Aft of radar tower, starboard side, 1.4m up from upper deck, right of two door close together directly below "CHECK YOUR AIR"
7	Between boat rest V's on stanchion, on octagonal plate, upper deck, port side
8	Upper deck, starboard side, aft of forward davit
9	Upper deck, starboard side, forward of aft door on wall approximately 1.4m from upper deck, aft of aft lifeboat cradle, aft of grill but forward of stairs
10	Upper deck, port side, between large square cut out and aft door approximately 20cm aft of door and 1m up from upper deck, forward of grill, directly below "CHECK YOUR AIR", yellow triangle and 2 x red arrows
11	Rear of blockhouse on wall, about 20cm left of pipes, upper deck
12	Stern, upper deck directly aft of 11, on aft of manhole cover
13	Stern, main deck, port side, on aft bollard
14	Stern, main deck, starboard side, forward of bollards on deck
15	Stern, main deck, starboard side, on forward bollard

Table 2. Corrosion potential, surface pH and average depth of the measuring points on the *Swan*.

Position	Metal	Average depth (m)	FOUR HOURS	ONE YEAR	FOUR YEARS	
			E_{corr} (14/12/97)	E_{corr} (30/11/98)	E_{corr} (26-27/3/02)	pH (26-27/3/02)
1	**Fe**	**21.7**	**-0.595**	**-0.506**	**-0.518**	**8.84**
2	**Fe**	**23.7**	**-0.577**	**-0.517**	**-0.514**	**8.59**
3	**Fe**	**22.3**	**-0.597**	**-0.522**	**-0.514**	**8.61**
4	Al	20.9	-0.586	-0.525	-0.558	8.13
5	Al	12.1	-0.597	-0.527	-0.410	7.99
6	Al	17.3	-0.563	-0.535	-0.554	7.64
7	**Fe**	**22.2**	**-0.500**	**-0.524**	**-0.550**	**7.47**
8	**Fe**	**20.3**	**-0.585**	**-0.532**	**-0.564**	**7.94**
9	Al	20.1	-0.556	-0.522	-0.546	8.26
10	Al	21.1	-0.522	-0.523	-0.382	8.15
11	Al	19.7	-0.559	-0.517	-0.368	nd
12	**Fe**	**20.3**	**-0.582**	**-0.508**	**-0.502**	**8.27**
13	**Fe**	**24.2**	**-0.605**	**-0.512**	**-0.368**	**8.29**
14	**Fe**	**21.8**	**-0.599**	**-0.509**	**-0.492**	**8.30**
15	**Fe**	**21.3**	**-0.584**	**-0.508**	**-0.508**	**8.28**

nd Not determined.

The inaugural corrosion survey on the *Perth* was performed on 26 November 2001, two days after the scuttling then repeated after six months (199 days) and sixteen months (473 days) post-scuttling. The surface pH of the metal surfaces were not measured until the sixteen-month survey. The measuring point positions are shown diagrammatically on the general arrangement plan of the former HMAS *Perth* in Figure 2 and their positional descriptions outlined in Table 3. The measuring point positions, 19 and 20 were inadvertently cut out some time after attachment, prior to scuttling. The corrosion potential and surface pH of each point measured on the *Perth* at the specified time intervals are shown in Table 4.

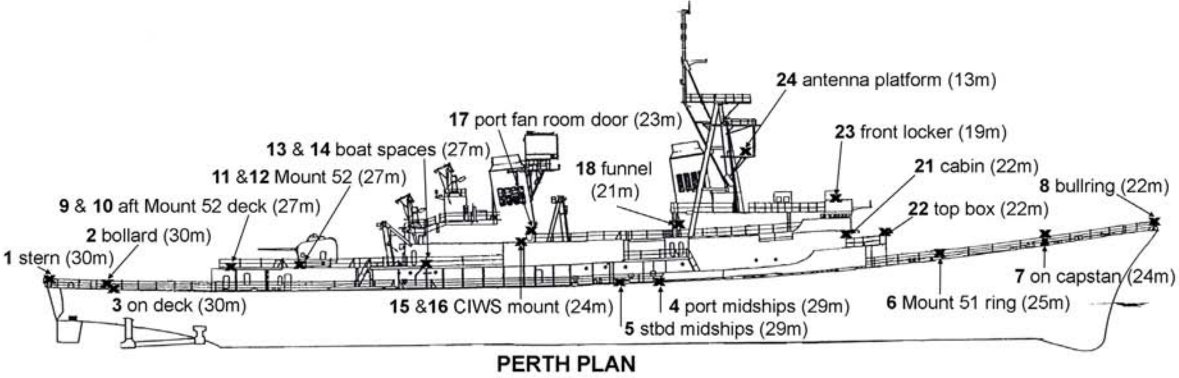

Figure 2. General arrangement plan of the HMAS *Perth* indicating the position of the 22 measuring points on the vessel.

Table 3. Positional descriptions of the measuring points on the *Perth*.

POSITION NO.	**POSITIONAL DESCRIPTION**
1	Base of aft anchor light support on 1 Deck (stern main deck)
2	Top of forward bollard on stbd side aft 1 Deck (stern main deck)
3	On main deck (~1m) forward of position **2** bollards on stbd side aft 1 Deck (stern main deck)
4	Port midships 1 Deck (main deck) attached to small plate on outside of scuppers
5	Stbd midships 1 Deck (main deck) attached to scupper aft of hawse and forward of bollards
6	Aft Mount51 ring forward 1 Deck (bow main deck)
7	On top of capstan centre forward 1 Deck (bow main deck)
8	Bullring on bow (main deck)
9	Port side aft end of Mount52 Deck (01 Level). Mounted on brackets on deck
10	Stbd side aft end of Mount52 Deck (01Level). Mounted on brackets on deck
11	Bottom aft edge port side Mount52 (01 Level)
12	Bottom aft edge stbd side Mount52 (01 Level)
13	Aft end of port boat spaces Mount52 Deck (01 Level)
14	Aft end of stbd boat spaces Mount52 Deck (01 Level)
15	Forward port corner of port CIWS mount base remains on Ikara Missile Deck (02 Level)
16	Forward stbd corner of stbd CIWS mount base remains on Ikara Missile Deck (02 Level)
17	Forward of port side fan room door (directly below aft funnel) ~1.5m above Ikara Missile Deck (02 Level)
18	Eyebolt on rear of forward funnel (~2m above deck 02 level)
21	Above cut out (~1.8m above deck) into captain's cabin on Torpedo Deck (01 level)
22	On top of box forward Torpedo Deck (01 level)
23	On front of (store locker) Ikara tracking unit platform (~1.5m above 03 level)
24	On stbd side ECM DF Antenna platform

Table 4. Corrosion potential, surface pH and average depth of the measuring points on the *Perth*.

Position	Metal	Average depth (m)	TWO DAYS	SIX MONTHS	SIXTEEN MONTHS	
			E_{corr} (26/11/01)	E_{corr} (11-12/6/02)	E_{corr} (12-14/3/03)	pH (12-14/3/03)
1	**Fe**	**28.8**	**-0.494**	**nd**	**-0.546**	**7.97**
2	**Fe**	**29.0**	**-0.504**	**nd**	**-0.531**	**7.99**
3	**Fe**	**29.3**	**-0.498**	**nd**	**-0.535**	**8.18**
4	**Fe**	**28.9**	**-0.510**	**-0.508**	**-0.538**	**8.15**
5	**Fe**	**28.9**	**-0.538**	**-0.498**	**-0.565**	**7.81**
6	**Fe**	**24.8**	**-0.520**	**-0.478**	**-0.525**	**8.22**
7	**Fe**	**23.2**	**-0.434**	**-0.480**	**-0.523**	**8.17**
8	**Fe**	**21.9**	**-0.504**	**-0.490**	**-0.534**	**8.06**
9	Al	26.9	-0.492	-0.500	nd	nd
10	Al	26.8	-0.496	-0.502	-0.554	7.98
11	**Fe**	**27.3**	**nd**	**-0.502**	**-0.556**	**8.19**
12	**Fe**	**26.8**	**-0.486**	**-0.502**	**-0.554**	**8.19**
13	Al	27.4	nd	-0.508	-0.567	8.12
14	Al	27.4	nd	-0.512	-0.564	8.11
15	Al	24.5	nd	-0.514	-0.570	8.05
16	Al	24.3	nd	-0.516	-0.570	8.17
17	Al	23.3	nd	-0.524	-0.579	6.38
18	Al	21.4	nd	-0.528	-0.581	nd
21	Al	22.5	-0.518	-0.510	-0.565	nd
22	Al	22.4	-0.518	-0.500	-0.552	8.17
23	Al	18.7	-0.518	-0.508	-0.560	8.17
24	Al	13.6	-0.510	-0.526	-0.569	8.16

nd Not determined.

Corrosion surveys of the *Hobart* were performed on 28 January 2003, two months (84 days) after the sinking and on 10 May 2003, six months (186 days) post-scuttling. The measuring point positions are almost identical to those of the *Perth* (Figure 2; Table 3) however, the Mount 51 gun on the main deck towards the bow of the *Hobart* remains intact. The corrosion potentials measured on the *Hobart* at the specified time intervals are shown in Table 5. No surface pHs of the metal surfaces have been measured to date.

Table 5. Corrosion potential and average depth of the measuring points on the *Hobart*.

Position	Metal	Average depth (m)	TWO MONTHS	SIX MONTHS
			E_{corr} (28/1/03)	E_{corr} (10/5/03)
1	**Fe**	**22.5**	**-0.512**	**-0.496**
2	**Fe**	**22.2**	**-0.520**	**-0.503**
3	**Fe**	**22.9**	**-0.521**	**-0.505**
4	**Fe**	**22.2**	**-0.534**	**-0.534**
5	**Fe**	**21.3**	**-0.525**	**-0.523**
6	**Fe**	**18.4**	**-0.494**	**-0.505**
7	**Fe**	**16.5**	**-0.505**	**-0.507**
8	**Fe**	**15.0**	**-0.515**	**-0.513**
9	Al	20.3	-0.531	-0.522
10	Al	20.2	-0.535	-0.520
11	**Fe**	**20.3**	**-0.532**	**-0.519**
12	**Fe**	**20.3**	**-0.531**	**-0.520**
13	Al	20.0	-0.543	-0.526
14	Al	20.2	-0.542	-0.524
15	Al	17.4	-0.554	-0.536
16	Al	17.4	-0.550	-0.539
17	Al	16.3	-0.561	-0.548
18	Al	13.2	-0.562	-0.568
21	Al	15.6	-0.551	-0.547
22	Al	15.4	-0.534	-0.543
23	Al	11.1	-0.540	-0.544
24	Al	6.2	-0.549	-0.550

3.2 Sediment Monitoring Programme

The baseline sediment survey of the *Swan* site was performed on 15 November 1997, one month prior to scuttling then five months (153 days) and twelve months (363 days) after the sinking. The heavy metal and TPH results are outlined in Table 6.

Table 6. Sediment analysis results for the *Swan*.

Contaminant	EA (2002) Guidelines[1]		BASELINE (15/11/97)		5 MONTHS (16/5/98)		12 MONTHS (12/12/98)	
	Screening	Max	Reference	Swan	Reference	Swan	Reference	Swan
Aluminium[2]	na	na	1450±71	1650±71	1000±0	965±191	1650±636	14000±0
Cadmium	1.5	10	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Chromium	80	370	11±1	25±1	14±1	17±1	14±7	47±1
Copper	65	270	2±0	3±0	2±0	7±2	<1	69±16
Iron	na	na	6400±141	6850±71	3500±283	2250±778	2500±141	88500±212
Lead	50	220	<1	<1	<1	7±7	<1	5±0
Zinc	200	410	5±0	5±0	3±0	19±18	8±3	80±3
TPH	na	na	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1

[1] Environment Australia (2002).

[2] All contaminants levels are quoted in mg/kg.

na Not applicable (no screening or maximum levels quoted in the EA (2002) Guidelines).

The baseline sediment survey of the *Perth* site was performed on 15 November 2001, 9 days prior to scuttling, then repeated after six months (174 days) and twelve months (388 days) post-scuttling. The heavy metal, TPH and TBT results are outlined in Tables 7, 8 and 9, respectively.

4. Discussion

4.1 Corrosion Monitoring Programme

4.1.1 General

The main objectives of the corrosion monitoring programmes are to measure the corrosion parameters of previously designated sites on each of the vessels at specified time intervals, to ascertain any discernible differences in the corrosion rates between the various locations on the vessels and to ultimately monitor the long-term stability of the vessels. The *Swan* lies 2.4km north-east of Point Piquet, Dunsborough in Geographe Bay, Western Australia (Figure 3) in 31m of water at high tide whilst the tower reaches to within 8m of the water surface. The vessel rests on the keel, the bow facing north-west with a 10° list to port.

Figure 3. Location of the *Swan* including the sediment sampling positions (Morrison, 1998).

The *Perth* lies in King George Sound, Frenchman Bay, Albany, Western Australia about 9.5km south-east of Albany (Figure 4). The vessel rests on the keel with the bow facing approximately east with no noticeable list to either side. The total depth to the keel at the sediment line is about 34m. The remains of the radar tower rises 4m out of the water surface to act as a navigation marker.

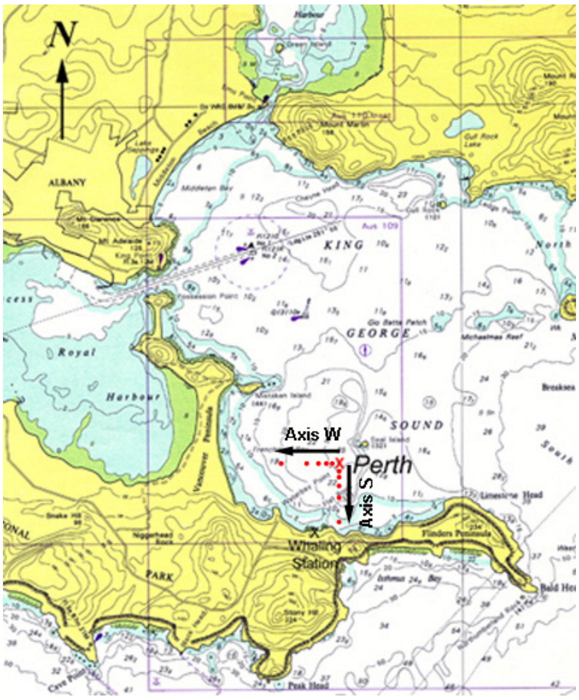

Figure 4. Location of the *Perth* including the sediment sampling positions (Richards & MacLeod, 2004).

Table 7. Baseline sediment analysis (15/11/01) results for the *Perth*.

Sample	**Al**[3]	**Cd**	**Cr**	**Cu**	**Fe**	**Hg**	**Ni**	**Pb**	**Sn**	**Zn**	**TPH**	**TBT**[4]
West 10m	5850±71	0.1±0.0	20±1	7±0	3750±71	0.02±0.00	5±0	6±0	0.45±0.07	9±4	8±0	0.5±0.0
West 50m	7050±354	nd	24±2	7±0	4550±354	0.02±0.01	6±0	7±0	0.55±0.07	9±0	5±3	0.5±0.1
West 125m	6850±636	0.1	22±2	8±1	4250±354	0.01±0.00	5±1	6±1	0.60±0.14	8±1	6±1	0.5±0.0
West 250m	6000±848	nd	20±2	6±1	3350±919	0.01±0.00	4±1	6±1	0.45±0.07	6±4	11±5	0.7±0.3
West 500m	5900±566	nd	21±3	7±0	3900±283	0.01	5±0	6±1	0.50±0.00	6±1	26±8	1.2±0.0
South 10m	5800±424	nd	19±1	6±0	3250±354	nd	4±1	6±1	0.50±0.00	4±0	54±26	0.5±0.0
South 50m	5550±212	nd	18±1	6±0	3050±212	0.01	4±0	5±0	0.50±0.14	9±4	60±28	0.4±0.0
South 125m	6300±283	nd	20±0	6±0	3400±141	0.01±0.00	5±0	6±0	0.50±0.00	10±1	35±5	0.4±0.1
South 250m	5050±636	nd	16±1	6±1	2500±566	0.01	3±1	5±0	0.45±0.07	6±2	65±30	0.5±0.2
South 500m	3000±283	nd	11±1	6±1	1100±141	nd	2±1	3±0	0.30±0.00	7±1	28±2	0.5±0.1
Reference 1	6550±1061	0.1	20±1	6±0	3750±919	0.01	4±1	6±1	0.60±0.00	6±1	115±49	0.7±0.2
Reference 2	7050±212	0.1±0.0	10±0	8±1	4250±212	0.01±0.00	4±0	12±8	0.60±0.00	10±2	115±7	0.5±0.1
Perth Site[1]	4950±212	nd	18±1	7±0	3000±0	0.01	4±0	6±0	0.50±0.00	6±3	82±1	0.7±0.2
Screening value[2]	na	1.5	80	65	na	0.15	21	50	na	200	na	5
Maximum value[2]	na	10	370	270	na	1	52	220	na	410	na	70

[1] Samples from the proposed *Perth* scuttling site prior to sinking.
[2] Environment Australia (2002) guidelines.
[3] All contaminant levels are quoted in mg/kg with the exception of TBT, which is quoted in µg/kg.
[4] Normalised to 1%TOC.
na Not applicable (no screening or maximum levels quoted in the EA (2002) guidelines).
nd Not detected (both replicates below Practical Quantitation Limit, PQL).

Table 8. Six month sediment analysis (7/5/02) results for the *Perth*.

Sample	**Al**[2]	**Cd**	**Cr**	**Cu**	**Fe**	**Hg**	**Ni**	**Pb**	**Sn**	**Zn**	**TPH**	**TBT**[3]
West 10m	9185±262	0.1±0.0	33±7	10±1	6050±636	0.03±0.00	8±1	10±1	0.7±0.0	20±2	nd	**39.9±56.1**
West 50m	10200±141	0.1±0.0	32±0	6750	6750±212	0.03±0.00	9±0	10±1	0.8±0.1	18±2	nd	0.2±0.0
West 125m	9965±474	0.1±0.0	32±1	8±0	6600±141	0.03±0.00	9±1	10±0	0.8±0.0	19±1	5±1	0.3±0.1
West 250m	8780±56	0.1	28±3	8±0	5700±141	0.03±0.00	8±0	8±0	0.6±0.1	14±1	3±1	0.3±0.0
West 500m	6335±1096	nd	23±1	6±1	4150±495	0.02±0.00	7±1	6±1	0.6±0.1	11±1	8±1	0.3±0.0
South 10m	8490±254	0.2±0.0	31±4	16±6	5500±283	0.04±0.00	10±3	8±1	0.6±0.1	24±8	21	0.2±0.0
South 50m	8920±792	0.1	30±3	14±1	5500±707	0.03±0.00	8±1	10±0	0.6±0.0	20±2	nd	0.2±0.0
South 125m	7670±976	0.1	26±2	8±2	4700±424	0.02±0.01	7±0	8±1	0.6±0.1	16±1	nd	0.2±0.0
South 250m	7885±318	nd	29±7	8±0	4750±212	0.02±0.01	6±0	8±0	0.6±0.1	14±1	nd	0.2±0.0
South 500m	6390±14	nd	20±1	7±0	3500±141	0.02±0.00	6±1	7±0	0.6±0.1	12±4	nd	0.5±0.2
Reference 1	6615±855	0.2±0.1	22±4	8±1	3700±566	0.02±0.00	7±3	8±4	0.8±0.1	10±1	7±1	0.4±0.1
Reference 2	18420±18498	nd	24±7	6±0	2850±71	0.01±0.00	4±1	6±1	0.5±0.0	10±4	nd	0.5±0.1
Screening value[1]	na	1.5	80	65	na	0.15	21	50	na	200	na	5
Maximum value[1]	na	10	370	270	na	1	52	220	na	410	na	70

[1] Environment Australia (2002) guidelines.
[2] All contaminant levels are quoted in mg/kg with the exception of TBT, which is quoted in µg/kg.
[3] Normalised to 1%TOC.
na Not applicable (no screening or maximum levels quoted in the EA (2002) guidelines).
nd Not detected (both replicates below Practical Quantitation Limit, PQL).
Bolded values indicate that the guideline screening value has been exceeded.

Table 9. Twelve month sediment analysis (17/12/02) results for the *Perth*.

Sample	Al[2]	Cd	Cr	Cu	Fe	Hg	Ni	Pb	Sn	Zn	TPH	TBT[3]
West 10m	7405±417	0.1±0.0	27±0	14±4	4850±495	0.02±0.00	7±0	12±6	1.0±0.2	24±2	6±1	3.2±2.7
West 50m	7855±276	0.1	27±1	7±0	4700±424	0.02±0.00	6±1	8±0	0.6±0.1	16±1	9±4	0.5±0.3
West 125m	7765±78	0.7	28±1	6±0	4750±212	0.02±0.00	7±1	10±4	0.6±0.1	12±1	5±1	0.3±0.1
West 250m	7075±417	nd	24±2	5±0	4050±212	0.02±0.00	5±1	6±1	0.4±0.1	10±2	4±0	0.2±0.0
West 500m	5905±262	nd	20±1	6±1	3350±353	0.01	4±0	6±1	0.4±0.0	8±1	6±1	0.3±0.0
South 10m	7640±396	0.2	22±8	9±1	4950±212	0.02±0.00	7±0	12±1	0.6±0.0	33±1	9±6	**48.4±17.7**
South 50m	8825±757	nd	31±1	7±1	5450±354	0.02±0.00	8±2	10±0	0.9±0.3	17±1	5±0	1.0±0.5
South 125m	9840±184	nd	33±11	7±0	6150±71	0.02±0.01	8±1	10±0	0.6±0.1	16±1	12±2	0.3±0.0
South 250m	8595±544	0.6	33±3	6±1	5450±354	0.01±0.00	7±0	9±0	0.6±0.0	14±1	8±1	0.3±0.3
South 500m	6735±841	nd	22±2	5±0	4400±283	0.02±0.01	4±1	7±1	0.4±0.0	11±1	9±1	0.3±0.0
Reference 1	6225±35	nd	20±0	5±0	3600±141	0.02	4±1	6±0	0.4±0.1	12±3	9±7	0.3±0.1
Reference 2	6075±559	nd	20±0	4±1	3400±283	0.01±0.00	4±1	6±1	0.5±0.1	8±1	6±4	0.4±0.1
Screening value[1]	na	1.5	80	65	na	0.15	21	50	na	200	na	5
Maximum value[1]	na	10	370	270	na	1	52	220	na	410	na	70

[1] Environment Australia (2002) guidelines.
[2] All contaminant levels are quoted in mg/kg with the exception of TBT, which is quoted in µg/kg.
[3] Normalised to 1%TOC.
na Not applicable (no screening or maximum levels quoted in the EA (2002) guidelines).
nd Not detected (both replicates below Practical Quantitation Limit, PQL).
Bolded values indicate that the guideline screening value has been exceeded.

The *Hobart* lies offshore, about 7.5km west of Marina St Vincent, Wirrina Cove in Yankalilla Bay, Gulf St Vincent, South Australia (Figure 5). It lies in a roughly east-west orientation with no noticeable list to either side, with the bow facing approximately east. The total depth to the keel at the sediment line is about 28m, the depth to the main deck is 23m, while the remains of the radar tower rises to within 5-6m of the water surface dependent on the tidal range.

Figure 5. Location of the *Hobart* (Richards 2003a).

The dissolved oxygen, salinity and temperature of the water column on each of the sites was measured at 0.5–1m intervals and the pH and redox potential of the seawater was measured at an average depth of 3–5m. The results are presented in Table 10.

Table 10. Seawater column measurements for the *Swan*, *Perth* and *Hobart*.

Vessel	Date	Average Salinity (ppt)	Average Seawater Temperature (°C)	pH Seawater	Redox Potential Seawater (V)	Average Dissolved Oxygen Content (ppm; % Sat)
Swan	30/11/98	34.7±0.1	19.3±0.1	8.21	0.221	7.87±0.14 85%@19°C
Perth	11/6/02	37.4±0.1	17.8±0.7	8.26	nd	6.92±0.09 72%@18°C
Perth	14/3/03	37.9±0.1	20.8±0.1	8.26	0.310-0.349	6.52±0.05 72%@21°C
Hobart	10/5/03	38.5±0.0	17.8±0.0	8.04	0.275	6.85±0.11 71%@18°C

nd Not determined.

The pH and the redox potentials measured on the sites indicated typical open circulation, well mixed, aerobic marine environments. There were no significant changes in the salinity with depth on the sites. The usual salinity range for the open ocean is 32–36ppt however, enclosed seas, embayments and estuaries may have higher average salinities, such as 38.6ppt for the Mediterranean and 41ppt for the Red Sea (Pearson, 1987, p. 4). Therefore, the higher average salinity for the *Hobart* site may be expected towards the head of the Gulf in the summer months due to decreased water exchange and increased evaporation and also during dodge tide periods when tidal movement is minimal. The temperature of the water columns did not vary significantly with depth, with the exception of the *Perth* site during the winter survey. The average water temperature was 17.8 ± 0.7°C and there was a marked temperature differential below 15m where the temperature decreased 1-2ºC, which would account for the relatively larger standard deviation.

The average dissolved oxygen contents are typical of aerobic seawater. Each site exhibited the general decreasing trend of dissolved oxygen concentration with increasing water depth, which is typical for an open circulation ocean environment. Factors contributing to this trend are decreasing water movement, which leads to less oxygen exchange with the atmosphere and decreasing photosynthetic activity due to less light penetration. The solubility of oxygen in seawater decreases with increasing temperature and salinity. Since the salinity of the seawater did not change significantly from winter to autumn on the *Perth* site, the dissolved oxygen concentrations measured in autumn were corrected for the 3°C temperature difference using Grasshoff's (1976) oxygen solubility in seawater table (Pearson, 1987, p. 5). Hence, the average corrected dissolved oxygen concentration of the water column in autumn was 6.95±0.05ppm and in winter the average dissolved oxygen content was 6.92±0.05ppm (~72% saturation at 18°C). When the dissolved oxygen contents are corrected for the temperature difference there is very little variability between the dissolved oxygen contents of the water column between winter and autumn. Since the cathodic reduction of oxygen is the rate controlling step in the corrosion of concreted metals in seawater, a knowledge of the seasonal variation of dissolved oxygen on a site is vital.

4.1.2 Corrosion Surveys

Corrosion monitoring of the vessels was facilitated by measuring the corrosion potentials of stainless steel bolts that had been attached to the hull and superstructure, prior to scuttling. This provided high profile, long-term electrical ohmic contact with the vessels, ensuring that the same positions were measured over the course of the monitoring programmes. The surface pH of the metal surfaces were not routinely measured until after at least one year of immersion to allow the vessel to attain some form of 'steady state' with the local environment. The physical structure and the nature of the alloys used in the original manufacture of these vessels will significantly affect the measured corrosion potentials. The sacrificial anodes that were attached to the steel hull under the waterline were probably not removed during the preparation of the vessels prior to scuttling, however there was a relatively large time lapse of at least 4-5 years between the ships being decommissioned and their sinking. Hence, any protective effect afforded by the sacrificial anodes would be minimal as they would have most likely been consumed during this time period. The range and average corrosion potentials for the iron and aluminium alloys measured on the *Swan*, *Perth* and *Hobart* are summarised in Table 11. The average surface pH of the iron and aluminium points measured on the *Swan* after four years were 8.29±0.40 and 8.03±0.24 and on the *Perth* after sixteen months were 8.09±0.13 and 8.12±0.07, respectively.

Table 11. The range and average corrosion potentials measured during the corrosion monitoring programmes for each vessel.

Vessel	Date	Time (yr)	Iron Alloy Corrosion Potential (V)			Aluminium Alloy Corrosion Potential (V)		
			Min	Max	Average	Min	Max	Average
Swan	14/11/97	0	-0.500	-0.605	-0.580±0.032	-0.552	-0.597	-0.569±0.018
	30/11/98	1	-0.506	-0.532	-0.515±0.009	-0.517	-0.535	-0.525±0.006
	26/3/02	4.3	-0.492	-0.565	-0.521±0.025	-0.369	-0.559	-0.470±0.092
Perth	26/11/01	0	-0.434	-0.538	-0.499±0.029	-0.492	-0.518	-0.509±0.012
	11/6/02	0.5	-0.480	-0.508	-0.494±0.012	-0.500	-0.528	-0.512±0.010
	12/3/03	1.3	-0.523	-0.565	-0.541±0.014	-0.552	-0.581	-0.566±0.009
Hobart	28/1/03	0.2	-0.494	-0.534	-0.519±0.013	-0.531	-0.562	-0.546±0.010
	10/5/03	0.5	-0.496	-0.534	-0.512±0.011	-0.520	-0.568	-0.539±0.014

The total amount of water movement generally decreases with increasing depth thereby reducing the total amount of oxygen flux to a metal surface. The general rate of deterioration of concreted metals on shipwreck sites is very dependent on the water depth and the flux of oxygenated seawater over the objects lying proud of the seabed. Therefore it is expected for concreted iron alloy artefacts that the corrosion potentials will decrease with increasing depth. The corrosion potentials and the average depths of the points measured at the specified time intervals for each vessel were graphed to ascertain if there was any emergent relationship between the two variables since the time of scuttling (Figure 6).

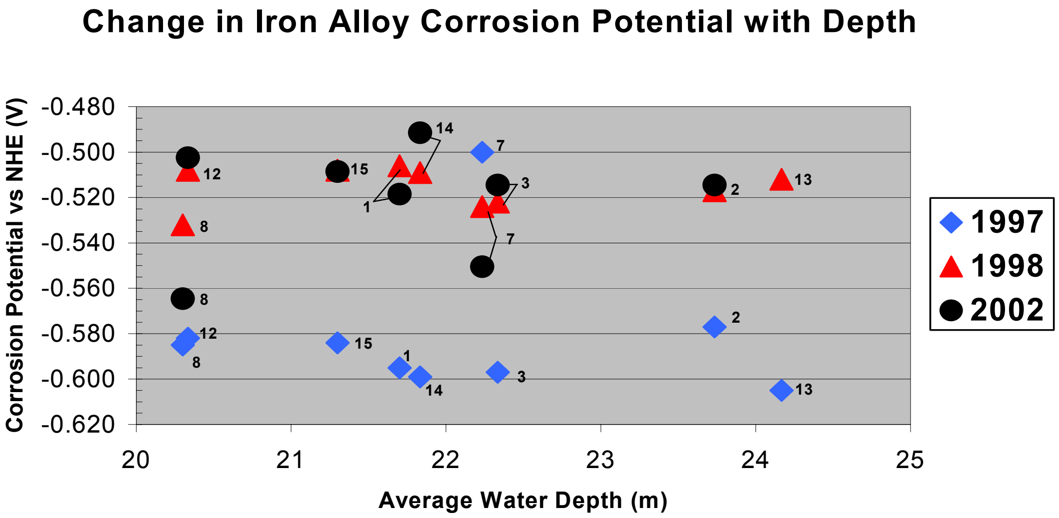

Figure 6. The relationship between the iron alloy corrosion potentials and depth for the *Swan*.

As is evident from Figure 6, there appears to be no correlation between changes in corrosion potential with average water depth on the *Swan* even after four years of submersion. There was also no emergent trend between the aluminium alloy voltages measured on the *Swan* and the average water depths. Similarly, the corrosion potentials for the iron and aluminium alloys on the *Perth* and the *Hobart* showed no correlation with increasing water depth. The lack of any apparent dependence of E_{corr} on depth is simply a reflection of the inter-connected nature of the structural elements of the vessel and that large sections of the ships are still electrically connected with each other and therefore the voltages expressed do not relate directly to the measurement point. The ships are very much still in the initial stages of deterioration and although there has been some colonisation of the vessel's surfaces, due to the anti-foul present below the waterline of the vessel and the protective paint systems, no significant concretion formation has occurred on the steel hulls during their period of immersion. Therefore, the usual film free iron corrosion mechanism applicable to concreted iron objects where the anodic and cathodic sites are separated by a semi-permeable concretion membrane does not apply to these vessels at this point in time. Experience with the wreck of the *Fujikawa Maru* (1944) in Chuuk Lagoon has shown that this wreck is only now just beginning to have E_{corr} values that are sensitive to water depth (MacLeod, 2003). The *Fujikawa Maru* has a very similar site orientation to the *Perth* in that it is lying upright on its keel on a flat seabed so it is expected that a decade or two will be needed before any E_{corr} values on the naval vessels show any systematic behaviour with regard to water depth.

It is vital that the data from the modern naval vessels are viewed in their own right since the fundamental corrosion microenvironment is different to that of historical concreted marine iron that has been immersed for more than 100 years. The different processes mean that the rate-determining step in the overall corrosion process at this stage is not the reduction of oxygen on the surface but the oxidation of the metal. All three vessels are painted with an anti-corrosive paint system, which will have an effect on the corrosion mechanisms and significantly reduce the corrosion rate of the underlying metals. In an attempt to understand changes in the corrosion potentials with time, the voltages of the aluminium and iron alloy points on each vessel were plotted against the time of submersion since the scuttling. In addition, by plotting the measured corrosion potentials and the corresponding surface pH's of the residual metal surface on the Pourbaix diagram for the appropriate metal, the thermodynamic stable state of the metal in that particular environment can be ascertained.

The corrosion behaviour of the *Perth* and the *Hobart* for the first six months is very similar, therefore only the *Perth* results will be presented. The aluminium alloy points on the *Perth* are reacting similarly to the iron alloy points (Figure 7) and there appears to be a relatively random scatter of points during the first six months of immersion. The baseline corrosion potential of point **7** on the *Perth* appears to be anomalous and may have been caused by partial electrical connection between the platinum electrode and the bolt during measurement. This random scatter for the *Perth* and the *Hobart* may reflect differences in the amount of sea water penetration through and under the paint film in the vicinity of the measuring points and this, in turn, would lead to a range of dry to wet corrosion cell mechanisms occurring under the paint layers. Therefore, interpretation of any differences between individual data points or sets of the same is not possible for the first six months of immersion. However, after sixteen months there was a small, relatively consistent decrease in the average corrosion potentials of both the aluminium (0.055V) and iron (0.045V) alloy measuring points on the *Perth*, reflecting more effective and uniform penetration of the seawater under the protective paint film and the establishment of a series of localised corrosion cells after a further ten months of submersion.

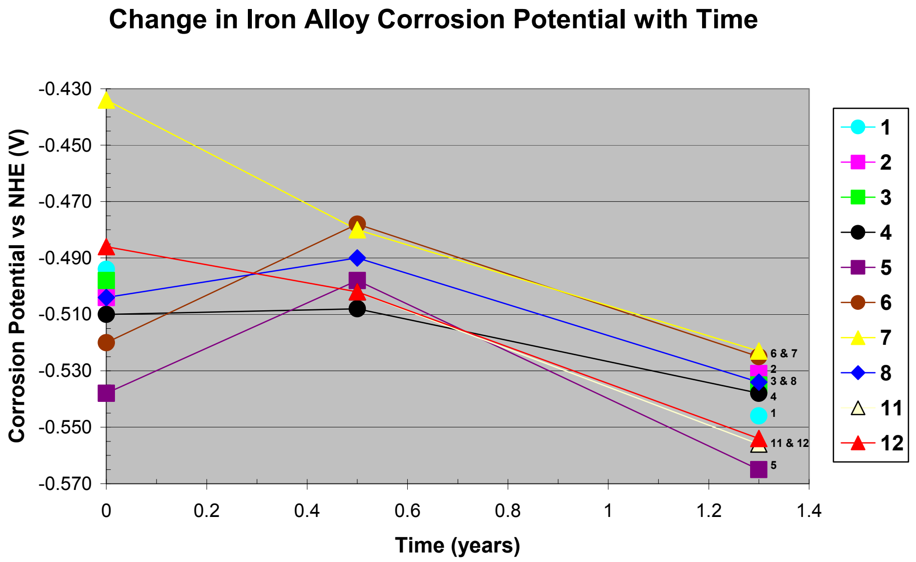

Figure 7. The change in iron alloy corrosion potentials on the *Perth* with time.

This decrease in the average voltages after sixteen months could also indicate a relatively small decrease in the corrosion rate of the vessel. This may be caused by the increase in secondary colonisation of the hull and superstructure after this time but there is no significant uniform formation of concretion, which would cause some partial separation of the anodic and cathodic sites effectively slowing the corrosion rate. Therefore, it may be that this decrease in the average corrosion potentials coupled with slightly more acidic pHs at the metal surfaces after sixteen months is more consistent with a slight increase in the corrosion rate due to the development of localised corrosion cells on the vessel as the seawater penetrates the paint layers, causing pitting corrosion of the iron and aluminium under this passive paint film. Unlike film free corrosion mechanisms, with pitting corrosion a decrease in corrosion potential indicates an increase in the corrosion rate.

The changes in the iron and aluminium alloy corrosion potentials of the *Swan* over the four years of submersion are shown graphically in Figures 8 and 9, respectively.

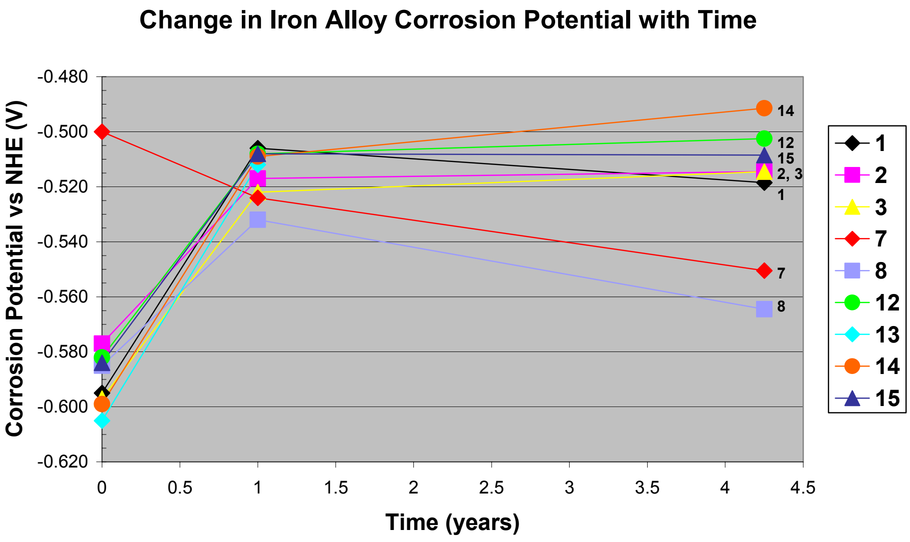

Figure 8. The changes in iron corrosion potentials on the *Swan* with time.

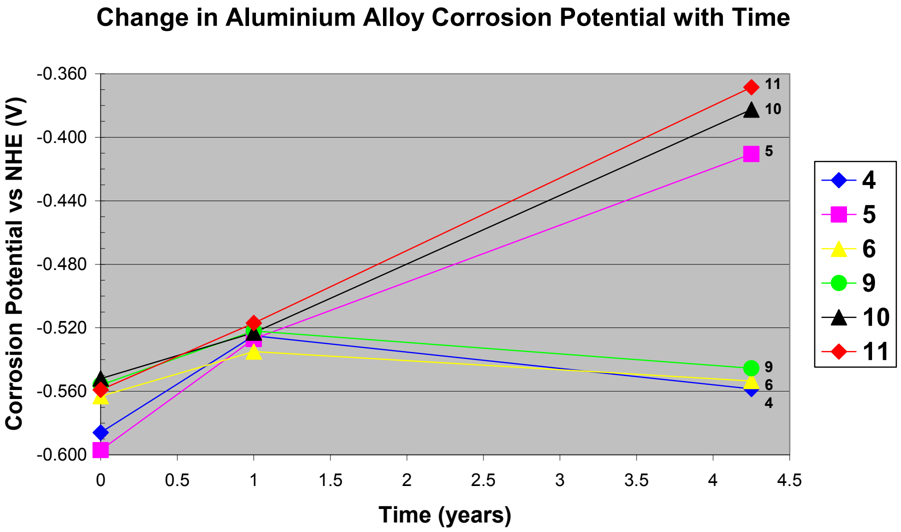

Figure 9. The change in aluminium corrosion potentials on the *Swan* with time.

The baseline iron and aluminium corrosion potentials measured fours hours after scuttling are indicative of dry cell corrosion mechanisms as the seawater would not have had time to effectively penetrate the protective paint system. Again the voltage of point **7** appears to be anomalous. After one year, the voltages become more positive, similar to the voltages measured on the *Perth* and *Hobart* after the first six months of immersion, reflecting increased deterioration and penetration of the paint barrier with seawater causing a corresponding increase in the formation of localised wet corrosion cells. However, after four years the vessel appears to have attained some form of 'steady state' with the local environment and differences in corrosion potentials are becoming more apparent, which may indicate some slow changes in corrosion mechanisms occurring on the vessel.

The more positive voltages of the iron alloys measured on the stern (**12**, **13**, **14** and **15**) and the bow (**1**, **2** and **3**) suggests that these areas are subjected to a more corrosive environment than the more protected points (**7** and **8**) located on the upper deck, midships on the vessel. There is a significant amount of scouring around the stern and bow of the vessel, which indicates that considerable water movement is occurring in these areas and increased water movement increases the oxygen flux to metal surfaces thus, in turn, increasing corrosion rates.

The voltage of point **13** at –0.368V is very close to the open circuit potential for iron in flowing seawater (-0.383V). This voltage could simply be erroneous but the more likely explanation is the bollard is not in good electrical contact with the rest of the hull. If the latter is the case then this supports the fact that isolated iron artefacts corrode at a faster rate than a large, intact iron structure. This is due to the massive difference in surface area and therefore, the current density is dispersed over a larger area and the corrosion rate of the hull will significantly decrease in comparison to the isolated iron fitting.

The aluminium alloy points are reacting similarly to the iron alloys with respect to total water movement and localised turbulence factors. The less negative corrosion potentials of aluminium points **5**, **10** and **11** indicate they are subject to a more corrosive environment than positions **4**, **6** and **9**. Point **4** is positioned on the port side corner of the bridge behind a large splash guard, point **6** is mounted on the wall on the rear of the radar tower and point **9** is mounted on the wall, behind a ladder on the starboard side of the superstructure. All three points are considerably more protected from excessive water movement than the other more exposed positions.

Galvanic corrosion may also be contributing to the emerging differences in the iron and aluminium alloy corrosion potentials on the *Swan*. The effects of galvanic corrosion are most readily discerned when the iron alloy hull and the aluminium of the superstructure are in direct electrical contact. When this occurs the aluminium will act as an enormous sacrificial anode for the steel hull promoting galvanic corrosion of the aluminium and protecting the steel structure. Naval architects make enormous efforts to ensure electrical isolation of the different alloys used in the construction of these vessels to prevent galvanic corrosion occurring during service so it will be only after the these insulating techniques have begun to fail and the seawater has penetrated the isolation barriers that galvanic corrosion will be observed. The anode or cathode resistances in the galvanic cells are controlled by protective oxide films and the resistance associated with the custom-made industrial paint system. Data from the *Swan* indicates that breaches in the electrical barriers have commenced but they appear to still be intact after six and sixteen months immersion for the *Hobart* and *Perth* respectively. The midships of the steel hull of the *Swan*, points **7** and **8,** appear to be receiving some cathodic protection by the aluminium superstructure after four years, while the stern and bow are the least protected (more positive voltages). It should also be noted that the structural profile of the bow and stern are such that they present zones of greater turbulence for the flowing seawater than in the midships areas. Preferential corrosion of the aluminium is also indicated by the decrease in the average pH of the aluminium elements and an increase in the pH of the iron measurement points. The absence of significant build up of concretion mitigates against ready discernment of such changes in local acidity and alkalinity.

Six months after being sunk the average corrosion potential of the iron alloy points on the *Hobart* was about 0.130V more negative than the open circuit potential of iron in seawater (-0.383V); the *Perth* about 0.160V more negative after sixteen months and the *Swan* about 0.120V more negative after four years. Normally cathodic protection will result in a 150 millivolt drop in average corrosion potentials but the differences between the E_{corr} of the vessels cannot be directly compared with the open circuit value of iron in seawater since the latter refers to bare iron and not the painted systems on the naval vessels. The intercepts of the iron and aluminium alloy points for the *Swan* on the corresponding Pourbaix diagrams (Figure 10 and 11) support the results from the potential/time graphs and also indicate the *Swan* is relatively protected even after four years immersed in an aerobic marine environment. The intercepts for the *Perth* and *Hobart* are very similar to the results for the 1997 and 1998 measurements on the *Swan* indicating these vessels are obviously less deteriorated than the *Swan* because they have been submerged for much shorter periods of time.

There were a significant number of discrete areas of aluminium corrosion products visible on the planar surfaces of each vessel’s aluminium superstructure, which increased significantly with the time of immersion. Pitting and crevice corrosion are causing this deterioration of the aluminium as the protective paint system is slowly failing in these areas but it has not significantly affected the overall corrosion rates even after four years of submersion. These results signify that these contemporary vessels are corroding albeit at a relatively slow rate and this is most probably due to the protection afforded by the paint barrier remaining on the vessels. The monitoring programmes for the *Perth*, *Swan* and *Hobart* are the first systematic corrosion survey programmes established in Australia for monitoring the long-term stability of twentieth century warships after scuttling as artificial reefs. Complex corrosion behaviour are being exhibited by these vessels but it is still too early in the monitoring programmes to make any definitive statements regarding the long-term stability of these vessels.

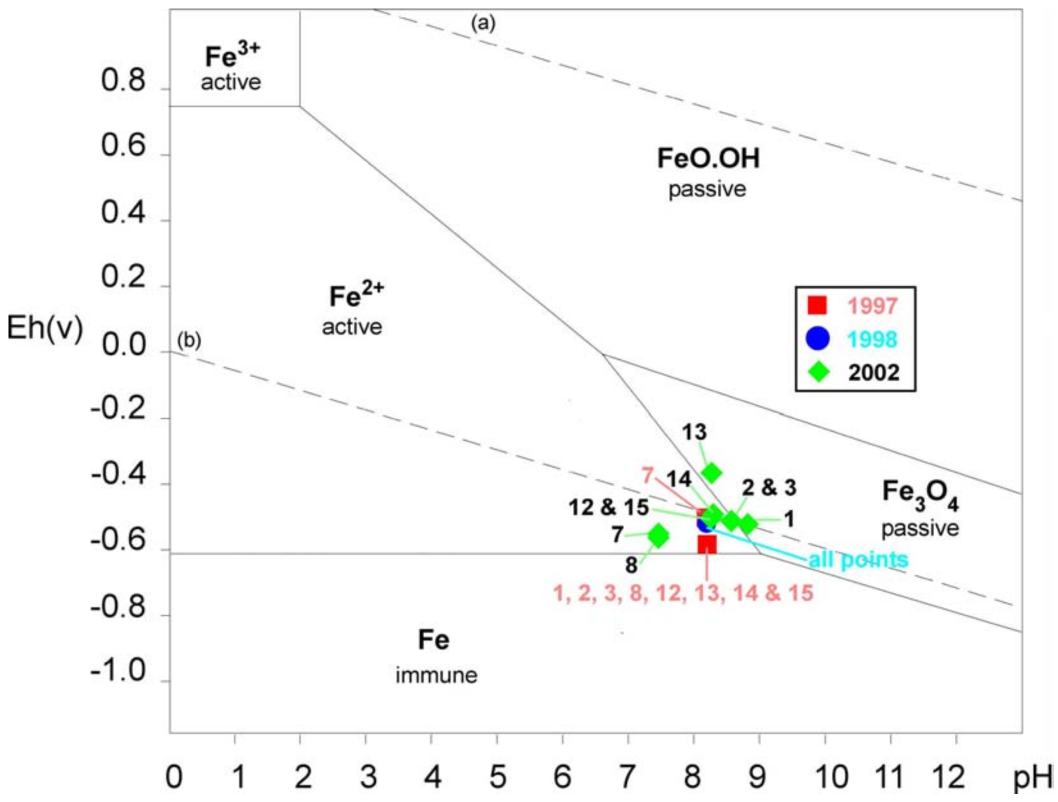

Figure 10. Iron (10^{-6}M) Pourbaix diagram in aerobic seawater at 25°C on the *Swan* after four years.

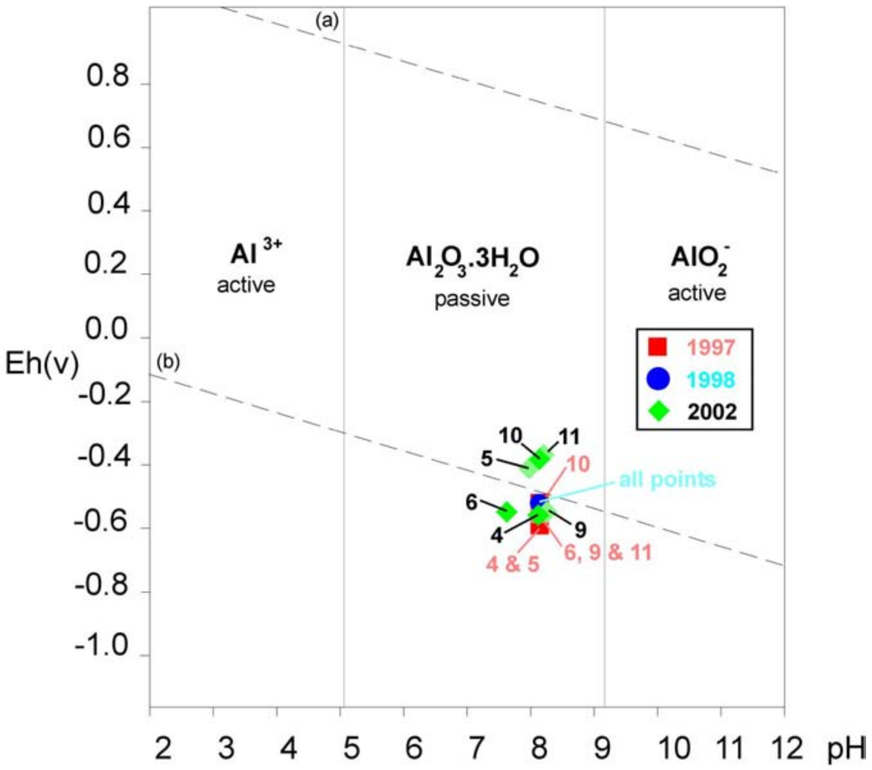

Figure 11. Aluminium (3.7 x 10^{-6}M) Pourbaix diagram for aerobic seawater at 25°C on the *Swan* after four years.

4.2 Sediment Monitoring Programme

The main objectives of the sediment analysis programmes are to ascertain any environmental impact resulting from the scuttling of these contemporary vessels, to ascertain the extent of metal enrichment of the sediments surrounding the submerged vessel, to ascertain if any change in corrosion mechanism has an impact on the extent of metal enrichment in the sediment and to ultimately monitor the long-term stability of the vessels. During the decommissioning of the ex-naval vessels significant quantities of metals and oil were removed as scrap for both the purposes of salvage and for reducing the potential for impact on the environment. Vast quantities of copper, brass, aluminium, lead and steel were removed however, it was not possible to remove all traces of metals, especially copper and brass from the engine rooms. The metals remaining on the vessels will corrode and diffuse into the surrounding environment, therefore it is imperative that the sediments in close proximity to these vessels are monitored for these major contaminants and the environmental impact assessed.

The results of the sediment surveys for the *Swan* are tabulated in Table 6. Prior to scuttling, chromium and iron were found to be significantly elevated indicating that the site had naturally elevated levels of these two metals compared with the reference site. No statistically significant differences in sediment metal concentrations between the reference and *Swan* site were noted after five months. After 12 months there was a marked enrichment of aluminium, chromium, copper, iron, lead and zinc in the sediments directly adjacent to the vessel. Only copper was found to exceed the Environment Australia (2002) guidelines and none of the sediments contained measurable quantities of total petroleum hydrocarbons from either site that were measured on the three sampling occasions.

Metal enrichment of sediments surrounding metal structures and jetties is common. Since the area of enrichment around such structures is dependent on distribution by currents, the sediments on the *Perth* site were monitored at increasing distances away from the vessel in the major current directions for that area. The results of the *Perth* sediment surveys are summarised in Tables 7, 8 and 9. The concentrations of these metals in the sediment have increased significantly since the baseline survey however, none are above the Environment Australia (2002) guideline levels. The concentration of cadmium and mercury did not increase significantly above the Practical Quantitation Limit. Whilst there was some variability in metal levels measured at the reference locations, none were statistically significant (Morrison, 2003b). The TBT results indicate that there has been some contamination of the *Perth* site at four locations within 50m of the vessel after one year however, the data shows that the TBT is below screening levels at all locations with the exception of one site 10m west of the vessel. It is possible that a paint flake had dislodged from the hull during the scuttling process and the prevailing current from the east deposited it on the seabed at this location. The significant variation between replicate samples supports this suggestion however, further sampling will investigate whether TBT is decreasing due to degradation or increasing through further contamination. The TPH concentrations have not increased since the baseline survey.

Typically the amount of metal enrichment in the sediment decreases with increasing distance from the vessel. On average, the metal concentrations in the sediments are relatively similar from the vessel out to a distance of 125m along both transects, decrease slightly at distances greater than 125m and then decrease markedly at distances greater than 250m away from the vessel. There appears to be no significant differences in the heavy metal distribution in the sediment measured along the west and south transects. Metal enrichment of the sediment surrounding the *Swan* and the *Perth* is a direct result of metal corrosion and the degradation of the protective paint layers. The major source of aluminium and iron in the sediment would originate from the corrosion of the superstructure and the hull, respectively. Aluminium flake is also a constituent in the primer applied to the keel up to the waterline and iron is a minor constituent in the alkyd resin topcoats. Galvanic corrosion of the aluminium in preference to the iron hull would cause significant increases in the levels of aluminium with a corresponding plateau or only very slight increases in the concentration of iron in the sediment. Hence, the increases in the aluminium and iron levels measured in the sediment over the one year monitoring period support the initial corrosion survey results, which indicate that minimal cathodic protection is being afforded by the aluminium superstructure to the steel hull after twelve months in an aerobic seawater environment.

Chromium and nickel are alloying metals in stainless steel however, corrosion of stainless steel occurs predominantly under anaerobic conditions and since both vessels lie essentially proud of the seabed in aerobic seawater this would be only a minor source of contamination. More likely the chromium has originated from the original yellow zinc chromate primer that is commonly used on aluminium alloys. Although some or all of the original coatings were replaced in the 1980’s and despite recent coating formulations that did not contain chromium salts, the extent to which the original coatings were stripped prior to repainting is unknown. The copper, zinc and tin in the sediment would originate from the corrosion of copper and copper alloy components on the vessel however, much of this material was removed prior to scuttling. Copper linear flex shaped charge explosives were used to scuttle the *Perth* and may have also contributed to the contamination however, if the explosives were the major source of the contamination then increases in the sediment copper levels over time would not be expected. It is more probable that the major source of copper and tin would be from the copper oxide and organotin, which are the major constituents of the recent anti-foul.

The anti-foul is a one pack, organotin based antifouling, self polishing copolymer (Intersmooth Hisol) used for vessels larger than 25m. The coating contains tributyltin and the dry copolymer film contains 2.2% tin. The biologically toxic organotin and copper compounds leach into the water column and prevent marine organisms attaching to the external immersed hull sections. The TBTO leaches into the water column and degrades slowly in the marine environment to the tributyl, dibutyl and monobutyl species and finally to inorganic tin. The environmental degradation of TBT is principally biologically mediated and closely follows first order kinetics. The speciation products of organotin degradation are complicated by accumulation and degradation processes, which occur at different rates depending on the environmental compartment. Hence, the relatively low levels of tin in the sediment after one year of monitoring suggests that the surrounding sediment is not significantly contaminated with organotin species at this stage.

The degradation of the original zinc chromate primer could account for some of the zinc enrichment but the major source would be from the zinc salts, such as zinc phosphates and zinc powder added to the more recent primers as corrosion inhibitors. Lead was used as ballast in these vessels but due to its biological toxicity it was all removed during the preparation process prior to the scuttling in accordance with the EMPs. No lead oxides were present in the most recent paint formulations however, they may have been used in some of the original coatings and could possibly be a source of the lead contamination. During the scuttling of the *Swan*, the explosives used were lead linear flex shaped charges, which would have contributed some lead to the surrounding environment and presumably to the seabed sediments. The elevated levels of lead found in sediments near the *Swan* may have resulted from the explosive charges. As a result, lead linear flex shaped charges are no longer used for scuttling vessels.

The sediment results indicate that after the first twelve months of immersion in an aerobic marine environment the metal components on the *Perth* and the *Swan* are corroding but minimal cathodic protection is being afforded to the vessels and the protective paint coatings are deteriorating albeit at a relatively slow rate. Overall, the results indicate that the scuttling of the *Swan* and *Perth* has had no adverse environmental impacts on sediments and it is unlikely the enrichment at these levels will impact significantly on marine life. However, the gradual increase in metals and TBT concentrations near the vessels should continue to be monitored and the sediment chemistry included as an integral part of the corrosion monitoring programmes over the next ten years as the corrosion rates of the vessels will probably increase significantly over this time period.

5. Conclusion

The results of the corrosion and sediment monitoring programmes have shown that the corrosion behaviour of the three vessels are very similar over the first twelve months of immersion and corrosion rates increase over time, especially after the first year. However, the vessels are still corroding at a slow rate even after four years exposed to a typical open circulation, aerobic marine environment. There is evidence of aluminium and iron corrosion on all vessels indicating pitting corrosion of the superstructure and steel hull but the anti-corrosive paint system, albeit failing in some areas, is still providing considerable protection to the vessels. The vessels are still in the initial stages of corrosion without encapsulation by concretion, although there has been considerable secondary colonisation of the metal surfaces. However, the corrosion mechanisms are slowly changing over time. The effects of galvanic corrosion are beginning to be discerned after four years, but the effect is not significant at this stage. The wrecks are successful dive sites and artificial reefs and the impact on local environments has been minimal after one year of submersion. Complex corrosion behaviour is being exhibited by these vessels and it is still too early in the monitoring programmes to make any definitive statements regarding the long-term stability of the vessels and their effect on the marine environment. Therefore, it is of paramount importance that these monitoring programmes continue so as much information as possible regarding the corrosion processes and the long-term environmental effects of these vessels is obtained.

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Corrosion and cathodic protection of iron in seawater: a case study of the *James Matthews* (1841)

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Abstract

Pre-disturbance measurements of the *in-situ* corrosion properties of iron fittings on the snow brig *James Matthews* (1841) have been used as conservation management tools for the site. The wreck of the former slave trader is historically significant and the potential impact of continued industrial activities associated with nearby dredging activities necessitated *in-situ* cathodic protection of exposed iron fittings. A laboratory simulation study of the impact of pH and chloride content on the corrosion of cast iron and mild steel was conducted. There was a linear relationship between the corrosion rate of cast iron and the log of chloride ion concentration in the pH range 7.8< pH >5.5 with only a small pH effect noted for the given range of conditions. Studies on a 19th century mild steel sample indicated that the corrosion rate was linearly dependent on the square root of the chloride ion concentration and the corrosion rate fell in a linear fashion as the pH was increased to strongly alkaline solutions of sodium hydroxide.

Keywords: conservation, corrosion-simulation, cast-iron, mild-steel, seawater, *in-situ* treatment, sacrificial anodes.

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1. Introduction

The wreck of the *James Matthews* was chosen as a test case for the Western Australian Museum to trial the minimal intervention site management strategies of the ICOMOS (1997) charter on the protection and management of underwater cultural heritage. The wreck is a rare example of a ship built as a slave-trading vessel, which is located about 15km south of the Museum Conservation laboratories and the industrial history of Cockburn Sound meant that any stabilisation activities would not have major negative impacts on an area that has suffered decades of industrial abuse. The Western Australian Museum has previously reported a number of *in-situ* treatments of iron fittings associated with historic shipwrecks (Carpenter & Richards, 1993; MacLeod et.al., 1986; MacLeod, 1986, 1989a, 1989b, 1993a, 1993b, 1995, 1996a, 1996b, 1998a, 1998b; Richards, 1996, 2001; Richards & Carpenter, 1998) and the most recent studies have included measurements on modern naval vessels that have been deliberately sunk to act as artificial reefs (Richards, 2003a, 2003b; Richards & MacLeod, 2004). Periodic monitoring of corrosion potentials makes it possible to predict the rate at which a metal object deteriorates and to determine the most appropriate time to recover the object (MacLeod, 1996b, 1989b, 2002). The benefits of attaching sacrificial anodes to metal objects include an immediate decrease in corrosion rate and commencement of an active conservation treatment. As the polarity of the object changes from positive to negative the removal of chloride ions is enhanced, resulting in less time required for conservation treatments in the laboratory (Carpenter & MacLeod, 1993; Gregory, 1999, 2000; MacLeod, 1993b; Soerensen & Gregory, 1998).

It is believed that the 107-ton snow brig *James Matthews* was built in France in the 1820's as a wooden vessel with copper sheathing fastened with copper, iron and wooden treenails, and was wrecked on 22nd July 1841. The wreck is located about 100m offshore in Cockburn Sound and is relatively protected against rough sea conditions in all weathers, with the exception of northwesterly winds, which predominate in winter. The wreck lies at an approximate depth of 1.8m±0.4m, covering an area about 25m x 7m x 2m. It is mostly buried to a depth of approximately 1.5-2m in calcareous sand. The water temperature increased from 17ºC in September to 24ºC in

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December 2000, but there was no significant temperature gradient throughout the water column. The seawater column was measured on-site between the 6-7 December 2000 and the mean temperature was 24.3±0.1ºC, the pH 8.25±0.04, the salinity 34.5±0.7ppt, the average dissolved oxygen content 7.81±0.11ppm and the average redox potential was 0.142±0.072V[2]. These measurements indicate an open circulation aerobic marine environment.

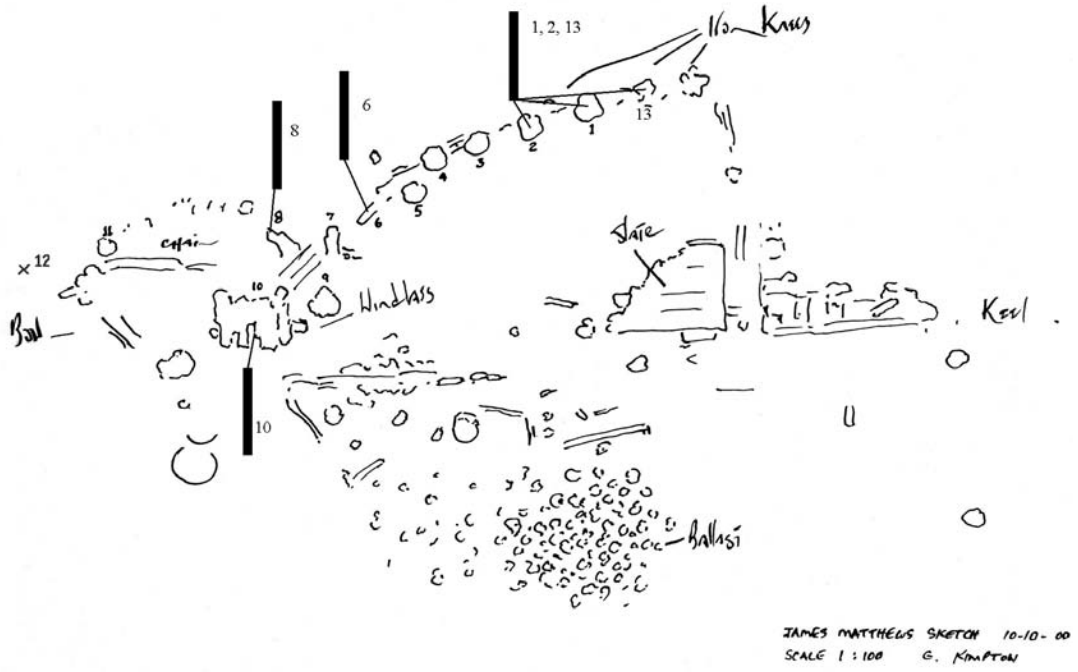

Figure 1: Sketch plan of the *James Matthews* detailing anode distribution.

The most exposed areas of the wreck are the iron deck knees on the starboard side, a slate mound towards the stern and the windlass located at the bow. The windlass is the highest profile artefact on the site and protrudes about 1.5m above the sediment. The exposure of the deck knees range from a few centimetres to about a metre. The concreted surfaces of the iron structures are quite densely covered with sessile marine organisms including mussels, sponges, barnacles, ascidians, tunicates and a variety of seaweeds. A pre-disturbance electrochemical survey of the major iron structures on the predominantly wooden *James Matthews* site was conducted prior to the attachment of zinc sacrificial anodes to a number of iron fittings. After attachment, the surrounding sediment was monitored at regular intervals to ascertain the impact of this method on the local environment. Exposed timbers exhibited extensive damage caused by marine borers (Richards, 2001). Sandbags were placed on the exposed timbers in April 2001 but the canvas cover degraded extremely rapidly and after three months very little textile remained. After six months there was only a thin layer (~1cm) of sand coverage aft of the slate mound however, coverage was slightly deeper (~10-20cm) on the starboard side edge of the wreck where the deck knees and windlass were located (Richards, 2003a).

2. Experimental

2.1 Measurement of the corrosion parameters

The surface pH of the iron elements was determined by using a BDH GelPlas flat surface pH electrode connected to a Cyberscan 200 pH meter sealed inside a custom-built plexiglass waterproof housing. The corrosion potential (E_{corr}) was determined with a high impedance digital multimeter mounted in the same

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[2] Voltage referenced to the standard hydrogen electrode (SHE) after correction for the $Ag/AgCl_{seawater}$ reference electrode potential of +0.254 V versus the SHE.

waterproof housing, connected to a platinum working electrode and a $Ag/AgCl_{seawater}$ reference electrode. The reference electrode was calibrated by measuring the voltage difference between a standard $Ag/AgCl_{3M\ KCl}$ electrode that had been previously calibrated using a standard saturated quinhydrone solution in a pH 4 buffer solution. The procedure for measuring surface pH and E_{corr} was to drill through the concretion and corrosion layers on the artefact until the residual metal surface was reached. Penetration of the concretion was effected using a 16mm masonry drill bit attached to a pneumatic drill powered off a SCUBA tank. Immediately after removal of the drill bit the pH electrode was inserted and held against the metal surface until the minimum pH reading was recorded. The E_{corr} was measured by establishing electrical contact between the metal and the platinum electrode that had been placed into the drill hole. The E_{corr} values were characterised by a steady voltage that varied by only one millivolt.

A standard divers depth gauge and thermometer unit was attached to the housing, as was a vernier calliper. After the corrosion parameters were measured, the total corrosion/concretion depth was determined with the vernier calliper.

2.2 Fabrication of the zinc anodes

Corrosion protection of iron objects in seawater can be effected by establishing electrical contact with a zinc anode via an insulated copper wire cable. Four zinc anodes were purchased for the experiment and one of them had three connection points so it could be simultaneously attached to three separate iron objects in order to gauge the impact of a three-fold increase in the surface area of the objects being protected on the efficiency of this anode arrangement.

The connection points between the crimped terminal at the exposed end of an insulated copper electrical wire and the cast iron G-clamp were silver soldered (50% Ag, 35% Cu, 15% Zn) and sealed using heat-shrink epoxy mastic (richard.garcia@museum.wa.gov.au). After attaching the commercial zinc anodes by securing the machined screw thread of the G-clamp via a pre-drilled hole through the concretion, the pH and E_{corr} were measured through a second drill hole and also directly on the anode. The impact of the anode corrosion products on the marine environment was quantified via analysis of the zinc content in the surrounding sediments, which were collected from beneath the anodes in polycarbonate corers (4.5x30cm) each time the corrosion parameters were measured. A piece of wood across the top opening of the tube protected the tube from being shattered as it was hammered into the seabed. Four baseline sediment samples were collected from the positions where the anodes were to be placed near iron deck knees **2**, **6**, **8** and the windlass **10** as shown in Figure 1. A control sample was collected off-site, approximately 20m south from deck knee **2**.

2.3 Corrosion simulation equipment

The cast iron and steel electrodes used in the corrosion simulation experiments were imbedded in epoxy resin after connecting insulated copper wires to the metal by brazing. Electrode surface area calibrations were performed using chronoamperometry with an Amel 551 Potentiostat connected to a flat bed XY-t recorder. The grey cast iron electrodes were fabricated from a commercially available washbasin, which had a very similar composition and microstructure to cast iron objects on the wreck. The cast iron electrode had an effective surface area of $12.6cm^2$ (surface roughness 13.6), a density of $7.3gcm^{-3}$ and a metal composition of Fe 96%, C 3.30%, Si 2.6%, Mn 0.46%, P 0.59%, S 0.06%, Cu 0.03% and Ni 0.01%. The 19th century mild steel electrode, which approximates wrought iron, had a surface area of $22.7cm^2$ (surface roughness 44), a density of $7.76gcm^{-3}$ and an elemental composition of Fe 99.98%, C 0.18%, Si 0.06%, Mn 0.69%, P 0.06%, S 0.06%, Cu 0.02% and Ni 0.02%. The real surface areas of the electrodes were separately determined using standard electrochemical techniques. The details of the method can be found in standard texts on the electrochemistry of solid electrodes based on comparison of the diffusion currents to standardised platinum electrodes and those observed on the iron systems (Adams, 1969). The aforementioned parameters were inserted into the software program, SoftCorr™ II, that calculated the corrosion rate of the metal surfaces exposed to the test solutions.

The effect of pH and chloride concentration on the corrosion rate of wrought iron and cast iron was assessed using the SoftCorr™ II program and a EG&G model potentiostat VersaStat (model 253) potentiostat using a standard three electrode configuration that sees the current pass between two graphite rod electrodes and the working iron electrode. The voltage is measured between the working electrode and a 3M KCl calomel reference electrode that was connected to the test solution via a Luggin capillary and a 2M $NaNO_3$ salt bridge (Princeton Applied Research, 1990). In order to avoid spurious concentration effects all variations in chloride concentration experiments were carried out at the same ionic strength, using $NaNO_3$ as the inert electrolyte. Generally, the most reliable method for analysis of the current voltage curves involved the use of one or both types of the Tafel analyses that fitted the curves to standard corrosion theory. A typical potentiodynamic scan involved recording of the relationship between the logarithm of the corrosion current and the voltage as it was scanned ±250mV from the rest potential or E_{corr} of the metal in the test solution. The Tafel slope relates to the region on the plot where there was a linear relationship between the log current and the voltage. Typically five Tafel slope scans were performed for each set of experimental conditions. The analyses sought to minimise the difference in the calculated result and the observed result as represented by a quantity defined as chi^2. A final chi^2 value of zero indicated a perfect fit of the data with typical values for good fits ranging between two and 100.

2.4 Laboratory corrosion experiments on cast iron and mild steel electrodes

The test solutions consisted of normal seawater and a range of chloride concentrations and pH values that reflect the increased alkalinity and reduced chlorinity that occurs during *in-situ* conservation treatments. The pre-disturbance *in-situ* pH was 6.85±0.27 with a mean E_{corr} of –0.224±0.022V vs SHE. The local seawater pH was 7.76 with a chloride concentration of 0.56M and the effect of chlorides at 0.01M and 0.001M at the same pH was examined. A 1.5M chloride solution at pH 5.50 represented a concreted microenvironment and the corrosion rate at 0.1M, 0.01M and 0.001M chloride were also examined. The NaCl solutions were prepared using AR grade chemicals from BDH and the pH was buffered to pH 5.50 and 7.76.

3. Results

Core samples were collected prior to anode attachment (29/11/01) and then 48 days (16/1/02) after attachment. The first 2cm and the next 10cm of the 30cm sediment cores were analysed for free zinc by Geotech Pty. Ltd and the results are listed in Table 1.

Table 1: Concentration of zinc in sediment samples collected before and after the use of sacrificial anodes.

Sample Name	29/11/2001 0-2 cm fraction [Zn] mg/kg	16/01/2002 0-2 cm fraction [Zn] mg/kg	29/11/2001 2-12 cm fraction [Zn] mg/kg	16/01/2002 2-12 cm fraction [Zn] mg/kg
Core 2	3	8 200	2	710
Core 6	5	18 400	2	980
Core 8	5	259 000	2	25 200
Core 10	12	1 380	2	53
Baseline	5	192 000#	2	12 500

This data point appears to be erroneous and may reflect sampling error.

4. Discussion

The colonisation of wrecks, which is dependent on a number of parameters including water depth, temperature and the season of the year, results in the separation of the anodic and cathodic reaction surfaces. Hard calcareous layers will reduce the corrosion rate of iron by virtue of the physical barrier it provides to dissolved oxygen (MacLeod, 1989b). *In-situ* pH and E_{corr} measurements have shown that a relative acidic and reducing environment exists inside the concretion in contact with the corroding iron where pH values can be as low as 4.2 and the chloride concentration higher than 1.5M. Acidity develops as a consequence of hydrolysis of the primary corrosion product $FeCl_2$ according to the equation described by North (1982).

$$2\,FeCl_2 + 2\,H_2O \rightarrow \beta\{Fe(OH)_2FeCl_2\} + 2H^+ + 2\,Cl^- \qquad 1$$

Both laboratory and shipwreck data indicates that corrosion is limited by the rate of the cathodic electrode process, i.e. by the rate of reduction of dissolved oxygen (MacLeod, 1995), thus the overall corrosion rate of iron is dependent on the flux of dissolved oxygen to the concreted surface. Analysis of data from a number of shipwreck sites shows that the logarithm of the corrosion rate of iron decreases linearly with increasing water depth (MacLeod, 2003). For iron objects that are totally buried under sediment the principal cathodic reaction involves the reduction of water, which is often facilitated by anaerobic bacteria.

4.1 In-situ conservation of iron objects using sacrificial anodes

Field measurements on the wreck were conducted between September 2000 and January 2002. The pre-disturbance corrosion potentials and pH values of the residual metal surfaces of the major structural iron features on the *James Matthews* site were measured (Table 2). In the outer zones, where the corrosion products are typically black, the potential measured is essentially a redox couple, measuring the ratio of Fe^{3+} to Fe^{2+}. Once the metal surface is reached and good electrical contact is established, this voltage will be the true corrosion potential (MacLeod, 1989a).

Table 2. Pre-disturbance electrochemical survey of iron on the *James Matthews* site.

Description	Surface pH	E_{corr} (V vs SHE)	Total drill bit penetration (mm)	Water depth (m)
Deck knee 1	7.12	-0.242	28-92	2.2
Deck knee 2	7.11	-0.274	8-20	2.2
Deck knee 3	7.95	-0.238	nd	nd
Deck knee 4	7.29	-0.226	nd	nd
Deck knee 5	7.45	-0.254	nd	nd
Deck knee 6	6.46	-0.320	18-105	2.1
Deck knee 7	7.37	-0.234	10-35	nd
Deck knee 8	7.37	-0.232	28-100	2.0
Windlass 10	6.31	-0.255	13-22	2.1
Chain 11	7.76	-0.266	25	1.8
Star picket 12	8.08	-0.344	5	1.8
Deck knee 13	7.01	-0.228	51-104	2.3

nd Not determined.

The iron structural features exposed to the oxidising marine environment present on this wreck site (Table 3) were covered with thick aerobic concretions heavily encrusted with secondary marine growth. Iron corrosion products are known biological stimulants so the overall depth of concretion is not surprising.

Table 3. Measured chemical and physical parameters on the *James Matthews* site.

Date	1 Nov 2001	7 Nov 2001	13 Nov 2001	15 Jan 2002
Water temp (°C)	20	22	24	nd
Depth (m)	2	2	1.3	2.2
pH seawater	8.32	8.24	8.40	8.56
E_h seawater (V vs SHE)	0.154	0.134	0.070	0.172
pH at sediment depth, cm	8.20 at 4.5	8.05 at 7	7.95 at 5	8.52 at 6
E_h at sediment depth, cm	-0.07 at 13	0.104 at 13	0.010 at 14	-0.056 at 13

The alkalinity of the seawater is significantly variable and this is largely a reflection of the level of industrial activity in the area of the nearby dredging spoil zone, which deposits calcareous plumes of debris on the site. Dissolved oxygen contents of sediments are notoriously difficult to measure accurately, therefore the E_h provides an indication of the level of oxygenation in the sediment. These results indicate that the wreck lies in a typical aerobic open circulation marine environment with the upper layer (<13cm) of sediment being slightly oxidizing and alkaline in nature and relatively mobile. By plotting the measured voltages and the corresponding surface pH's on the Pourbaix diagram for iron at 10^{-6}M in aerobic seawater at 25°C the thermodynamic stability of the iron can be ascertained. The results are shown in Figure 2.

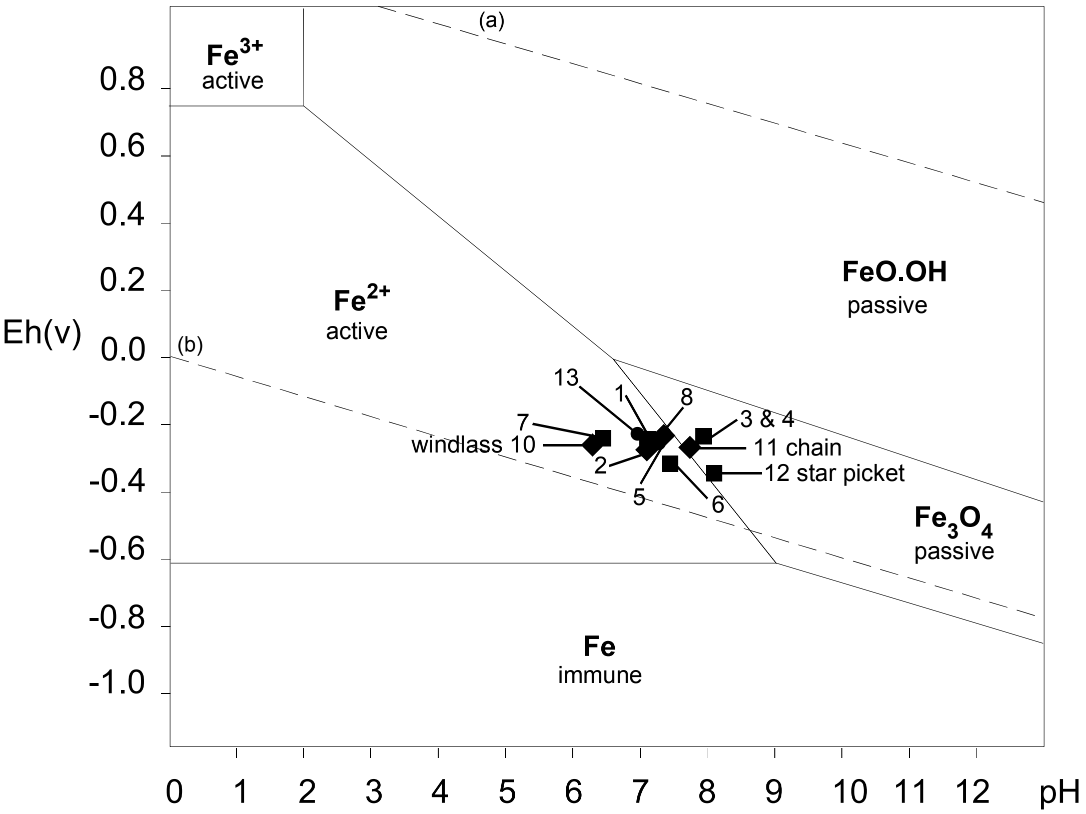

Figure 2. Pourbaix diagram for iron (10^{-6}M) in aerobic seawater at 25ºC on the *James Matthews*.

The Pourbaix diagram clearly shows that the windlass **10** and deck knees **1**, **2**, **5**, **6**, **7**, **8** and **13** on the *James Matthews* site are actively corroding. The deck knees and chain are wrought iron and the star picket is mild steel. The windlass **10** is a combination of cast and wrought iron however, the measuring and attachment holes on the windlass were drilled into a wrought iron bar. Cast irons typically contain 2-6% carbon by weight and this can be manifested in E_{corr} values that can be up to 50mV more positive than wrought iron in the same microenvironment. It should be noted that the differences in E_{corr} are also interdependent on the metallographic microstructure of the alloys. The pre-disturbance values of E_{corr} and pH measurements for deck knees **3**, **4**, chain **11** and star picket **12** indicated that these objects were in the passive zone of the Pourbaix diagram. In the case of knees **3** and **4** and the chain **11**, the value of the pH and E_{corr} is more a reflection of the advanced state of decay of the objects, since there was very little solid metal remaining so the driving force behind the build up of acidity has been diminished. It is not possible to make any direct comparison of the data from the star picket **12** with the deck knees owing to their different metallurgical composition and the vastly different times of immersion, since the star picket relates to field excavations in the 1970's. For the *James Matthews* site the average surface pH, for original artefacts with residual iron, was 6.85±0.27 and the mean E_{corr} was –0.224±0.022V at an average water depth of 1.8±0.2m. It should be remembered that Pourbaix diagrams can only be used as an indication of the thermodynamic stability of a metal in a specified environment (Pourbaix, 1974) and do not reflect differences in corrosion rates.

It was not possible to accurately assess the depth of corrosion on the *James Matthews* site since this would have involved removal of some of the protective concretion subsequently increasing the corrosion rate of the already extensively corroded iron fittings. The total depth of corrosion and concretion ranged from 5-105mm with an average of about 55mm. If we use the standard corrosion rate for iron in aerobic seawater at 0.1mmy^{-1} (La Que, 1975) and assume corrosion has been active on both sides of the fitting, a metal loss equivalent to about 32mm would leave a 50mm thick fitting with about 20mm of metal after 159 years. Given that some knees showed little to no residual metal, it could be safely assumed that some of these iron structures, with very large total depths of corrosion, have been corroding at an accelerated rate. Although it was not permitted to deconcrete the objects, plots of the average drill penetration (mm) against the E_{corr} data gives the following relationship,

$$\log_{\text{conc. thickness}} = 4.20 + 10.25\, E_{corr} \quad \ldots 3$$

for which the R^2 value was 0.989. This equation shows that there is a direct relationship between the log of the corrosion rate of iron, as measured by the concretion thickness and the corrosion potential. This assumes a direct connection between marine growth and the availability of iron as a growth stimulant. This data indicates that the *in-situ* E_{corr} data does provide a direct measure of the way in which the corrosion rate varies over the site.

Sandbagging the site in April 2001 resulted in a general lowering of the E_{corr} values since sediment had built up in the more exposed regions of the site and the deck knees and other higher profile material were partially reburied. Owing to the archaeological significance of the *James Matthews* and the mobility of the sediment, and since by November 2001 the previously reburied areas were re-exposed, it was decided to stabilise the heavily degraded knees *in-situ* through the application of sacrificial anodes. During the galvanic corrosion process chloride ions, which have accumulated as a result of the *in-situ* corrosion reaction, migrate towards the surrounding seawater. Although aluminium is more economical than zinc it has a tendency to passivate in aerobic seawater and it is unsatisfactory when buried under sediment, whereas zinc performs well in both environments and has good overall current efficiency (Morgan, 1993). The number of anodes and their size is calculated according to standard formulas in the cathodic protection literature, which take into account the wetted area of the iron structure to be protected (Shrier, 1976). Sacrificial zinc anodes were attached to selected deck knees (**1**, **2**, **13**, **6** and **8**) and the windlass (**10**) and the effectiveness of the treatment was gauged over time. The results of the electrochemical survey of the protected iron structures are shown in Table 4.

Table 4. Electrochemical survey of the protected iron objects during treatment.

Description of Iron Material	pH object 7 days	E_{corr} vs SHE 7 days	E_{corr} vs SHE 69 days	pH anode 7 days	E_{corr} anode vs SHE 7 days	E_{corr} anode vs SHE 69 days
Deck knee 13	8.01	-0.348	-0.466	7.02	-0.658	-0.676
Deck knee 1	n.d.	-0.520	-0.558			
Deck knee 2	8.35	-0.608	-0.590			
Deck knee 6	8.04	-0.738	-0.732	6.83	-0.748	-0.748
Deck knee 8	8.08	-0.453	-0.532	7.46	-0.638	-0.662
Windlass 10	8.35	-0.570	-0.608	7.43	-0.602	-0.620

Deck knees **1**, **2** and **13** were attached to the same anode with a spider-like arrangement and the E_{corr} data showed better protection after a further nine weeks. After 10 weeks of use the anodes had a loose covering of corrosion products that were cleared before E_{corr} was measured; the pH of the windlass anode was 5.74, which showed it is actively corroding. The surface pH of the iron objects after one week of treatment was directly linked to their E_{corr} values by the relationship,

$$pH_{object} = 4.76 - 0.64\ E_{corr} \ldots\ldots 4$$

Deck knee **6** did not conform to this relationship, which had an R^2 of 0.9383, as it was originally corroding at the lowest rate and had become totally protected with the anode. The other fittings generally demonstrated a more cathodic E_{corr} after a further nine weeks of treatment than that which was observed after one week. The increase in the pH of the iron objects is a direct measure of the *in-situ* treatment consuming acidity at the metal-concretion interface. Corrosion potential values of the iron objects on the *James Matthews* site before and after cathodic protection are shown on a Pourbaix diagram for iron in aerobic seawater (Figure 3).

Interpretation of the *James Matthews* pre-disturbance data is facilitated by a comparison with the *Xantho* shipwreck, where the mean E_{corr} of 25 measurements was –0.268V, at an average water depth of 3.5m (MacLeod 1986). This value is marginally more cathodic than the mean *James Matthews* E_{corr} value of -0.258V, as would be expected from the deeper site conditions. After the zinc anodes had been attached the drop in the corrosion potential was in the range $0.417<\delta E_{corr}>0.236$V, which is a greater degree of protection than was obtained on the *Xantho* stern where the drop in E_{corr} was only 0.115V but the anode was protecting a much greater surface area (MacLeod, 1986, 1996b). The submarine *Resurgam* had an average E_{corr} of –0.393V and this fell by 0.040V immediately after zinc anodes had been attached (Gregory, 2000), which indicated good connection but that the large vessel had not been polarised within the diving period. These voltage drops on the *James Matthews* site exceed the nominal value of 0.150V needed for reasonable protection. Full cathodic protection is afforded at voltages more negative than –0.610V (Shrier, 1976), therefore only deck knee **6** and the windlass **10** had effectively ceased corroding but the other fittings were undergoing active conservation treatment *in-situ* (Morgan, 1993).

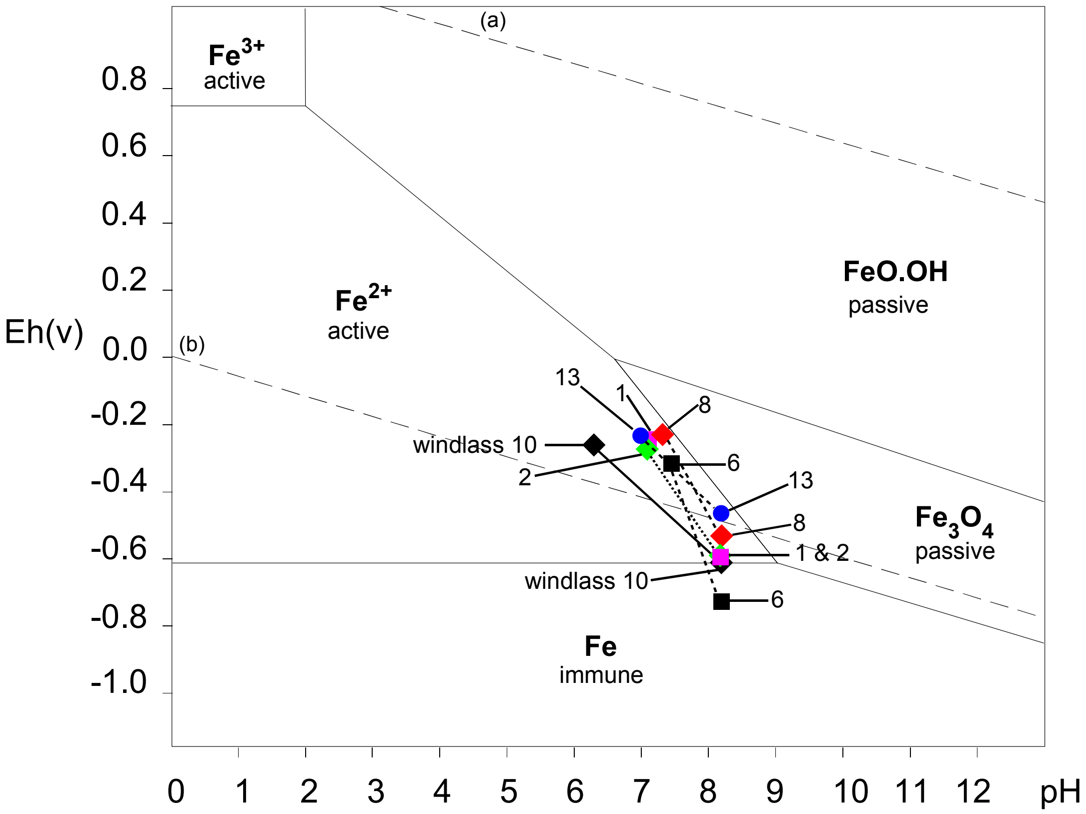

Figure 3. Pourbaix diagram for iron (10^{-6}M) in aerobic seawater at 25ºC, showing pre-disturbance measurements and those after two months of cathodic protection.

All the data on the *James Matthews* confirmed that the overall rate of iron corrosion has been dramatically reduced. The anode attached to deck knee **6** had achieved the greatest protection and this was reflected in the surface pH of the anode being the lowest at 6.83, as the result of hydrolysis of Zn^{2+} from the corrosion reaction. The differences in the apparent efficiency of the anodes is likely to be due to the surface areas being protected rather than being due to poor electrical connection to the objects. When the data in Table 4 was compared with the pre-disturbance values it was found that after 90 days, the changes in E_{corr} were related to the original E_{corr} values by the following,

$$\delta\, E_{corr} = 0.196 + 1.89\ {}^{original}E_{corr} \quad \ldots\ldots 5$$

which had an R^2 of 0.9964. Although there were only three of the data points that lay on the line, namely deck knees **2**, **6** and **13**, the other knees **1** and **8** followed a similar trend, along with the windlass **10**, as shown in Figure 4. Thus the changes in corrosion potentials were seen to be consistent in that the knees that were corroding at the slowest rate, those with the lowest E_{corr} values, were the most protected by the anodes whilst those which were corroding at a faster rate had the smallest change in E_{corr}. All this implies is that it will take longer to stabilise the objects that are most at risk.

The zinc analyses of the sediments (Table 1) indicate that the zinc corrosion products are generally retained in the sediments close to their position on the seabed. Although the concentrations of zinc in the sediments immediately below the anodes exceed the 410mg/kg limit of the Australian and New Zealand Environmental and Conservation Council Interim Ocean Disposal Guidelines (ANZECC, 2000), the impact of such localised concentrations on the marine ecology needs further ecotoxicological assessment. Toxicity testing of these levels of zinc on the local marine biota needs to be investigated as it appears that much of the zinc has precipitated in the sediment and may not be in a biologically available form (Morrison, 1999).

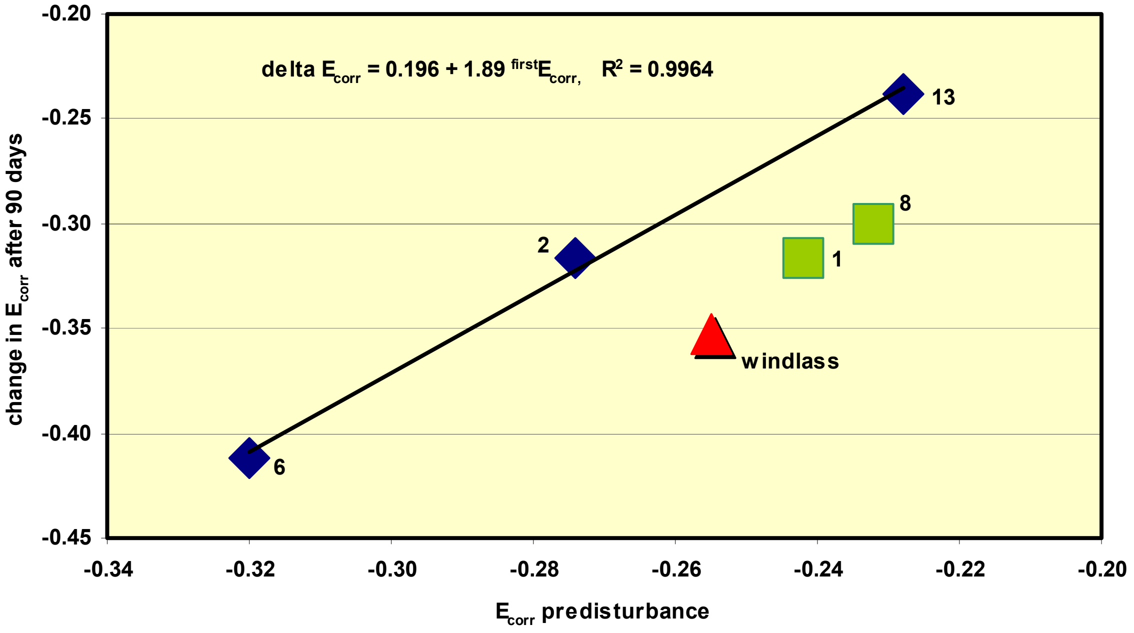

Figure 4: Plot of the change in E_{corr} as a function of the pre-disturbance values.

4.2 Laboratory corrosion experiments on cast iron and mild steel electrodes

Corrosion testing of the iron electrodes provides a measure of the corrosion rates when the corroding, chloride rich acidic interface of the concreted alloys are suddenly directly exposed to dissolved oxygen in the seawater. It is understood that experimental observations relate directly to the laboratory environment but the trends in corrosion behaviour will reflect aspects of the *in-situ* environment. Although the final outcome of the *in-situ* treatment of the *Sirius* carronade, which removed more than 80kg of chloride on the seabed, was a stable conserved object, little is known about the changes to the object that occurred on the seabed (MacLeod, 1998b). The data obtained with the experiments using the cast iron electrode is summarised in Table 5 and Figure 5 but the most significant feature was that the corrosion rate was linearly dependent on the log of chloride ion concentration. Thus the direct effect of reduced chloride ion activity on the corrosion rate is less than might have been simplistically predicted.

Table 5: Cast iron corrosion rate as a function of chloride and pH.

Medium	Corrosion rate, mm/year	Standard deviation	pH
Seawater	0.460	*	7.76
1.5 M Cl^-	0.890	0.062	5.58
0.100 M Cl^-	0.587	0.015	5.26
0.010 M Cl^-	0.330	0.013	5.49
0.010 M Cl^-	0.326	0.030	7.98
0.001 M Cl^-	0.097	0.100	5.30
0.001 M Cl^-	0.151	0.018	8.18

* Passivation of the electrode resulted in only two reliable data sets.

The corrosion rate of cast iron in seawater was lower than would have been predicted solely on the basis of chlorinity due to effects such as the activity of carbonate ions in the seawater. In 0.001M and 0.01M chloride, the change in pH from 5.50 to 7.76 had little effect on the overall corrosion rate. The implications of this observation is that during the *in-situ* conservation of cast iron objects, the increased alkalinity of the solution under the concretion will have a much smaller effect on the overall corrosion process than the reduction in the chloride ion concentration. Increased alkalinity in the concretion matrix brings about precipitation of a number of iron corrosion products, which increases the resistivity of the concretion and lowers the corrosion rate.

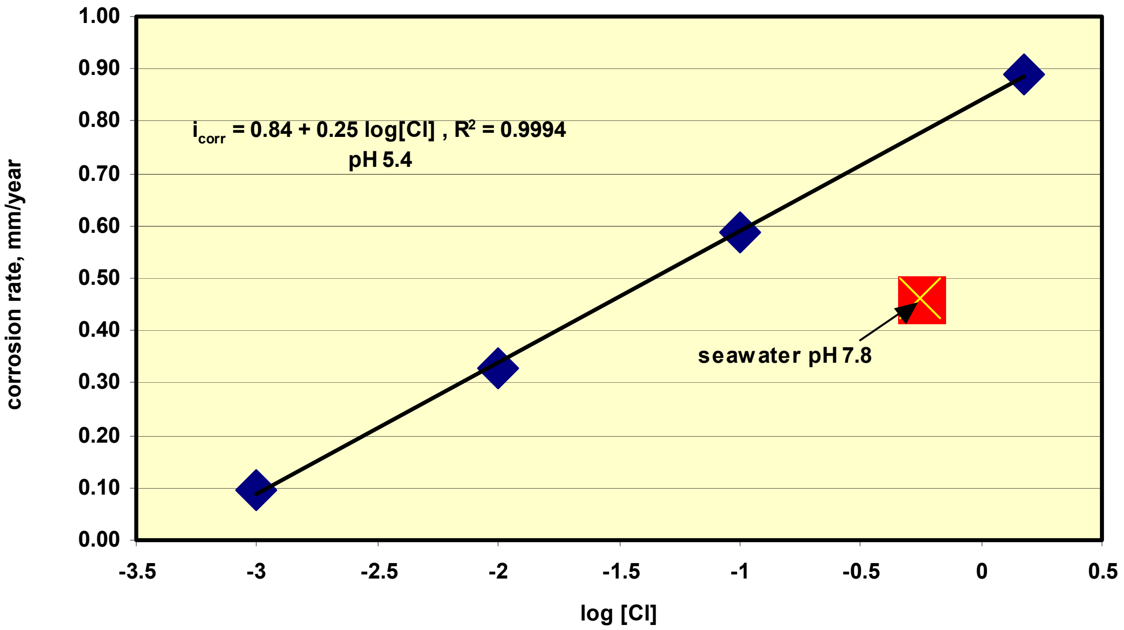

Figure 5: Effect of chloride concentration on the corrosion rate of cast iron at pH 5.40.

The general relationship between the cast iron corrosion rate in mmy^{-1} and chloride ion concentration is given by

$i_{\text{corr}} = 0.84 + 0.25 \log [\text{Cl}^-]$ 6

which had an R^2 of 0.9994 for the four points noted in Figure 5, which were in the more acidic environment with an average pH of 5.41±0.15. It is noted in Figure 5 that the corrosion rate in seawater is lower than in the same pH predicted by the equation. This lower rate in seawater is likely to be due to the specific effects of pH through the presence of carbonates. The overall impact of the more alkaline environment is seen by the relationship,

$i_{corr} = 0.50 + 0.11 \log [\text{Cl}^-]$ 7

where the mean pH was 7.97±0.21with an R^2 of 0.947. More measurements and testing over a wider range of pH values is needed to confirm the nature of this apparent trend reducing the effect of the chloride ion concentration on the corrosion rate. The different intercept values of the two equations also support the observation that corrosion rates decrease in more alkaline solutions. The corrosion rates at either pH would be the same when a chloride ion concentration of $3.7\text{x}10^{-3}$M was reached. An indicator of the way in which the corrosion mechanism changes with chloride concentration is found in the relationship between the anodic Tafel slope β,

$\beta_{anodic} = 3.57 - 8.65 \log [\text{Cl}^-]$ 8

which has an R^2 of 0.9343 for the six data points that conformed to the above relationship. In simple terms this means that the amount of corrosion overpotential needed to bring about a ten-fold increase in the corrosion rate i.e. β_{anodic} increases as the amount of chloride decreases.

The corrosion rates on the 19th century mild steel electrode were examined over the pH range of 8.2 of seawater to fresh sodium hydroxide solutions at pH 13.8 and the corrosion rate was found to conform to equation 9,

$i_{corr} = 0.328 - 0.0194\,\text{pH}$ 9

which had an R^2 of 0.9922 for the four data points. In simple terms this means that the corrosion rate in normal seawater is 0.17mmy^{-1}, which is not widely removed from the average long-term corrosion rate of iron in open seawater (0.1mmy^{-1}) (La Que, 1976) and the corrosion rate will fall by 11.4% per unit increase in pH. Thus it can be seen that the increased alkalinisation of the concreted deck knees will result in a significant fall in the overall corrosion rate. When the reciprocal of the polarisation resistance was plotted as a function of chloride it was found that the following relationship existed, namely

$1/R_p = 0.0002 + 0.0016\,[\text{Cl}]^{½}$ 10

Further work is needed to determine the precise nature of the reasons for the 19th century mild steel and the cast iron having different corrosion dependencies on the chloride ion concentration. However, the main point to note is that the use of *in-situ* conservation treatments for iron fittings will not only remove chloride ions but will reduce the corrosion rate through a combination of increased alkalinity and decreased chlorinity.

5. Conclusion

Samples of some 19th century steel, which simulates aspects of the corrosion behaviour of wrought iron, have been shown to increase the corrosion rate with the square root dependence on the chloride concentration. This dependence may be a reflection of diffusion controlled processes dominating the oxidation of the iron metal. Cast iron electrodes showed an increased corrosion rate that increased linearly with the logarithm of the concentration of chloride. The differences in corrosion mechanism of the iron alloys are likely to be due to their different microstructures. The site of the *James Matthews* was used to demonstrate the value of obtaining pre-disturbance survey data on the *in-situ* pH, E_{corr} and thickness of the iron marine concretion. The application of zinc sacrificial anodes to effect *in-situ* conservation of the objects has been shown to be an effective method of site stabilisation.

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SS *Great Britain* iron hull: modelling corrosion to define storage relative humidity

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Abstract

Brunel's wrought iron ship Steam Ship *Great Britain* is corroding in its dry dock in Bristol. Corrosion control will involve sealing and desiccating the dock. The corroding iron hull forms chloride rich βFeOOH and during desiccation ferrous chloride is likely to form. βFeOOH/iron and $FeCl_2.4H_2O$/iron were subjected to controlled relative humidity (±1%) and corrosion thresholds were experimentally determined. Iron in contact with these compounds corroded above the thresholds but not below them. Iron did not to corrode in the presence of $FeCl_2.2H_2O$. The stability of this compound to moisture was determined. Corrosion was extremely slow just above corrosion thresholds, but increased significantly as relative humidity values rose to 30%. These results are being used to set an operational relative humidity for the desiccated environment around the ss *Great Britain* and to offer new conservation options for other historic ships.

Keyword: iron, corrosion, ferrous chloride, β-ferric oxyhydroxide, relative humidity, storage.

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1. Introduction

1.1 ss *Great Britain*: Historical context

The 1843 wrought iron steamship ss *Great Britain* was salvaged from the Falkland Islands in 1970 and placed in the Great Western Dockyard in Bristol, which had been constructed especially for building the ship, making it the first integrated iron shipbuilding yard in the world (Figure 1). In its open air dry dock the iron hull of the ss *Great Britain* equilibrated with its environment, which rarely drops below 70% due to climate, seepage of water through the docksides, faulty drainage and a leaking caisson (Cox and Tanner 1999, Turner *et al* 1999).

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Figure 1. ss *Great Britain* in the historical Great Western Dockyard Bristol.

Initial evaporation of seawater from the hull left behind highly soluble and deliquescent chloride salts, which are unlikely to be present in their solid crystalline form, due to the high ambient relative humidity in the dock. They will be solvated within corrosion layers, micro cracks, pits and in the overlaps between iron hull plates at rivet points. In this state their contribution to the electrolytic corrosion of the iron will be significant; even though rain-wash over the years and an aqueous pressure wash, which was used as an early conservation method, will have reduced their concentration. The hull is rapidly corroding in the high relative humidity within the dock environment and engineering reports estimate that it will be structurally unsafe in about 25 years (Turner *et al* 1999).

1.2 Conservation programme

Early conservation and maintenance of the hull had involved 10,000 psi aqueous pressure blasting and traditional shipyard practices that applied 'protective' coatings (Turner *et al* 1999). Understandably these measures failed to either stop corrosion or to appreciably slow its progress (Figure 2).

Figure 2. Ongoing corrosion of the ss *Great Britain* hull in dry dock.

A long-term development plan adopted a mission statement in 1998:
"To preserve the ship, ss Great Britain, and it's building dock for all time for the public benefit of all, and to place the same upon public display as a museum for the enhancement of public understanding and appreciation of her social, commercial, scientific and technological context and significance."

The decision from the ss *Great Britain* Trust *"to conserve fully to the highest standards the extant fabric of the ss Great Britain (1843-1970) and its building dock"* (Cox and Tanner 1999) defined future preservation by firmly recognising it was a conservation task, rather than a restoration programme. The corroded wrought iron plates of the hull are considered an essential part of the ship's fabric and are to be conserved in situ, with their corrosion in place, rather than replaced with mild steel replicas.

The current conservation plan identified the condition of the ship and reviewed conservation options (Turner *et al* 1999). It was clear that the condition of the iron and the length (322 feet) of the hull rules out many conservation approaches. Methods employing stripping or traditional surface treatments for ships would damage the badly corroded hull (Table 1). Treatments designed to remove or inhibit the action of chlorides are unpredictable and offer technical limitations on a large scale project (Table 2). The amount of chloride that remains in iron after chloride extraction procedures have been applied cannot be known. It will remain as an unknown threat to the future stability of the iron.

Condition	**Percentage of hull**
Good condition	3%
Areas covered with GRP, concrete or timber	8%
Areas severely corroded – likely to disappear upon abrasive cleaning	17%
Areas in fair condition – much iron likely to survive abrasive cleaning	29%
Areas of severe corrosion – likely to be perforated by abrasive cleaning	43%

Table 1. Assessment of condition of the ss *Great Britain* hull (data from [2])

Treatment	**Comment on treatment within context of ss Great Britain conservation plan**
Aqueous wash	Inefficient and unpredictable level of chloride extraction; aerated environments provide lower chloride extraction than deaerated (Selwyn and Logan 1993, Scott and Seeley 1987, Watkinson 1982 and 1996).
Alkaline sulphite	Better aqueous chloride extraction due to alkali and deaerated environment, but normally less than 90% chloride removed; caustic solution; impractical on scale required (Gilberg and Seeley 1982, Knight 1997, North and Pearson 1975, Rinuy and Schweizer 1982, Selwyn and Logan 1993,Turgoose 1985, Watkinson 1996).
Sodium hydroxide	Between 55% and 80% chloride removed in aerated environments; caustic solution; impractical scale (North and Pearson 1978, Watkinson 1982, 1983 and1996).
Alkali wash	Sodium Carbonate wash; used with Holland 1 submarine; efficiency as chloride remover unknown; practical application problems with very corroded structures; disposal of treatment solution (Barker *et al* 1997, Knight 1997).
Electrolysis	Varying reports on efficiency and stability; disposal of electrolyte is a problem; challenging on a large scale; better with substantial metal cores; hull is extensively mineralised in places (Knight 1997, Selwyn and Logan 1993, Selwyn *et al* 2001).
Hydrogen reduction	Effective chloride removal; reactive pyrophoric iron produced; ethically questionable; impractical on scale required (Barker *et al* 1982, Birchenall and Meussner 1977, Tylecote and Black 1980).
Inhibitors	Inhibitor action is unpredictable on heavily corroded iron surfaces that are contaminated with chloride; toxicity limits choice (Argryropoulos *et al* 1997, Skerry 1985, Turgoose 1985) .
Cathodic protection	Hull lacks metallic continuity due to areas of total mineralisation that are being retained as part of the conservation rationale.

Table 2. Limitations of more traditional interventive methods used on chloride infested iron.

In order to employ a conservation method whose effectiveness could be successfully modelled and tested prior to implementation, it was decided to conserve the iron hull by controlling the availability of water to support the corrosion processes (Turner *et al* 1999). Desiccation is the both the least interventive and least unpredictable method for preserving the ss *Great Britain*. As part of their ethical framework the ss *Great Britain* Trust was pleased to be able to choose a treatment option that retained the iron corrosion layers on the hull.

To implement this conservation option the corrosion processes occurring on the hull need to be identified and their response to relative humidity assessed by modelling corrosion in the laboratory. In this way the degree of desiccation required to prevent them occurring can be measured. This data can then be used to design a controlled storage environment that moderates or prevents corrosion.

Desiccating the environment around the hull is a technically challenging task that involves constructing an envelope around the ship and controlling the relative humidity within this space. Consulting with architects and climate control engineers produced an option that would roof the dry dock with glass, from the waterline of the ship to ground level at the dockside. The interior of the ship would be modified to produce an environment with minimum air leakage between the lower and upper decks. Within this space encompassing the exterior and interior of the hull below its original water line, moisture levels will be controlled to a value that will either dramatically reduce or prevent chloride and chloride bearing compounds contributing to corrosion of the iron hull. Visitors would have access to both the interior of the hull below the waterline and the dry dock facility (Figure 3). The hull will appear to float in its dry dock, as the roof will have water across it. Above the waterline the hull has lower chloride levels and is in good condition, making it suitable for a coating system.

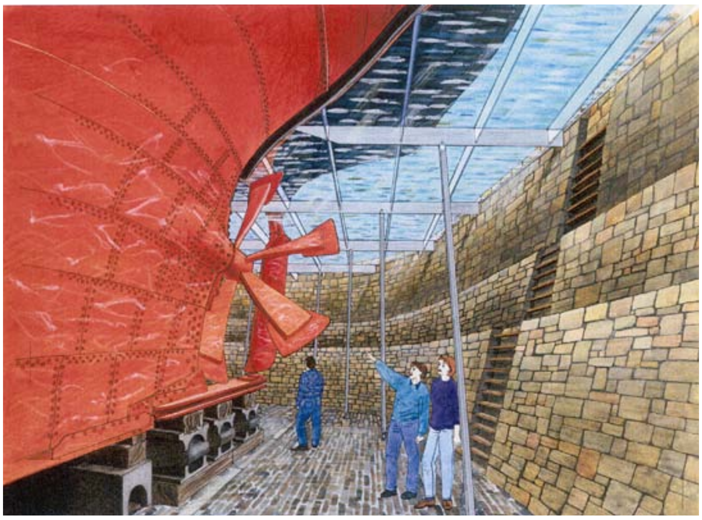

Figure 3. Artist's impression of the controlled dock space enclosing the ss *Great Britain's* hull.

1.2 Desiccation for corrosion prevention

Desiccation of iron has been employed for over 40 years, with varying degrees of success, to store and preserve archaeological iron (Watkinson and Neal 1998). Remarkably, very little investigation of this process has been carried out, yet it remains the storage mainstay for archaeological iron. Turgoose (1982a and b) and Selwyn *et al.* (1999). provided some information on the corrosion of chloride infested iron during burial and following excavation, there are no accurate figures on the level of desiccation necessary to prevent corrosion of chloride infested iron.

The design for successful desiccation depended on the ss *Great Britain* Project identifying how relative humidity affected corrosion reactions that could occur on the hull. The cost of dehumidifying an environment is closely linked to the target relative humidity. Very low relative humidity values will cost much more money to achieve and sustain, due to plant requirements for dehumidification and tolerances in the architectural design of the controlled space.

The ss *Great Britain* Trust sought to:

- Determine how corrosion reactions occurring on the iron hull were influenced by relative humidity.
- Identify the relative humidity at which corrosion of iron in chloride infested environments ceases.
- Explore how the rate of corrosion of chloride infested iron changes with relative humidity.
- Use this data to model a storage environment that will enhance the life of the iron hull by either preventing or reducing corrosion rate according to the resources available to them;
- Offer this model as part of an £8.4 million bid to the Heritage Lottery Fund for support to conserve the ss *Great Britain* and its historic dockyard.

1.3 Corrosion of the ss *Great Britain* iron hull

Analysis of the hull revealed significant amounts of soluble chloride in the corrosion product and the presence of βFeOOH (Akageneite), Fe_3O_4 (Magnetite) and other FeOOH (ferric Oxy-hydroxide) polymorphs. βFeOOH was identified by XRD (Figure 4) and Soxhlet extraction of corrosion products from various parts of the hull revealed chloride levels within the 160 to 3200 ppm range (Turner *et al* 1999). Since chloride is concentrated at anode sites at the metal surface overall chloride levels in the hull are likely to be much higher than the measurements suggest (Ishikawa *et al* 1988, Selwyn *et al* 1999, Turgoose 1982a,Watkinson 1983).

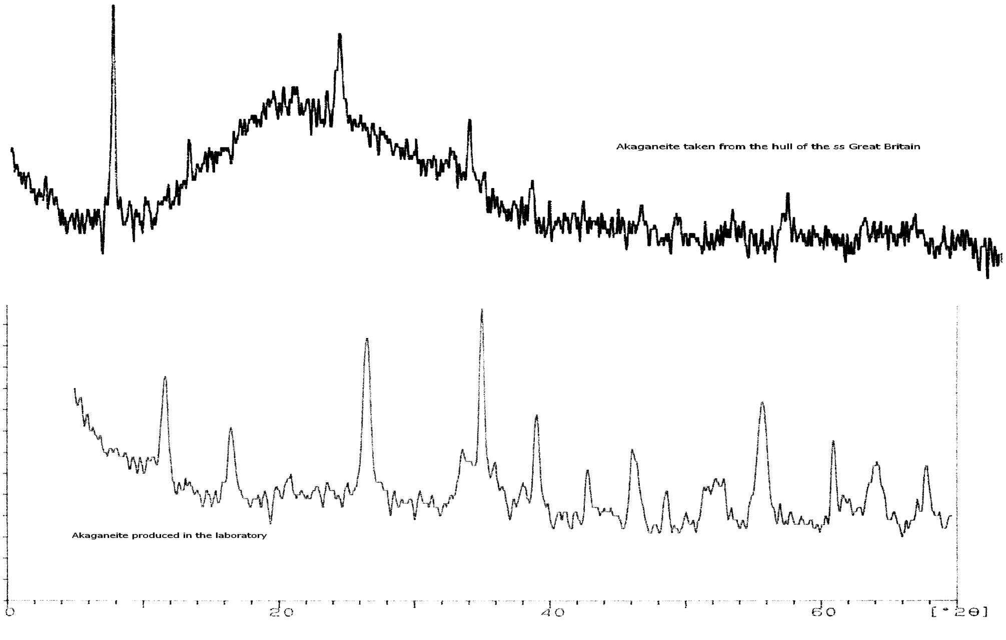

Figure 4. Comparison of XRD spectra for laboratory produced βFeOOH (Akaganeite) (bottom) and a sample taken from the hull of the ss Great Britain (top). The broad hump in the upper spectra was due to mounting the sample on a glass plate. (International powder diffraction files JCPDS 42-1315 and 34-1266.)

The presence of these corrosion products fits the corrosion model suggested by Turgoose (1982a and 1982b) in which Fe^{2+} is oxidised and resulting acid can attack iron directly to free more Fe^{2+}. There is also free chloride in solution acting as an electrolyte (Equation 1). Selwyn *et al* (1999) cited a cycle involving acid attack on iron by HCl, which is also described for pitting by Jones (1992).

$$4Fe^{2+} + O_2 + 6H_2O \rightarrow 4\beta FeOOH + 8H^+ \qquad [1]$$

In the environment within the dock area the iron hull is currently corroding rapidly due to high ambient relative humidity that allows the soluble chloride to act as an electrolyte to support corrosion. This situation will change when the hull is dried within its new controlled storage environment. Chloride will concentrate as the moisture within the iron evaporates. Anode sites will become increasingly acid due to hydrolysed Fe^{2+} and this provides low pH conditions in which solid $FeCl_2.4H_2O$ may form (Jones 1992, Turgoose 1982a).

1.4 Low humidity corrosion of chloride infested iron

Turgoose (1982a) identified iron corrosion processes involving $FeCl_2.4H_2O$ and βFeOOH that occur at low relative humidity. Iron corrodes when mixed with ferrous chloride at 20% relative humidity, but it does not corrode when the relative humidity is 15% (Turgoose 1982b). This is attributed to the stability of $FeCl_2.4H_2O$ at the higher humidity and $FeCl_2.2H_2O$ at the lower humidity. The water in $FeCl_2.4H_2O$ is thought to support electrolytic corrosion, whereas $FeCl_2.2H_2O$ does not contain enough water to do this.

Turgoose (1982b) postulated that βFeOOH is hygroscopic and that this contributes to corrosion of iron in contact with it. βFeOOH contains chloride in its crystal structure and adsorbs it onto its surface when it forms in chloride rich environments (Ishikawa *et al* 1988). This chloride can become mobile in moisture that is attracted to its surface and it may be this that facilitates either the electrolytic corrosion of iron or direct acid attack on iron (Lewis and Watkinson, forthcoming).

1.5 βFeOOH on the hull of the ss *Great Britain*

The hull of the ss *Great Britain* will carry two forms of βFeOOH. The first will have formed in the atmosphere during the past 35 years. Much of this βFeOOH is subject to rain wash, which is likely to have removed most of its surface adsorbed chloride. If mobile surface adsorbed chloride causes iron in contact with βFeOOH to corrode, then washed βFeOOH should not corrode iron.

βFeOOH will also be present as a corrosion product in areas of the ship that are not rain-washed and it will form as iron corrodes during the proposed desiccation of the hull. This βFeOOH will retain its surface adsorbed chloride and present a corrosion threat to iron that it is in contact with, provided the storage relative humidity supports the βFeOOH/iron corrosion reaction.

It is reported that βFeOOH is metastable with respect to αFeOOH over a 25 year time period (Gilberg and Seeley 1981). This offers dangers for the ship as its transformation to αFeOOH will release chloride that can potentially act as an electrolyte. An FTIR assay of a 23-year-old sample of βFeOOH that was stored in a closed glass jar in the conservation laboratories at Cardiff University, revealed the same composition as when it was produced. It is also known that pH influences transformations of βFeOOH. These are areas that require further study.

Based on the corrosion model involving βFeOOH and ferrous chloride, experiments were carried out to link relative humidity to corrosion of chloride infested iron in low humidity environments. Results were used by the ss *Great Britain* Trust to help design their storage environment.

2. Experimental Procedure

2.1 The experiments carried out in this study aimed to:

- Confirm that iron does not corrode in the presence of $FeCl_2.2H_2O$
- Identify the highest relative humidity at which $FeCl_2.2H_2O$ exists before it converts to $FeCl_2.4H_2O$
- Examine the corrosion of iron mixed with $FeCl_2.4H_2O$ at various relative humidities.
- Establish the relative humidity at which iron mixed with βFeOOH ceases to corrode.
- Examine the corrosion of iron mixed with unwashed βFeOOH at selected relative humidities.
- Remove surface adsorbed chloride from βFeOOH (this simulates rain-wash of this corrosion product) and determine whether washed βFeOOH corrodes iron.

Results of the experiments were used to recommend:

- A relative humidity below which iron does not corrode if mixed with ferrous chloride
- A relative humidity below which iron does not corrode if mixed with βFeOOH
- Offer comment on the rate of corrosion of ferrous chloride/iron and βFeOOH/iron mixtures at relative humidity values that were slightly above the “no-corrosion” relative humidity identified above.

This data was used by engineers and architects to design climate control plant and the tolerances of the dock and hull seals that would create the storage space around the ss *Great Britain* Hull.

2.2 Research method

Analar grade $FeCl_2.4H_2O$ and pure iron powder were purchased and βFeOOH was synthesised by exposing pure iron powder and ferrous chloride to 92% relative humidity until the iron oxidised completely, which took several months. The resulting assay showed 99% βFeOOH and 1% αFeOOH (Figure 4).

Washed βFeOOH was produced by subjecting synthesised βFeOOH to aqueous Soxhlet wash until no more chloride was being released into the wash solution, as determined by specific ion meter. At this point it was deemed that mobile surface chloride is lost from the βFeOOH and only the chloride locked in the crystalline hollandite tunnel structure of the βFeOOH would remain (Childs *et al* 1980, Gilberg and Seeley 1981, Ishikawa and Inouye 1972, Ishikawa and Inouye 1975). Unless otherwise stated all βFeOOH used in experiments reported here is unwashed.

Testing involved the use of a climatic chamber that controlled relative humidity to ±1% (established by test calibrations) and $\pm 0.5^{o}C$. Test samples were placed on a balance (accuracy 0.0001g) in the chamber. The balance was calibrated for accuracy and drift using a standard weight, exposed to 20% relative humidity at $20^{o}C$ for several days. Systematic error was reproducible and slight balance drift could be accounted for when analysing trends.

The chamber can be programmed to operate either at a particular relative humidity or on a particular relative humidity programme. Weight changes were dynamically monitored to file every five minutes. Visual inspection, XRD and FT-IR were used to determine change in the sample composition and attribute weight change to one or a combination of; iron corrosion; oxidation of corrosion product; desiccation or hydration. In this way the influence of relative humidity on the corrosion process could be monitored and graphic results show weight variation of test samples against time for fixed humidity values. All tests were standardised at $20^{o}C$ enabling conversion between relative and specific humidity. For consistency results are hereafter reported in terms of relative humidity.

3. Results

Samples of $FeCl_2.2H_2O$ and $FeCl_2.4H_2O$ were mixed with iron powder and exposed to differing relative humidities. A sample comprising $FeCl_2.2H_2O$ and iron powder did not gain weight after 20000 minutes (13.9 days) at 19% relative humidity (Figure 5). This showed that $FeCl_2.2H_2O$ is the stable form of ferrous chloride at 19% relative humidity and iron does not corrode in the presence of $FeCl_2.2H_2O$. Both hydration to $FeCl_2.4H_2O$ and oxidation of iron to FeOOH would have produced a weight increase. In contrast $FeCl_2.4H_2O$ mixed with iron powder gained weight at 22% and 27.5% and 35% relative humidity. This confirmed that $FeCl_2.4H_2O$ is the stable form of ferrous chloride at 23% relative humidity and above and that it corrodes iron in contact with it. Corrosion is slow at 22% relative humidity but speeds up appreciably at 35% relative humidity.

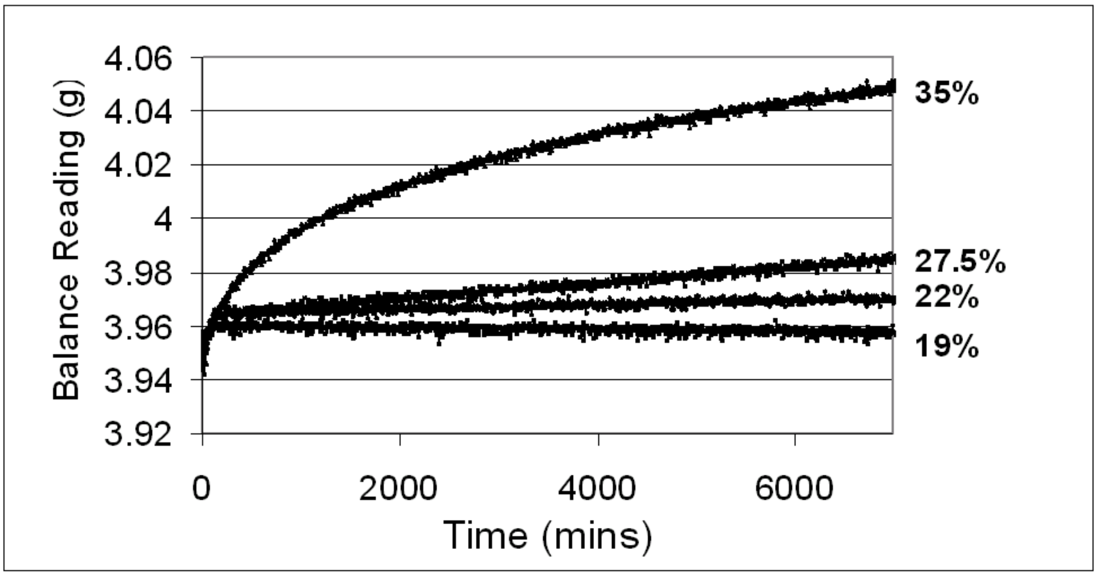

Figure 5. The line at 19% relative humidity is $FeCl_2.2H_2O$ mixed with iron powder. The lines at 22%, 27.5% and 35% relative humidity are $FeCl_2.4H_2O$ mixed with iron powder. All samples exposed for 14 days

The corrosive effect of $FeCl_2.4H_2O$ on iron at different relative humidities is seen in Figure 6. Samples comprising 2g of $FeCl_2.4H_2O$ mixed with 2g of iron powder were exposed to differing relative humidities. Percentage weight change at 4000 minutes is compared. Below 25% relative humidity corrosion is limited. As relative humidity rises corrosion increases and is ten times greater at 30% relative humidity as compared to the rate at 25% relative humidity.

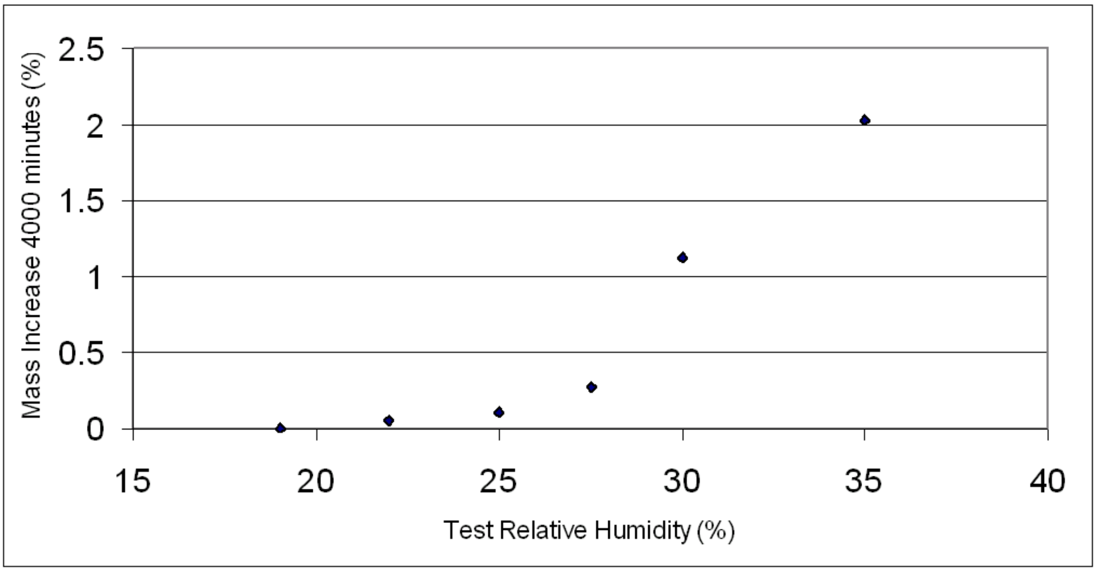

Figure 6. The response of 2g $FeCl_2.4H_2O$ /2g iron powder mixtures to relative humidity. Increase in mass as a percentage, after 4000 minutes at a particular humidity.

Using the 19% no-corrosion marker for iron chloride mixed with iron powder determined in Figure 6, a mixture of βFeOOH and iron powder was exposed to 19% relative humidity for 4000 minutes (2.8 days). Initially weight was lost due to dehydration of the βFeOOH and this masked any corrosion taking place. At 2000 minutes the sample started to gain weight due to corrosion of the iron, whose contribution to weight gain exceeded any continued weight loss due to dehydration (Figure 7). Corrosion then continued at a slow steady rate. Iron in contact with unwashed βFeOOH corrodes at 19% relative humidity.

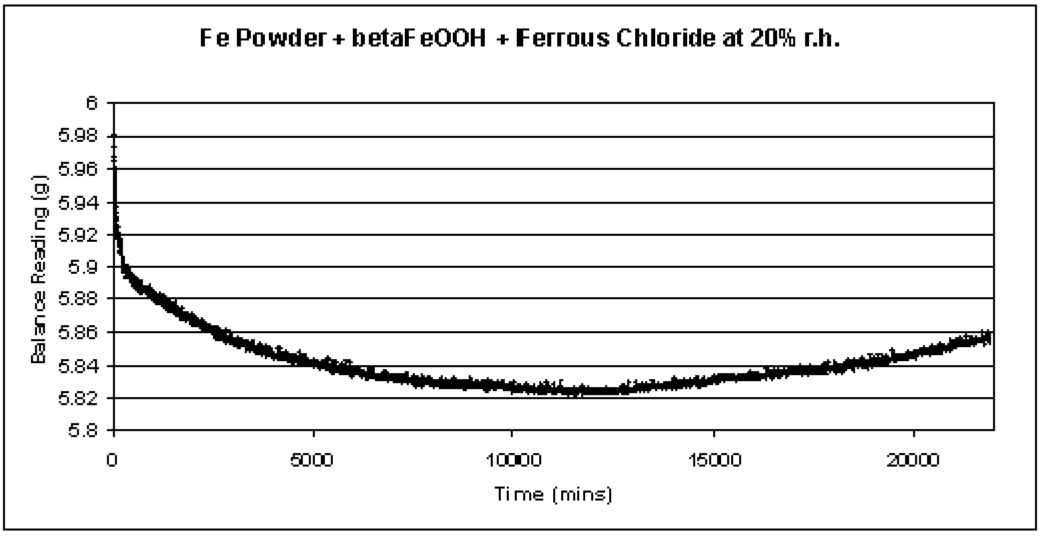

Figure 7. βFeOOH mixed with iron powder exposed to 19% relative humidity for 4000 minutes.

Mixtures of unwashed βFeOOH and iron powder were exposed to a range of relative humidities to determine the point at which the corrosion of iron ceased when in contact with unwashed βFeOOH (Figure 8). All samples showed a rapid initial desiccation of βFeOOH. Iron/βFeOOH mixtures did not measurably corrode at 12% relative humidity over the duration (16000 minutes) of the test but clearly corroded at 15% relative humidity.

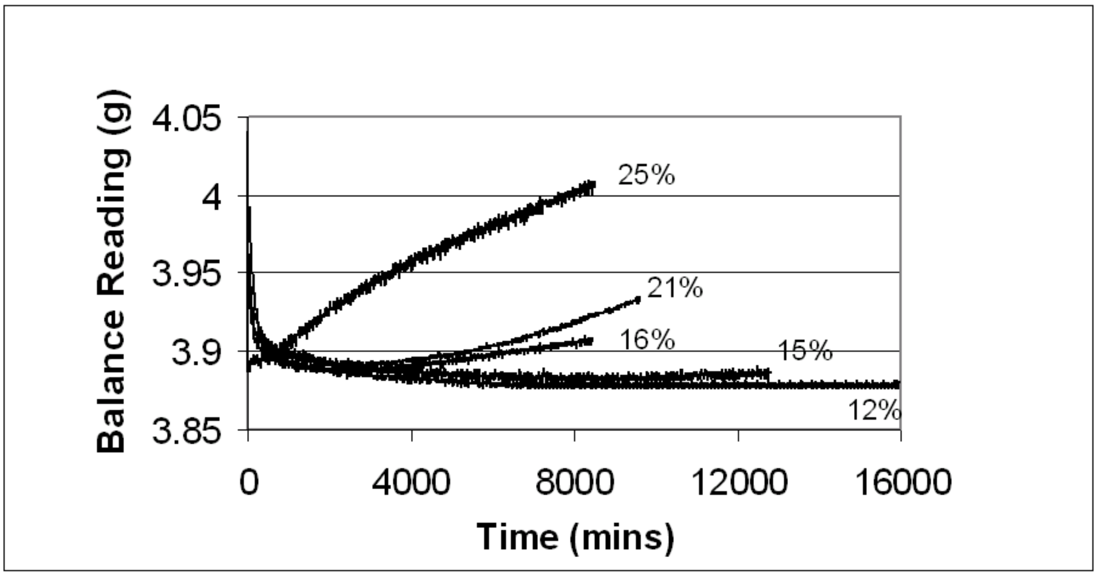

Figure 8. Samples comprising 2g of βFeOOH mixed with 2g of iron powder exposed to 12%, 15%, 16% 21% and 25% relative humidity.

A sample of washed βFeOOH/iron powder was exposed to 19% relative humidity. When compared to the unwashed sample at 19% relative humidity (Figure 7), it is clear that removal of surface chloride has eliminated the immediate aggressive corrosive effects of the βFeOOH on iron (Figure 9). The lack of weight loss by the sample may indicate that surface adsorbed chloride is responsible for the majority of the hygroscopic behaviour of βFeOOH. Our initial comments are that this may be due to the association of chloride with water and subsequent production of HCl on the surface of the βFeOOH, which then attracts water. Once chloride has been removed surface sites are occupied by hydroxyl ions from the wash solution. More research is required to investigate this theory.

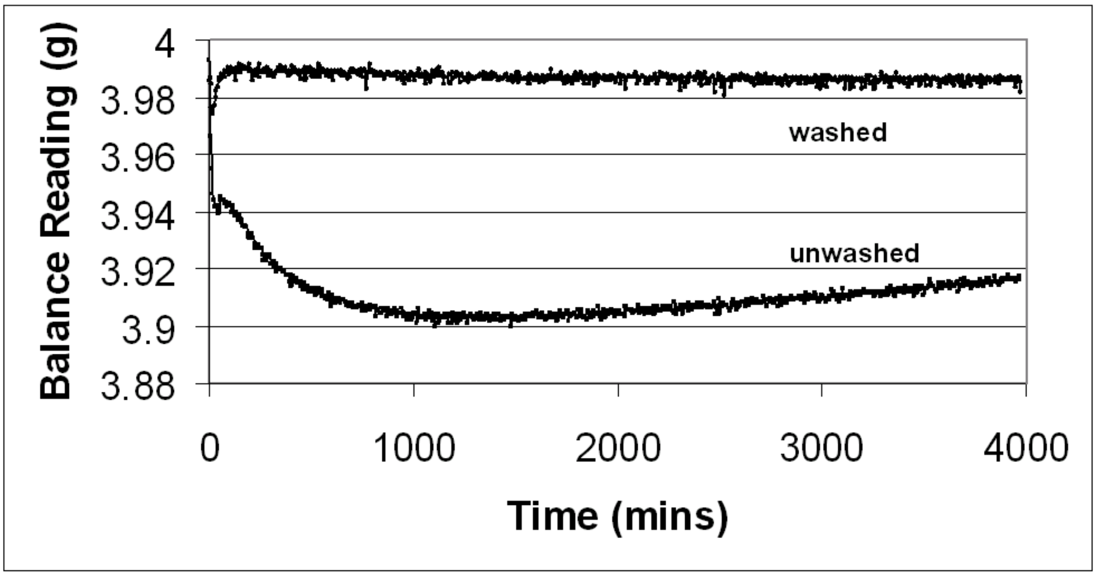

Figure 9. Washed βFeOOH/iron powder mixture exposed to 19% relative humidity, as compared to an unwashed sample of βFeOOH/iron powder.

A mixture of 2g quantities of $FeCl_2.4H_2O$, unwashed βFeOOH and iron powder was exposed to 20% relative humidity. A significant loss in weight occurred from dehydration of the corrosion products during the first 12000 minutes (8.3 days) (Figure 10). This was followed by steady weight gain due to corrosion of the iron. Corrosion of iron in contact with βFeOOH will occur at 20% relative humidity. Since $FeCl_2.2H_2O$ is stable at 19% relative humidity and $FeCl_2.4H_2O$ at 22% relative humidity, any hydration of $FeCl_2.2H_2O$ will be slow at 20% relative humidity. Any contribution from ferrous chloride to corrosion will be negligible in the time frame of the experiment here.

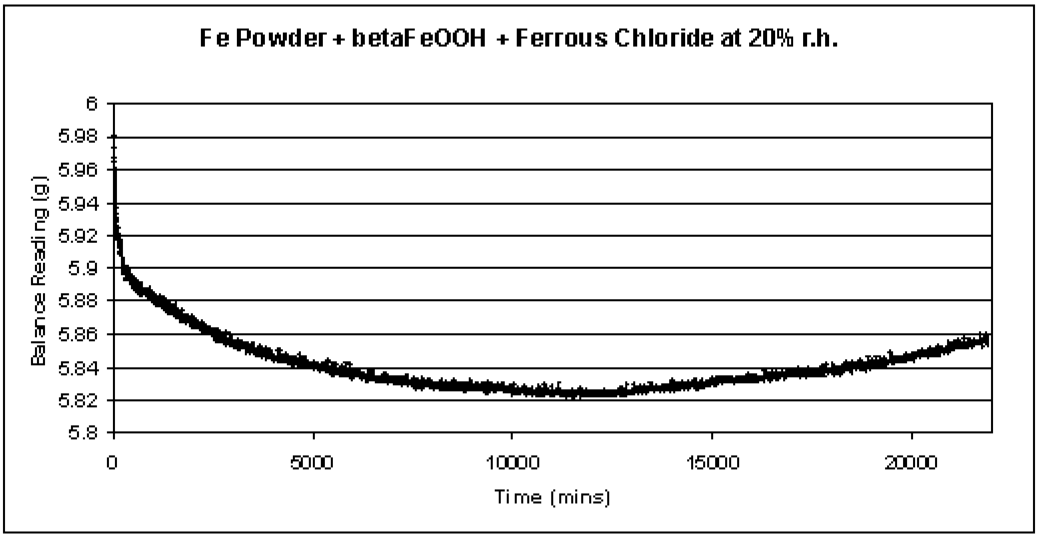

Figure 10. Unwashed $βFeOOH/FeCl_2.4H_2O$/iron powder mixture exposed to 20% relative humidity.

4. Discussion

The results reported here endorse the principle of desiccation as a means to preserve the iron hull of the ss *Great Britain*. The hull of the ss *Great Britain* contains a range of iron corrosion products that include βFeOOH. As it dries in its new storage environment, it is likely that $FeCl_2.4H_2O$ and fresh (unwashed) βFeOOH will form. The experiments reported here show that βFeOOH and $FeCl_2.4H_2O$ are capable of corroding iron that is in contact with them. To prevent $FeCl_2.4H_2O$ corroding iron relative humidity will have to be lowered to 19% to form $FeCl_2.2H_2O$. To prevent βFeOOH corroding iron requires a relative humidity of 12% or less. Where both compounds are present a relative humidity of 12% or less is necessary to stop the corrosion of iron in contact with them. If βFeOOH has been washed to remove surface adsorbed chloride, it does not measurably corrode iron in comparison to unwashed βFeOOH. Rain-wash of the ship's hull may have produced this effect on βFeOOH on its surface.

Desiccating the 322 feet long hull of the ss Great Britain to 12% relative humidity would be costly and technically challenging, with potentially high maintenance costs. Examining the influence of $FeCl_2.4H_2O$ and βFeOOH on the rate of iron corrosion, as measured by the weight increases shown in Figures 6 - 8 indicates that corrosion is many times slower at 20% relative humidity, as compared to 25% or 30% relative humidity. It is worth taking a pragmatic view of the βFeOOH /$FeCl_2.4H_2O$ iron corrosion model and considering the overall effect of relative humidity on the rate of corrosion (Figure 11). The stability of the iron hull of the ss *Great Britain* could be significantly enhanced and its life-span prolonged by storage environments that control relative humidity to 20%.

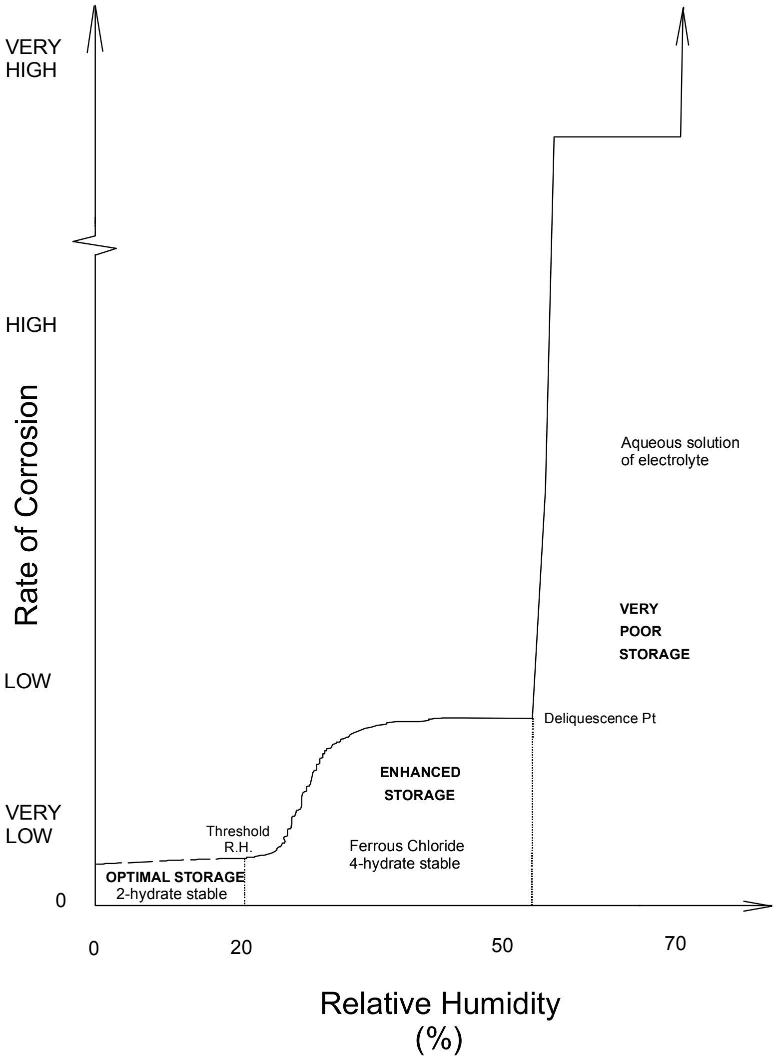

Figure 11. Schematic diagram of proposed corrosion rate/ relative humidity model.

Cost effectiveness often promotes compromises. The results of these experiments allow informed decisions as to the effectiveness of a particular humidity for the preservation of chloride infested iron. Capital expenditure and future income can be related to best value decisions for the long-term preservation of the iron hull (Table 3). At the ss *Great Britain* it is planned that costs will be minimised by controlling relative humidity in the immediate vicinity of the hull. The ss *Great Britain* Trust plans to force dried air over the hull to create and sustain a localised relative humidity that prevents or significantly reduces corrosion of the type examined in this research. Currently experiments are underway to determine the effects of small short-lived fluctuations in relative humidity above the chosen control relative humidity. Simulations of the effect of catastrophic plant failure on corrosion rates are also underway. The results of this work successfully supported a £8.4 million grant from The Heritage Lottery Fund in the UK.

Storage category	Relevance for the ss Great Britain
very poor	Current storage conditions for the ss Great Britain. Humidity lies above the deliquescence point of ferrous chloride (~55% relative humidity). Corrosion will be accelerated very greatly due to the presence of the very strongly conducting electrolyte.
enhanced	Humidity is below the deliquescence point for iron chloride and above the corrosion threshold established for ferrous chloride/iron mixtures in this research. Within this region the rate of corrosion increased significantly with increasing relative humidity.
optimal	Any relative humidity beneath the 'threshold humidity' for the corrosion of ferrous chloride and iron powder mixtures. Ferrous chloride no longer contributes directly to the corrosion of the iron. βFeOOH still contributes to corrosion.

Table 3. Storage categories for chloride contaminated wrought iron.

The results of these laboratory experiments are discussed in the context of the ss *Great Britain* and the juxtaposition of these corrosive products and iron on the hull must be considered in any corrosion model. The large surface area contact provided by powders used in the experiments and the large quantities of reactants are not duplicated on the hull. The physical nature of the corrosion layers on the ship will be likely to have a very significant effect on reaction rates. However, experience with chloride infested archaeological iron suggests that corrosion can be rapid and invariably occurs at the interface between metal and corrosion layers, creating spalling of the corrosion layers.

The results of this research and their successful implementation offer a new model for the conservation of large iron ships. Both the level of relative humidity and its effects have now been linked to specific chloride based corrosion reactions. When compared to chloride removal treatments for corroded iron, desiccation can now offer greater predictability, with the option of monitoring effectiveness to maintain standards. It also provides its user with measurable choices. Since its efficacy can be graded according to the prevailing relative humidity, it is possible to model the level of corrosion control that a particular sum of money can buy, in terms of plant and operational costs. The application of this conservation technique can be extended to other chloride contaminated iron objects, both large and small.

Acknowledgements

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