Metal corrosion on shipwrecks: Australian case studies

Ian Donald MacLeod

Department of Materials Conservation, Western Australian Maritime Museum, Cliff Street, Fremantle, Western Australia 6160

INTRODUCTION

The study of corroded metal objects recovered from historic shipwrecks provides conservators with a unique chance to look at the effects of salts, water movement, depth of burial and the level of dissolved oxygen on the degradation of a wide range of artefacts. Normally the chronology of shipwrecks is well defined and this helps quantify the rates of deterioration that occur. Previous work in these laboratories has concentrated on the identification of corrosion processes and how, through a study of deterioration, we can improve our techniques for stabilising the artefacts(North 1976, MacLeod 1987).

The routine measurement of electrochemical parameters, such as the surface pH of degrading artefacts and the corrosion potentials of metal objects on wreck sites, has a very recent history. Following the early work on the *Rapid* (1811), corrosion scientists have found that the knowledge obtained through these on-site measurements is an invaluable aid in understanding the corrosion mechanisms and the modes of deterioration of materials on archaeological sites. The significance of this work has only recently been reassessed and shown to be a very powerful tool in not only determining what has occurred over the past centuries but also in providing the practitioner with a rational and non-destructive form of assessment of the inherent archaeological potential of metal objects that are scattered on a wreck site.

CORROSION POTENTIAL MEASUREMENTS

The determination of corrosion potentials is effected by reading the voltage recorded by a digital voltmeter housed in its waterproof case. The measured voltage refers to the difference in electrical potential of a reference electrode, such as a silver chloride electrode in the sea water, and a working electrode such as platinum. Platinum is used because it is electrochemically inert and it does not corrode in sea water and therefore the measured voltages refer to the object itself and are not part of the nature of the experimental apparatus. When we look at the basic construction of a concreted artefact on the sea bed as shown in Fig.1, we see that after many years of immersion, an acidic and chloride-rich microenvironment is established in which the corroding metal object is placed.

The acidity results from hydrolysis of metal ions. As corrosion proceeds, chloride ions from the surrounding sea water diffuse through the marine growth and corrosion products to the corroded metal interface to achieve electrical neutrality of the corrosion products. Corrosion
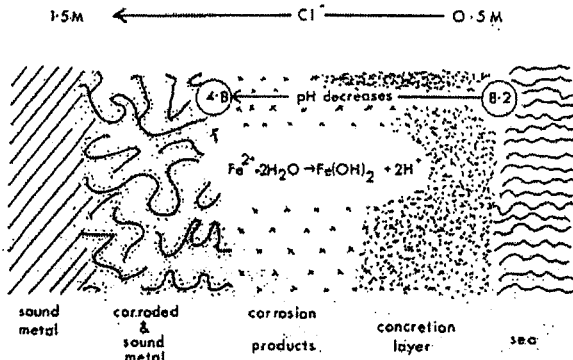
Figure 1: A schematic view of corroded and concreted iron showing the increase of chlorinity and acidity under the concretion.

potential measurements are made by drilling through the marine growth, more recently with the aid of a compressed air-driven drill with a masonry bit, placing the platinum electrode into the hole with the reference electrode adjacent to the point of measurement and reading the voltage. Correct determination of the corrosion potential is normally indicated by the obtaining of a very steady voltage, i.e. a reading that varies by only 1 to 2 millivolts over several minutes.

Because the corrosion rate is controlled by the diffusion of dissolved oxygen to the concreted interface there is a linear relationship between the logarithm of the corrosion rate and the corrosion potential for the artefacts measured under aerobic conditions. Small changes in corrosion rate are therefore readily detected in changes in the value of $E_{corr.}$, the corrosion potential. For an iron artefact, covered with concretion and lying proud of the sea-bed, the anodic current is due to the oxidation of iron to ferrous ions,

$$Fe \rightarrow Fe^{2+} + 2e^- \quad \ldots \ldots \ldots \ldots 1$$

The cathodic reaction is controlled by the rate at which oxygen will

accept electrons to produce the hydroxide ion. The rate of this reaction is largely determined by the rate at which the oxygen dissolved in the solution can diffuse to the corroding interface. The typical variation of corrosion and redox potential and pH with depth of concretion is shown in the Pourbaix diagram in Fig.2. In the outer zones, where the corrosion products are typically red-brown, the potential is essentially a redox couple measuring the ratio of Fe^{3+} to Fe^{2+} ions whereas once electrical contact is made with the metal itself, the voltage is the true corrosion potential. The data for Fig.2 was obtained from a cannon on the wreck of the Rapid(1811). It should be stressed that the corrosion potential is not a true thermodynamic function in that it is essentially a kinetic variable that reflects a non-equilibrium or steady-state situation. The primary corrosion product occurring underneath the concretion has, after many years of controversy and research, been established as
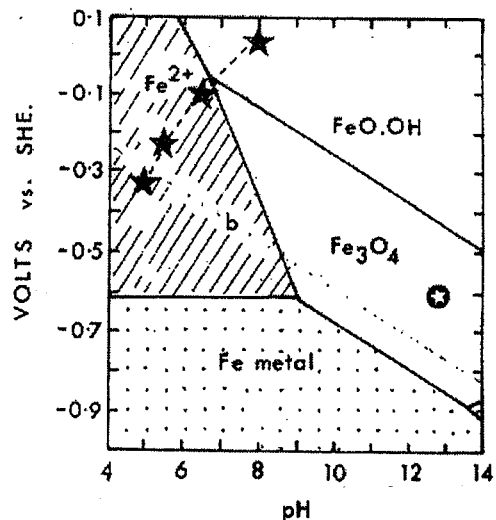

Figure 2: Pourbaix diagram showing the $E_{corr.}$ and redox potentials for a concreted iron cannon on the Rapid (1811) wrecksite and in treatment ✱.

ferrous chloride. Ferrous chloride subsequently undergoes hydrolysis to β(Fe(OH)$_2$.FeCl$_2$.). As the ferrous chloride solution diffuses out through the concretion matrix and undergoes hydrolysis, the resultant increase in acidity causes the dissolution of the calcium carbonate in the marine deposits. Some iron carbonate precipitates along with concomitant oxidation of iron (II) corrosion products to iron (III).

CORROSION ON THE WRECK OF HMS SIRIUS(1790), NORFOLK ISLAND

The flagship of the First Fleet to Australia was wrecked on Norfolk Island in March 1790. The vessel was heavily salvaged at the time and two hundred years later the remaining artefacts are scattered around the main site which is located some 70 metres offshore as a very gently sloping plane of hard calcareous rock in water varying in depth from 1.5-4.5 metres. The wreck site consists of flat beds of overlying coralline reef materials with a series of gullies and depressions in the sea floor. The very nature of the island and the location of the wreck site means that apart from the odd calm day the objects are subjected to the effects of continuous breaking surf. The wave action is sufficient to shift a 1.5 tonne concrete plinth thirty metres across the sea bed during a storm. The most significant remains are several hundred concreted cast iron ballast blocks and a few anchors. Smaller artefacts are either trapped within the coralline matrices or under the ballast. The warm sea water (20.80 ± 1.96°C), a mean annual salinity of 35.77± 0.04‰ or ppt and dissolved oxygen levels of 7.7 ± 0.3 ppm mean that the materials are in a corrosive environment.

SACRIFICIAL ANODES AND IN-SITU ARTEFACT CONSERVATION

In March 1985 the best bower anchor of HMS Sirius was raised from the

wreck site and brought alongside the Kingston jetty on Norfolk Island. A small section of concretion, approximately 50 cm x 10 cm, had come away as the anchor left the seabed. Within two hours the exposed part of the shank was covered with a red-brown iron (III) oxy-hydroxide film. Corrosion potential measurements on the anchor showed that the oxidation rate had increased significantly from its predisturbance value. Monitoring continued for 96 hours until the corrosion potential (E_{corr}.) eventually plateaued at -0.340 volts vs Ag/AgCl. The positive shift of 240 mV in E_{corr}. corresponds to a shift in corrosion rate from approximately 0.1 mm/year to 5 mm/year! Given that no commercial sacrificial anodes were available on Norfolk Island, a 30 kg engine block made of an aluminium - magnesium alloy was attached to the anchor using heavy gauge copper cable. Within a few minutes the E_{corr}. value had fallen to its predisturbance value (MacLeod, 1987). Measurements on the anchor showed that although it was still in an active corrosion zone, the corrosion rate was greatly reduced.

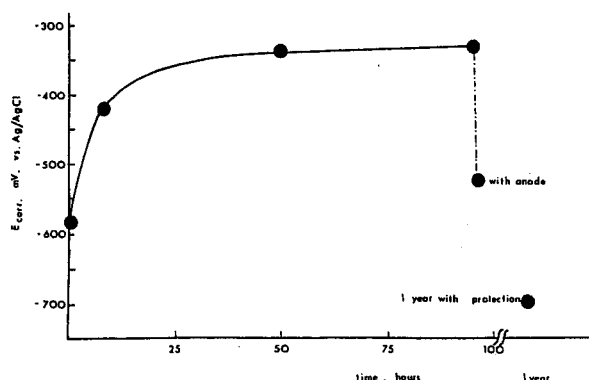The anchor was left in shallow water which was well oxygenated by the

Figure 3. Plot of E_{corr}. for the HMS Sirius anchor after disturbance and with cathodic protection.

surge and wave action. After one year of cathodic protection the "scar" on the shank had "healed" and the copper cable was also covered with a white calcareous layer. The anode had lost half of its weight and the corrosion potential of the anchor at -700 mV vs Ag/AgCl was 120 mV more negative than the predisturbance value, which shows that it had been effectively protected from any corrosion during the year in the sea by the pier. Although no surface pH measurements were made, the calculated pH was 7.43, assuming that the pH is in equilibrium with the voltage determined from the corrosion potential. This increase of the pH represents a significant reduction in acidity by a factor of more than four hundred during the year of cathodic protection. On breaking the concretion seal, copious amounts of gas were released. As electrons flow into the concreted anchor hydrogen ions will be reduced to hydrogen gas and the chloride ions will diffuse out. Based on a net consumption of 7 kg of aluminium, the approximate current density delivered by the engine block anode to the anchor was of the order 150 mA.m^{-2} which will protect iron metal from corrosion in the marine environment (Fischer, 1983).

Inspection of the anchor at the end of the electrolysis treatment programme in sodium hydroxide solutions showed that large areas of original surface had been retained. It was noted during the deconcreting process that the calcareous matrix was extremely hard (Carpenter, 1986) and that the underlying metal was not so prone to spalling as is generally found with wrought iron anchors that have been in the sea for several hundred years. The most likely explanation for these features lie in the pretreatment that the anchor received during its year of cathodic protection. It should be noted that most of the original surface has very little mechanical strength and is very

prone to disbondment. The properties of the various zones of wrought iron have been well documented (Chilton and Evans, 1955) and they relate to the distribution of impurities in the bands of metal and their effect on the corrosion mechanism. In the extensive hot working of the final surface, the iron was decarburised and sulphur impurities would have been removed by oxidation. Prior to treatment, the anchor was sampled by drilling and the results are shown below in Table 1.

The total amount of chloride released during treatment was 1.63 wt%. The low level of sulphur in the anchor indicates that the wrought iron had probably been produced using charcoal rather than coal as the reducing agent in the furnace. Given that nickel and copper promote the zonal corrosion which results in the typical woodgrain finish of corroded wrought iron, the low levels of these noble metal impurities will have helped in reducing the localised corrosion rate, and so help retain vestiges the original surface. It should be noted that the original surface details on the anchor would have been lost if the electrolysis treatment had been too severe. A formal representation of one of the many processes occurring during the cathodic protection of the anchor on the sea bed is given by the equation

$$3\ FeCl_2 + 4\ H_2O + 6e^- \rightarrow Fe_3O_4 + 3H_2 + 6Cl^- \quad \ldots \ldots \ldots 2$$
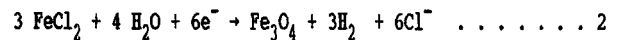
Reactive iron chloride-containing corrosion products are changed from the acidic forms present underneath the concretion into the stable black corrosion product magnetite, Fe_3O_4. In the same process the chloride ions diffuse through the concretion into the surrounding sea water and the acidity of the solution under the concretion is reduced. The reduction in acidity shifts the iron metal towards a more stable environment. Since the acid from metal ion hydrolysis had dissolved

Table 1: Composition of a *Sirius* wrought iron anchor (wt%).

Area	C	S	Si	Ni	Cu	Mn	P	Cl
Outer layer	0.25	0.05	0.2	<0.005	0.015	0.090	0.035	1.12
Inner zone	0.10	0.04	0.1	<0.005	0.015	0.015	0.015	0.61

calcium carbonate, the reduction in acidity will tend to promote redeposition of calcium/magnesium carbonates (magnesium calcites) and the deposition of the iron carbonate siderite, $FeCO_3$.

Such a redeposition would harden the concretion which, with the production of more magnetite, would act as a "cement" to bind together the original surface material which normally falls away from the corroded metal. The filamentous nature of the slag inclusions, $SiO_2.2FeO$, may also act as a matrix for reinforcing the redeposited minerals.

Corrosion potential measurements on the second *Sirius* carronade showed that it was actively corroding. Since the weapon is of great historic and archaeological significance it was decided to begin conservation treatment as soon as possible whilst it remained in-situ. A 20 kg lump of an aluminium alloy (a truck engine block) was attached via a specially fabricated giant "G" clamp to the concreted carronade. Prior to the connection of the anode the E_{corr} of the carronade was measured and the result was within 10mV of the value previously determined two years previously after 198 years of equilibration. The reproducibility of the results proves that the method of measuring E_{corr} causes no real change in the micro-environment of the object.

Within ten minutes of the anode being connected the E_{corr} had fallen 165mV which showed that a good

current flow had been established. The chloride and acid removal process had begun. During a violent winter storm in 1989 the bracket became dislodged which halted the treatment. Measurements in 1990 confirmed that the initial treatment of the cannon had an increased surface pH and that E_{corr}. had shifted to more negative values. A second anode was attached and after three years of extra treatment the final E_{corr}. was -0.482 volts vs. NHE with a calculated equilibrium pH of 8.14, the same pH as the local seawater. Upon recovery, the carronade was found to be stabilised in that the surface was not prone to the normal rapid oxidation where the colour can change from black to red-brown in minutes.

Recent work on a concreted iron cannon from the *Batavia* (1629) has shown that chloride ions diffuse out from the dense concretion under the influence of the electrical current flowing from the sacrificial anode at rates up to 8.7 g m^{-2} hr^{-1} (MacLeod, 1988). Given that the rate of chloride removal from concreted cannon is approximately one third of that obtained during electrolysis of deconcreted guns it can be seen that the *Sirius* carronade had received at least the equivalent of one years electrolysis on the seabed prior to recovery.

CORROSION MEASUREMENTS ON THE HMS *SIRIUS* SITE

It was decided in 1988 to survey the corrosion potentials and surface pH of the corroded cast iron ballast.

The results of the survey would be very valuable to conservators and corrosion scientists since, for the first time on a major shipwreck site, there was a statistically large enough number of apparently identical objects, which had corroded in the same environment, to enable proper assessment of the reliability of corrosion potential measurements as an index of corrosivity of the site. One of the biggest problems that has been faced over the last 15 years of research is that there have only been one or two cannon, one or two anchors available for measurement on a given site. Since many shipwreck sites are in locations where the different water temperatures would have had varying effects of marine growth it had not been possible to see if there were any overall correlations between site variables and overall corrosion.

It was rather surprising to find that a large degree of variation existed in the corrosion potentials. The difference between the highest and the lowest values of E_{corr}. was greater than 160 millivolts. This indicated that the objects were showing markedly different corrosion rates. Inspection of the artefacts previously raised on other expeditions showed that there was indeed a wide range of corrosion behaviour of the cast iron ballast. The least corroded ballast pig had been recovered from the sheltered lagoon area whilst the most corroded pig had been recovered from a section of the site that was quite exposed to the ocean surge.

Under the strong surge conditions experienced on the site the measurement of surface pH is very difficult. Reliable data was obtained using a compressed-air driven drill with a masonry bit the same diameter as the flat-surface pH electrode. The lowest pH had a value of 4.18. The most acidic microenvironment previously recorded on iron artefacts was on the *Batavia*

wreck site where the typical value was 4.8, a factor of more than four times less acidic. Inspection of the digital read out of the pH meter showed that equilibrium values were obtained within two minutes. Our measurements have confirmed that the HMS *Sirius* site is the most aggressive of all those measured by the author. It should be noted that all the objects have corrosion potentials that are in the active corrosion region of the Pourbaix diagram.

The surface pH is apparently related to the corrosion process through the partial hydrolysis of the primary corrosion product ferrous chloride,

$$FeCl_2 + H_2O \rightarrow \tfrac{1}{2}\{FeCl_2.Fe(OH)_2\} + H^+ + Cl^- \quad\ldots\ldots\ldots 3$$
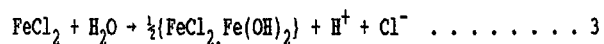
The partial hydrolysis of the ferrous chloride controls the in-situ pH of the corroding iron artefacts. For wrought iron the relationship is given by equation 4,

$$E_{corr.} = -0.029pH - 0.100 \quad\ldots\ldots\ldots\ldots\ldots 4$$

where the corrosion potential is measured in volts relative to the normal hydrogen electrode. Cast iron objects showed the same pH dependence as the wrought iron anchors and anchor fluke, but the intercept value was different.

CORROSION POTENTIALS AND THE EFFECTS OF WATER DEPTH

The data collected during the 1988 *Sirius* inspection showed the highest (the least negative) corrosion potentials were found in the shallowest water whilst those with more negative values, reflecting less corrosive environments, were found in deeper waters. Objects lying proud of the seabed had higher corrosion potentials than other objects at the same depth which were more buried in the surrounding reef platform. Since direct comparison of the E_{corr} values of cast and wrought iron is not possible, owing

to their different composition, the *Sirius* data was compared with other sites. The cast iron pigs were compared with a cast iron propeller from the steam ship *Xantho*, trypots from the *Lively* and cannon from a number of other sites. The *Sirius* anchors were compared with other wrought iron anchors and objects such as whaling hooks and chain plate.

The rate at which the corrosion potentials changed with water depth was essentially the same for both wrought iron and cast iron and the E_{corr} values fell by 18.9 ± 1.5mV per metre of water depth.This behaviour was not expected on the basis of the previously understood model (MacLeod & North, 1987) where the concentration of dissolved oxygen had been considered to be of paramount importance. Standard oceanographic data shows that the level of dissolved oxygen generally increases slightly with water depth up to approximately 30 metres, owing to the greater hydrostatic pressure. If the rate of corrosion was dependent primarily on the dissolved oxygen concentration, the observed decrease in corrosion rate with increased water depth could not be explained. However, one parameter that does decrease most markedly with increasing water depth is the total amount of water movement. Such movement depends on the combined action of the channelling effects of reefs and the topography of the seabed (MacLeod, 1989). The combined data from all the cast and wrought iron objects measured on ten different sites show that the corrosion potential is determined by the oxygen flux available to the corroding metal.

The rate of corrosion depends not only on the absolute value of oxygen dissolved in the sea water at the time of measurement but also on the rate of supply of the oxygen. If the rate of the corrosion reaction is determined by the rate at which oxygen can diffuse to the surface of
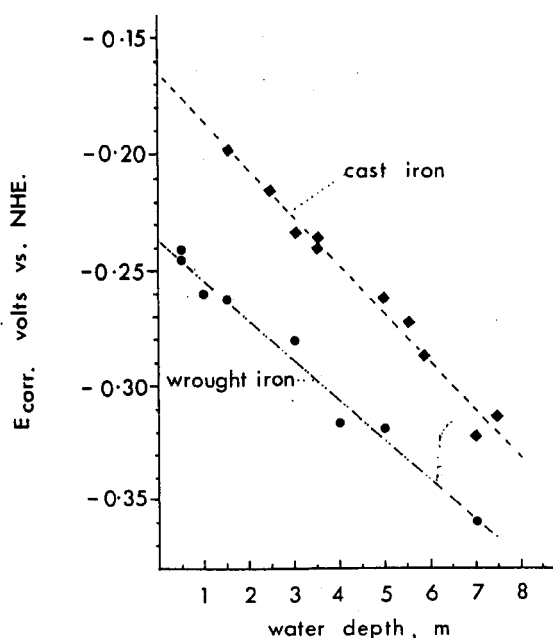

Figure 4. Water depth dependence of E_{corr} for wrought and cast iron objects on wreck sites.

the object any factor that reduces the diffusion layer thickness (the boundary layer) will increase the corrosion rate. In shallow depths there is much greater total water movement than in deeper sites; the higher the profile of an artefact on the seabed the greater localised turbulence and the greater the corrosion rate. This new understanding was catalysed by the analysis of the corrosion potentials on the *Sirius* site. The impact is of major significance to the understanding of corrosion phenomena on shipwrecks.

Recent work in these laboratories has shown that there is a direct relationship between the thickness of the marine concretion and the weight per cent of phosphorous in the metal(MacLeod,1988). If the rate of corrosion was partly dependent on the thickness of the concretion, i.e. on the electrical resistivity of that pathway, then the artefacts with a greater

percentage of phosphorous in them might be expected to be corroding at a slower rate owing to the increase of resistance due to a greater thickness of concretion. Given that the extent of corrosion on ballast pigs recovered from different parts of the site varies by a factor of approximately four between the ballast pig recovered from the inner part of the site compared with the outer, it is not possible to test this hypothesis because of the relatively small size of the perturbation due to thickness of concretion compared with the effects of the variations in water movement.

On Norfolk Island one of the causes for the differences in corrosion potential of similar materials appears to lie in the presence of the black long-spined sea urchin *Heliocidaris tuberculta* (Lamarck, 1816) which has the habit of burrowing into the marine growth on the artefacts thereby short – circuiting one of the rate determining parameters in the corrosion cell, namely the electrical resistance of the concretion layer. Currently research is underway to determine if the sea urchins are using the iron corrosion products as an energy source. Inspection of the carronade and ballast pigs' surfaces shows that the hemispherical depressions in the cast iron are due to the burrowing of the marine organisms.

CORROSION OF COPPER AND ITS ALLOYS

A study of the corrosion characteristics of a series of copper, brass and bronze fittings from the wreck of HMS *Sirius* has shown that the bronzes are very sensitive to the amount of dissolved oxygen in seawater (MacLeod,1993). The electrochemical data has shown how differences in the distribution of alloying elements in the same object can lead to major variations in the materials performance of the artefact. The sensitivity of

bronzes to the amount of dissolved oxygen indicates that artefacts recovered from the low-oxygen microenvironments, such as found under the concretions associated with iron objects, should be very well preserved without the need of direct galvanic protection.

Minor amounts of impurities such as antimony and iron are seen to have a major influence on the corrosion mechanism of archaeological bronzes. Differences in performance of copper fastenings and sheathing can be rationalised in terms of the influence of arsenic and the metallurgical microstructure. The turbulent and highly oxygenated nature of the HMS *Sirius* wreck site has a direct influence on the extent of corrosion of the artefacts and alerts the conservator to the special care that is needed to treat such materials.

CONSERVATION OF THE METALS

Having established the corrosion mechanisms for the various fittings from the shipwreck of HMS *Sirius*, it is essential to look at the practical consequences of these observations. The largest difference in corrosion is normally noted with iron artefacts since they are inherently more reactive than copper and its alloys. A cast iron carronade from the *Sirius* site released a total of 26.09 kg of chloride ions (5.36 wt%) during conservation treatment while a cannon of similar weight from the more sheltered site of the *Rapid*(1811) released a total of 4 kg (1.12 wt%) of chloride ions (MacLeod 1989). When the amount of corrosion on the more sheltered site is corrected to account for 21 years less corrosion, the chloride content would only increase to 4.6 kg (1.29 wt%). After such a correction, the cannon from the *Sirius* is seen to be four times more "corroded" than the similar object from the *Rapid* site.

In a similar way the copper, brass

and bronze alloys recovered from the *Sirius* wreck site had higher chloride contents than similar materials that came from a number of wreck sites off the Western Australian coast. Sesquicarbonate treatment of the bulk of the copper sheathing on Norfolk Island released 0.07 wt% chloride which is almost three times the average amount extracted from other wreck sites. The effect on brass and bronze artefacts was even more marked since the average amount of chloride removed under similar conditions was 0.52 wt%, a factor of more than eight times that of average sites (MacLeod 1987).

Measurements of the corrosion potential of artefacts on the site can now be used as a guide to the level of conservation that will be needed after the materials are recovered. The in-situ E_{corr} value of a copper bolt from the gun carriage of the remaining carronade was −0.121 V (vs.NHE). This voltage is the same as the laboratory measurement on a copper clinch ring in oxygen saturated sea water. The coincidence of these corrosion potentials means that laboratory studies may be able to be used to model the way in which corrosion varies on the site as levels of dissolved oxygen change with the archaeological profile. Further studies are needed to confirm the reliability of such indicators.

EFFECTS OF DIFFERENT CORROSION RATES

One of the practical archaeological implications of these corrosion measurements on wreck sites is that since we know the way in which corrosion potential and water movement varies with water depth, we can now state fairly unequivocally that, for all other parameters being equal, the cannon or anchor with the lowest corrosion potential will be the least corroded. Recent work on the *Sirius* and other Australian sites has shown that it is possible

to obtain a clear understanding of the nature of corrosion and deterioration forces working on a shipwreck site through the measurement and interpretation of both surface pH and corrosion potentials.

The most important thing to note is that the data obtained by the underwater conservator measuring these parameters gives the archaeologist a very valuable tool in helping them to decide what artefacts are to be raised. The data also helps to establish if the site is in danger and subject to strong forces of deterioration with major resource management implications. The results from the limited number of *in-situ* cathodic protection experiments indicates that these procedures retain the maximum amount of information for the maritime archaeologists.

Future work may involve the routine pre-treatment of artefacts on the sea-bed prior to them being excavated in subsequent seasons. Not only would this minimise the treatment time above the ground but the procedures would also halt corrosion during the remaining time on the sea bed.

METAL CORROSION IN A NON-CONCRETING MARINE ENVIRONMENT
A study of the *City of Launceston* (1865), Port Phillip Bay, Victoria

In order to test the applicability of the model developed for corroding concreted iron in warm tropical to sub-tropical waters, it was decided to perform measurements on a wreck in waters that were in a relatively confined system that was free of the concreting organisms. The wreck of the *City of Launceston* in Port Phillip Bay, Victoria fitted the assessment criteria.

On the evening of November 19 1865, the *City of Launceston* was rammed by the *Penola* and the ship rapidly

sank. The wreck lies in 20-22 metres of water on a flat bottom of shingle and silt. Apart from the loss of the poop deck, the two masts and funnel, the vessel is largely structurally intact. The wreck lies in the main western shipping channel of Port Phillip Bay and so caution needs to be exercised when working the site. A silt mound has formed along both sides of the hull with the top of the silt on the port side currently almost one metre below the top of the deck. The silt reaches to within two metres of the top of the vessel on the starboard side. It has been reported that the area around the site is subject to stratification in the values of dissolved oxygen, salinity and temperature. The complexity of the system is best summarised by the following quote "The Bay is at various times unstratified, stratified by temperature, stratified by salinity, or stratified by both temperature and salinity"(Cowdell et al, 1985).

The bottom temperature was 15 °C on both days and there was less than one degree difference between the surface and bottom temperatures. It has been calculated that the average residence time for water in Port Phillip Bay is one year. Data obtained from the Marine Science Laboratories (Cowdell et al, 1985) showed the surface values (at a depth of 1 metre) of dissolved oxygen had a mean annual value of 5.7 ± 0.2 ppm. Dissolved oxygen levels can fall as low as 68% saturation at a depth of 22 metres. The mean difference between the top readings and those at the bottom is 5.0 ± 6.7% saturation. The mean monthly temperature for April was 18.3 ± 0.7 °C while the mean annual temperature was 15.8 ± 0.6 °C. The mean value of the pH was 8.0 ± 0.2 while the corresponding salinity data gave a mean value of 34.8 ± 1.2 parts per thousand. Salinity differences of up to 0.6 ppt. can also occur at times that are dependent on the rainfall and the

fresh water run-off from the rivers that drain into the bay.

MARINE BIOLOGY OF THE SITE

Port Phillip Bay is a large mass of water that sees four major changes each day with the ebb and flow of the tides. Since the wreck site is in the centre of the bay it is not prone to currents of up to 5 knots associated with other sites, such as the *William Salthouse* near the entrance to the Heads. However it is subjected to a reasonable amount of water movement despite the depth of the site. During the inspection on the first day, a small current of approximately 0.5 knots took the silt away from the area that had been disturbed by the action of the compressed air drill. It was readily apparent that the extent and maturity of colonisation of the wreck was significantly different at the bow and the stern compared with the middle section of the vessel.

These differences are very similar to the phenomena that have been reported on the boiler on the wreck of the *S.S.Xantho* in Western Australia where the site has been shown to be periodically exposed and buried under a compacted layer of fine sand, macerated sea grass and a clayey-like material. On the *Xantho* site the level of the sea bed changed by more than 1.75 metres in the space of only eight months.

Because of the West-SW to East-NE orientation of the vessel it acts as a natural barrier to the flow of sediment in the bay. Scouring of the silt occurs at the bow and the stern in response to the barrier that the vessel presents to the flow of sediment from the waters to the north of the site. This means that the filter feeding marine organisms are provided with a steady supply of nutrients and so are free to grow to maturity, however the sedentary organisms in the mid-sections appear to be subject to periodic burial.

The burial results in the death. of
the algae and the tunicates and once
the hull plates are exposed again
the whole process of re-colonisation
takes place once again. Since the
silt mound is always deeper on the
port side of the wreck it is likely
that the main source of the deposit
is coming from the northern end of
the bay where the silt from the
dredging of the Yarra River is
dumped. The current eddies on the
northern (starboard) side of the
vessel prevents the build up of too
much material, but once the energy
of the water has been partially
dissipated the remaining silt falls
to the sea floor and so increases
the depth of sediment on the port
side.

Reports at the time of the shipwreck
stated that the work being done by
the divers and salvage crews was
clearly visible from the surface.
This indicates that the initial
environment was significantly
different to that which currently
exists. It is reasonable to assume
that the major changes in the nature
of the site occurred at the time of
the development of the Port of
Melbourne in 1890's and that the
City of Launceston was in a clean
microenvironment for the first 25
years of immersion. Further works
took place in the period up to the
1920's and since that time no major
changes have taken place. It is
possible that the site has therefore
been subject to a silty environment
for the last 100 years.   It was
noted during the site survey that
the extensive colonisation normally
found on iron wrecks in warmer
waters was absent. This in turn
means that the marine growth will
probably be less efficient at
protecting the corroding iron metal
from the direct effects of dissolved
oxygen than concretions of a more
dense and calcareous nature.
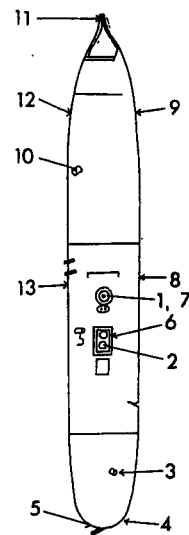
CORROSION STUDIES

A series of corrosion potential

Figure 5: Site plan of the City of
Launceston showing location of
objects and measurement points.

measurements were made at a variety
of points so that the materials on
the deck of the ship as well as the
structural members of the vessel
could be assessed. The locations
included the engine, bow and the
stern sections, the propeller and a
number of sites along the port and
starboard sides of the wreck. The
aim of these measurements was to
gauge the overall micro-environment
of the remains. The results of the
measurements are summarised in Table
2. The copper pressure vessel was
covered with a thin layer of a deep
blue corrosion product, which is
most probably the copper sulphide
covellite, CuS. Although the site
is presently exposed it must at some
stage have been covered by at least
25-40 cm. of sediment to produce the
necessary conditions to facilitate
the formation of sulphides. The
fine silt found on the site would
readily provide a suitable diffusion
barrier to oxygen and so lead to the
development of an anaerobic
microenvironment. - The same blue
corrosion product was also found on
a bronze tallow pot and the main
copper steam pipe on top of the

TABLE 2:   Corrosion potentials of ferrous and non-ferrous materials, *City of Launceston* (1865).

Site Location	Object	E_{corr} vs Ag/AgCl
1&7	Copper pressure vessel	-0.133
2	Cast iron engine cylinder	-0.289
5	" " propeller	-0.557
3	" " drum	-0.545
10	" " drum	-0.557
6	Wrought iron engine block	-0.584
4	Hull plates-counter stern	-0.579
8	" " mid starboard	-0.583
9	" " fwd starboard	-0.590
11	" " bow	-0.586
12	" " forward port	-0.589
13	" " mid port	-0.593

S.S.Xantho(1872) engine which had been buried under 40 cm. of sediment for various intervals. Although the *City of Launceston* site is essentially an aerobic site, the presence of the sulphide patina shows very clearly that the mid section of the vessel must have been covered by silt to produce the anaerobic corrosion product. The source of the sulphide ions is most probably associated with sulphate reducing bacteria such as *desulfovibrio salixigens*.

The value of the corrosion potential is typical of copper objects covered with a patina of copper sulphides. For example, the main copper steam pipe from the SS *Xantho* had an E_{corr} of -0.140 volts which is 7 mV more negative than the value for the fitting lying exposed on the upper deck of the *City of Launceston*. Both metal objects were measured at a time when they were exposed after a period of burial; the similarity of the E_{corr} values reflects the same microenvironment. Comparison of corrosion potentials only makes sense when the materials are in a

similar micro-environment. For example, the E_{corr} of a copper bolt on the rudder of another wreck in Port Phillip Bay, the *Empress of the Sea*(1853), was 47 mV more negative than the copper pressure vessel on the *City of Launceston*. The more negative potential could be interpreted as indicating that it is corroding at a slower rate but such an assessment cannot be made owing to the differences that the corrosion product layers exert on the current-voltage curves for the metals. Although no surface pH measurements were taken on the wrecksite, previous measurements on other sites show 7.5≤ pH ≥6.5. With this information it is possible to place the corrosion data on an appropriate Pourbaix diagram.

CAST IRON FITTINGS

The corrosion potential of the cast iron engine cylinder on the *City of Launceston* had a value of -0.289 volts (see table 2) which indicated that the fitting is in an advanced state of decay. The other cast iron fittings such as the drums, associated with the ill-fated attempts to raise the vessel in the 19th century, and the massive propeller had average corrosion potentials of -0.553 ± 0.004 volts. The very high corrosion potential of the engine cylinder is typical of data associated with a corroded matrix of cast iron where very little solid metal remains. The closeness of the values for the different objects indicates that they are all corroding at a similar rate since they are in a similar microenvironment. Iron fittings on the *Empress of the Sea*, which appear to be made of cast iron, gave average corrosion potentials of - 0.514 ±0.004 volts at a water depth of 7-8 metres. Given that the latter site is subject to greater water movement than the *City of Launceston*, the 39 mV more anodic potentials (less negative) value of the corrosion potentials is

consistent with a faster rate of corrosion. Iron objects from the *William Salthouse* gave E_{corr} values of -0.440 volts at a water depth of 10 metres. The 74 mV anodic shift is due to the increased amount of water movement associated with this site since it is subject to much greater current flow, hence a greater flux of dissolved oxygen, than the site of the wreck of the *Empress of the Sea*.

Owing to the different nature of the encrusting organisms on iron in Port Phillip Bay, it is unwise to attempt to make direct comparisons of corrosion potentials of these cast iron fittings with data collected on shipwrecks that have been colonised with calcareous concretions.

WROUGHT IRON MATERIALS

Since wrought iron has a much lower carbon content than cast iron, the corrosion potential of a wrought iron fitting will be more negative than a cast iron object in an otherwise identical environment. The average value of the corrosion potential for the hull plates from all areas of the *City of Launceston* is -0.586 ± 0.005 volts, which is 33 mV more negative than the cast iron fittings. It should be noted that this difference is smaller than the value of approximately 70 mV noted for the difference in the corrosion potentials for artefacts in the warm waters of Western Australia where the concretion is much more protective. The E_{corr}. for iron hull plates on the *Eliza Ramsden* was -0.399 volts, some 187 mV more anodic than the iron plates on the *City of Launceston* which is at a similar water depth. It should be noted that there was evidence of a recent scour near the measured hull plates on the *Eliza Ramsden* and this could have caused some elevation of the corrosion potential, as was noted for in the case of the *Sirius* anchor. The fundamental reason for the difference between the two sets of data lies in the amount of water

movement that the two sites experience. The more anodic E_{corr}. values are associated with a site that is at the entrance to the Bay which is subject to massive water movement. The flux of dissolved oxygen experienced by the artefacts with each ebb and flow of the tide is much larger than that found on the site of the wreck of the *City of Launceston*. On the basis of other data from a variety of sites, the differences in E_{corr} between the two wreck sites corresponds to a ten-fold higher corrosion rate for the *Eliza Ramsden* than for the *City of Launceston*.

EFFECTS OF MICROENVIRONMENT

An example of the differences in corrosion potential with depth of burial is found in the values of E_{corr} for modern iron materials associated with site stabilisation work on the wreck of the *William Salthouse*. Mild steel reinforcing mesh lying proud of the sea-bed, at a water depth of 9.3 metres, had a corrosion potential of -0.504 volts while the iron at the base of the artificial sea-grass mound gave a voltage reading of -0.581. The difference in potentials of 77 mV may indicate a difference in effective corrosion rates equal to a factor of somewhere between two and three. Although the presence of gas bubbles emanating from a freshly drilled iron concretion is often associated with release of hydrogen and methane, it has not been possible to equate these observations with in-situ pH measurements on the site of the *William Salthouse*. The reason for this may lie in the nature of the concretions. However, on the site of the *Empress of the Sea* an isolated and heavily concreted iron bar gave off gas and had an E_{corr} of -0.281 volts vs. NHE. Assuming that hydrogen is in equilibrium with the voltage of the metal, the corrosion potential corresponds to a pH of 4.74, which is typical of data obtained on a number of other sites in Western Australia.

GENERAL OBSERVATIONS

The series of measurements on iron fittings on a variety of shipwrecks in Port Phillip Bay has shown that it is possible to gain a good understanding of the corrosive forces that are determining the rate of deterioration of historic materials in those waters. Further work is needed to establish a data base for corrosion studies that can be used as a management tool. All the indications are that the *City of Launceston* is capable of being protected from further corrosion through a series of sacrificial anodes being attached to the vessel in its current location.

CORROSION OF SHIPWRECKS IN FRESH WATER - A STUDY ON WRECKED BARGES AND PADDLE STEAMERS IN THE RIVER MURRAY, SOUTH AUSTRALIA

The River Murray was the major trading route for much of inland areas of Victoria and South Australia in the 19th century. A substantial number of submerged and partially submerged wrecks form a unique heritage resource that needs to be assessed and properly managed. Since the turbid waters of the river precludes visual inspection methods, a study of the corrosion potentials of metals on the sites can act like a sensitive set of "remote sensing" eyes since the traditional imaging methods of assessment cannot be used in the river. It is proposed to use the $E_{corr.}$ measurements as a data base for monitoring changes in the site conditions; this will be the first time that corrosion data has been used for this purpose under *black water* conditions.

By plotting the average corrosion potentials for the iron frames and engine components from different sites on a Pourbaix diagram it is easy to see the different nature of the sites. Some of the data is shown in figure 6. When the site parameters are summarised in this
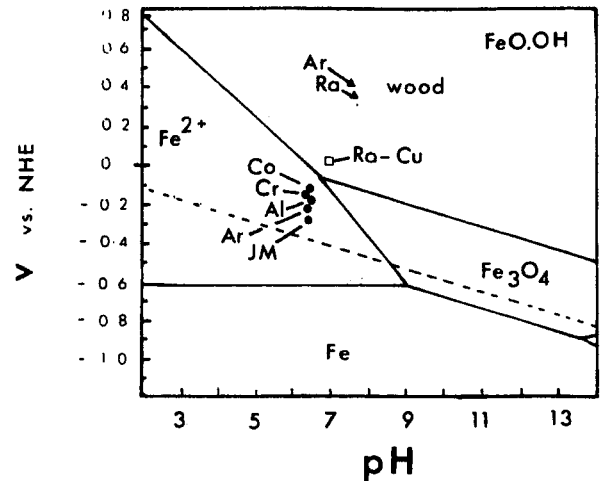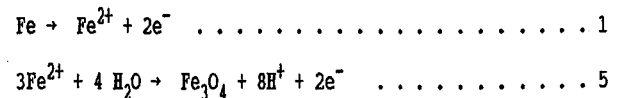

Figure 6. Pourbaix diagram showing average corrosion and redox potentials for fittings on the wrecks of the *William Randell(Ra)*, *Cobar(Co)*, *Albion(Al)*, *Crowie(Cr)*, *Jolly Millar(JM)* & *J.G.Arnold(Ar)*.

form we see that all the average $E_{corr.}$ values for sound iron are in the region of active corrosion. The equilibrium reactions appear to be related to the corrosion of iron to produce Fe^{2+} ions which are in equilibrium with magnetite, Fe_3O_4 according to the following reactions,

$$Fe \rightarrow Fe^{2+} + 2e^- \qquad \dots \dots \dots \dots \dots \dots \dots \dots 1$$

$$3Fe^{2+} + 4 H_2O \rightarrow Fe_3O_4 + 8H^+ + 2e^- \qquad \dots \dots \dots \dots 5$$

The pH of the microenvironment associated with this equilibrium is given by the relationship

$$E^0 = 0.980 - 0.2364 \text{ pH} - 0.0886 \log[Fe^{2+}] \qquad \dots \dots \dots \dots 6$$

which for the pH of 6.46 observed on the concreted sections on the *Uranus* at Goolwa, gives a ferrous ion concentration of 3.9×10^{-5}M or roughly 2.2 ppm Fe^{2+} in equilibrium with magnetite. Assuming that this pH value is typical, the average corrosion potentials on the *Jolly Miller* correspond to approximately 200 ppm Fe^{2+} ions in the immediate

vicinity of the corroding metal. The individual $E_{corr.}$ measurements on the extensively corroded iron materials on the *Wm. Randell* and the *Cobar* are seen to be in the region where FeO.OH is the stable form of iron. This data also is consistent with the observation that these fittings appeared to be extensively degraded. In a similar fashion we see that the voltages recorded for the wooden beams on the *J.G. Arnold, Wm. Randell* and the *Ventura / Undaunted* are typical of iron(III) corrosion products such as FeO.OH being impregnated into the matrix.

A summary of the average corrosion potentials for the iron fittings and iron structural material on the vessels is found below in Table 3. It is interesting to note that each of the pairs of vessels at each of the main sites at Goolwa, Morgan and Waikerie presented similar values of the corrosion potentials. The more corrosive environment measured for the vessels at Morgan, compared with Goolwa, are probably a reflection of the greater amount of water movement over the wrecks located at Morgan since those at Goolwa were in only what could be described as a very sheltered environment. The average potentials for the *Cobar* are significantly higher than those measured for the four vessels at Goolwa and Morgan. This is probably due to the much more exposed nature of the metal frames and plates that were being measured.

The more negative $E_{corr.}$ values for the vessels upstream of Waikerie, Loxton and Berri are in part due to the greater depth of water over the sites. It has been observed on ocean sites that water depth has a major affect on the values of $E_{corr.}$ and on the corrosion rate (MacLeod, 1989.2). Although the corrosion mechanism has not yet been validated for river sites, it is most likely that the reduction of dissolved oxygen is involved in the rate determining step. Support for this mechanism is found in the way in

Table 3 : Corrosion parameters for wrecks in the River Murray.

Wreck	Water depth metres	$E_{corr.}$ volts vs. NHE
ALBION	1-2	-0.176±0.025
URANUS	1-2	-0.163±0.007
COROWA	2-3	-0.156±0.024
CROWIE	1-2	-0.150±0.019
COBAR	1-2	-0.111±0.006
Wm. RANDELL	1-4	-0.145±0.052
J.G. ARNOLD	6	-0.229±0.025
JOLLY MILLER	6-8	-0.282±0.033
VENTURA II-UNDAUNTED	4-6	-0.227±0.016

which the individual corrosion potentials vary with site conditions. A good example of this is seen on the site of the *Jolly Miller* where the $E_{corr.}$ of the iron in the silt was 82 mV more negative (less corrosive) than values obtained on similar iron sections at shallower depth which were lying proud of the river bed (see fig 7).

The changes in the nature of the River Murray water are indicated by the changing pH and chloride content of the water measured on the various sites that ranged from being close to the mouth at Goolwa to being some three hundred miles away at Loxton. The data is dramatically portrayed in table 4.

It is essential that future studies are done on these wrecksites as it will only be possible to asses the stability of the sites by comparing data collected over an extended period. Any parameter that increases the water movement in the area of the wrecks will increase the rate of deterioration of the metals. The banning of water skiing would
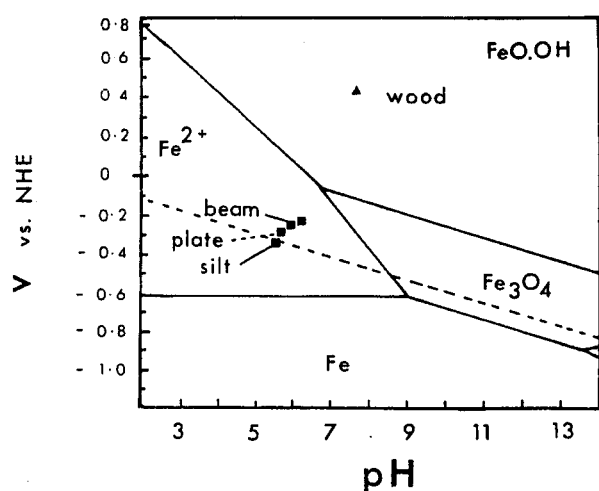
Figure 7. Pourbaix diagram showing the effect of water depth on E_{corr}. for the Jolly Miller.

help the wrecks by removing the effects of the wash from the speed boats. An example of the effects of water movement on the preservation of timber is seen in the degradation patterns on the bottom of the P.S.Colonel. The area adjacent to the wash from the paddles is less eroded than in the sections where the water flow is less turbulent. The iron corrosion products have apparently "preserved" the wood in the vicinity of the bolts.

The timber has apparently been degraded to a much greater extent in the area adjacent to the wash from the paddles than in the sections where the water flow is less turbulent. Iron is normally associated with the increased rate of chemical and biological deterioration of timber in a marine environment. The apparent "preservation" of the wood impregnated with iron corrosion products may be due to inhibition of microbial degradation. Further work need to be done to clarify the mechanism of this apparent reaction. Specific biological degradation mechanisms may be associated with the riverine and riparian

environments.

EFFECTS OF CORROSION ON THE KINETICS OF DESALINATION OF CAST IRON CANNON.

One of the common problems found with the conservation of corroded iron cannon recovered from historic shipwreck sites is that it is very difficult to predict how long the treatment will take. This review draws on data collected in the laboratories of the Western Australian Museum over the last twenty years where eighteen cannon have been successfully stabilised. Apart from laboratory studies, data obtained from in-situ corrosion measurements on ten wreck sites has also been vital in determining what factors control the nature of the desalination of corroded cannon (Carpenter & MacLeod 1993).

CANNON CORROSION ON WRECK SITES

The composition of cast iron cannon results in a metallurgical structure that consists of varying proportions of graphite flakes in a matrix of cementite, pearlite and ferrite (Samuels, 1980). When the cannon corrodes, the phases that have the highest iron content will be preferentially oxidised and this ultimately results in a corroded zone that is essentially graphitised cast iron. The corroded cast iron has lost most of its original mechanical properties but it still retains the original surface details and overall dimensions. The retention of the original surface is the primary aim of the overall conservation treatment and the archaeological rationale for excavation.

The collection of cannon came from a variety of historic shipwrecks that included one from the Trial (1622), seven from the Dutch Eastindiaman Batavia (1629), three from the Vergulde Draeck (1656), one Zuytdorp (1722), five from the whaler Lively

Table 4 : The effect of distance from the sea on pH and chlorinity.

Nearest town	pH	Miles from the sea	[Cl⁻] ppm.
Goolwa	7.90	5	410
Morgan	7.86	199	185
Waikerie	7.67	224	168
Pyap	7.67	298	154
Berri	7.61	326	113

Table 5: Corrosion depths for cannon on the Rapid(1811)

Location	RP4090	RP4288	RP4031	RP4205	RP4206	RP4207	RP4147	RP4032
Muzzle *	16	17	10	4	10	14	4.5	12
Cascabel *	16	15	5	4	10	10	4	8
Mean *	16	16.7±1.5	7.5±3.5	4	10	12.0±2.8	4.25±0.4	10.0±2.1
Annual d_g	0.096	0.101	0.045	0.024	0.059	0.072	0.026	0.059

* Corrosion/graphitisation depths measured in mm.

(1810), eight from the American China trader Rapid (1811), one Cumberland (1830) and two from the Fairy Queen (1875). The Rapid site was the first excavation at which in-situ corrosion measurements were taken (MacLeod,1981). This site also has the most accessible archaeological records. In order to facilitate comparisons of the rate of corrosion on a variety of sites that have been immersed in sea water for times varying from 114 to 365 years, the corrosion data can be averaged over the number of years of immersion. Since corroded cast iron retains its original dimensions, the rate of corrosion can be gauged by measuring the total depth d of corrosion/graphitisation of the cannon and dividing the result by the number of years of immersion. The annual mean corrosion rate is the depth of graphitisation d_g in units of mm.y⁻¹. This is effected by drilling into the artefact with a 5 mm. steel bit until the resistance of the uncorroded metal is felt.

The Rapid cannon provide an interesting example of how the microenvironment on the site dictates the extent of corrosion; the data is listed in table 5. It should be noted that the average long-term corrosion rate for iron in a marine environment is roughly 0.1 mm per year[7]. Inspection of the data shows that two cannon from the Rapid had the "average" corrosion rate for an open ocean site. The wreck lies in seven metres of water inside an offshore reef and at the time of the initial site inspection only one cannon was seen lying proud of the sea bed. It is this cannon (RP4288)

which is the most extensively graphitised. The carronade(RP 4090) with the higher corrosion rate was found under a mound of ballast. There were a significant number of copper artefacts located on the site in the general vicinity of the carronades. There were upwards of 850 copper artefacts within a two metre grid line found 6-8 metres from the guns. Copper fastenings in close proximity to the cannon showed significantly less corrosion than those artefacts further away. Previous studies on the corrosion phenomena on this site (MacLeod 1980 & North,1989) and on the site of the *Hadda* in the Abrolhos Islands (Carpenter et al,1992) have confirmed the existence of proximity corrosion which is a form of long-range galvanic coupling. Such phenomena may be the underlying cause for the increased corrosion rate for the carronade RP 4090. Three other cannon were partially exposed on the seabed and they exhibited the next highest corrosion rate with an average value of the mean annual depth of graphitisation being 0.064±0.007 mm.year^{-1}. Two of the cannon (RP 4206 & 4207) were a "crossed pair" ie. they were found concreted together in a scissor formation.

The other two cannon (RP4147 & RP4205) and the two carronades (RP 4031 & RP4090) were found under the mound of ballast stones and amongst the general wreckage of the vessel. The two buried cannon had an average annual mean corrosion rate of 0.025±0.001 while the carronades had rates of 0.045 and 0.096 mm.year^{-1}. Site excavation records are incomplete, but the divers notes indicated that the carronades were placed at a higher level in the sediment than the cannon and this is reflected in the higher levels of corrosion. Generally it can be seen that, in the absence of specific effects of galvanic coupling, there is a lowering of the rate of corrosion with the increasing depth of burial on the site. This is

primarily a reflection of the decreased amount of water movement combined with lower concentrations of dissolved oxygen.

Only one cannon (RP4205) had its corrosion potential ($E_{corr.}$) recorded on-site and the reading of -0.412 volts vs. NHE which indicated that it was corroding at a relatively slow rate. Using the relationship between $E_{corr.}$ values and the extent of corrosion on wreck sites (MacLeod,1989), the calculated depth of corrosion was 0.034 mm.y^{-1}. The calculated value is within the range of the standard deviation of the observed rate of 0.024 mm.y^{-1}.

The wreck of the *Lively* (c.1820) on the Rowley Shoals is characterised by a scattered deposit of metallic remains. No wooden structure remains and this is consistent with the much higher energy of the site, compared with the much more sheltered *Rapid* site. The wreck lies in a gully on the edge of a coral atoll and the water depth varies from seven to zero metres at the reef top. The corrosion parameters for the five cannon recovered from the site are listed above in table 6.

For convenience, all reported values of corrosion potentials are relative to NHE and are calculated from the on-site data collected with Ag/AgCl electrodes of known voltage. Analysis of the corrosion potential data shows that there is a linear relationship between the corrosion potentials ($E_{corr.}$) and the logarithm of the average annual rate of graphitisation, i.e. log d_g. The in-situ $E_{corr.}$ values of the cannon fall into two sets of data which have the same slope for the $E_{corr.}$ vs. log d_g plots but different intercepts. The relationship is given by,

$$log\ d_g = 2.34\ E_{corr.}\ -0.459\qquad\ .\ .\ .\ 7$$

for the cannon RS24, 25 & 124. For the RS125 and RS26 the intercept is -0.603. It is possible that the difference in intercepts is due to

Table 6: Corrosion parameters for cannon from the *Lively* (1810)

Location	RS125	RS24	RS 25	RS26	RS 124
Muzzle *	16	14	14	10	18
Cascabel *	12	14	10	10	16
Mean value *	14±2.8	14.3±0.6	12.0±2.8	10	17.0±1.4
Annual d_g	0.085	0.089	0.075	0.062	0.106
E_{corr}. volts	-0.200	-0.262	-0.273	-0.252	-0.219

* Corrosion/ graphitisation depths measured in mm .

some chemical or metallurgical difference in the cannon or that the nature of the water movement around these objects is different.

Data on the net effects of temperature on cannon corrosion are not unambiguous. Although the concentration of oxygen in sea water increases with decreasing temperature, the diffusion coefficients fall and this often cancels out the apparent increase in the rate of supply of dissolved oxygen to the corroding surfaces. With cooler water the extent and nature of the marine growth also changes and this in turn alters the amount of "protection" that a concretion can provide. Two cannon from the site of the *Sydney Cove* (1797) in Bass Strait provide data from a much colder site. Although the site is subject to storms, it has a sandy bottom and the average water temperature is 14.5±2.3 °C at a water depth of 3-5.5 metres (Clark, 1986). The average graphitisation depth was 7.3±2.3 mm which gives an d_g value of 0.041 ± 0.013 mm.y^{-1} which is similar to one of the carronades on the *Rapid* site, where the average temperature is 24.4±2.0°C⁶.

Another *cold* site is that of the *Cumberland* (1830) off Cape Leeuwin where the average water temperature is 18.6±1.5°C and the average annual corrosion rate was calculated at

0.028 mm.y^{-1}. Again this corrosion rate is of the same order as two of the cannon from the *Rapid* site, where the cannon had been protected under the ballast mound. Observations on a large number of submerged iron materials indicates that the corrosion rate of concreted iron in sea water is relatively temperature independent (North, 1992).

Given that a common corrosion mechanism controls the deterioration of the cannon, it is not unexpected to find correlations between the amount of chloride ions extracted during conservation and the extent of corrosion. Analysis of treatment data for ten cannon from five sites, for which complete data sets are available, shows that the total number of kilograms of chloride ions is directly related to the depth of graphitisation d via the relationship

$$\Sigma \ Cl = 0.0367 \ d^2 + 2.61 \quad \cdots \cdots \quad 8$$

where Σ Cl is the weight of chloride ions in kg and d is the depth of graphitisation, measured in mm. Since the corrosion rate settles down to a pseudo steady-state after some years, it is not unexpected to find the parabolic relationship (equation 8) between the total amount of chloride in the cannon and the depth of graphitisation. Where cannon do not follow this expression it is due to factors such as the

Zuytdorp cannon having corroded only on the "outside" since the tompion in the muzzle had sealed the bore from the sea water (MacLeod, 1988). Equation 8 can be used to calculate the total amount of chloride that should be extracted from concreted iron cannon that have corroded in sea water where the salinity ranges from 34 -37 ppt.

CHLORIDE EXTRACTION RATES

The diffusion controlled nature of the washing process has been well documented(North, 1978 & 1987) and one consequence is that chloride ions diffuse out at a rate that is linearly dependent on the square root of the treatment time. Once a plateau has been reached it is time to change to a fresh solution of sodium hydroxide. The chloride ions then diffuse out at a slower rate until the next plateau is reached and the solution changed again. Regular monitoring of the wash solutions of the cannon has provided the basic information as to when solutions need changing and when the treatment is complete. Many of the electrolysis times are in excess of five years. At the end of the electrolysis process the total amount of chloride ions released can be calculated from values of the plateau levels (corrected for background levels of the water) and from a knowledge of the solution volume.

We have applied the same methods of data analysis as for the desalination of copper and its alloys (MacLeod,1987) where the release rates were standardised as x mg.cm^{-2}.hr^{-1} by multiplying the rate in ppm of chloride per hour[1] by the solution volume in litres and dividing by the geometric surface area of the cannon in cm^2. It should be noted that the contribution of surface roughness and effective porosity have been ignored in the calculations owing to our inability to accurately assess their values. The common microstructure and composition of the iron cannon means that corroded cannon are closely related in their physical properties. Analysis of the wash data for fifteen iron cannon shows that the rate of release of chloride ions is directly related to the "porosity" of the corroded metal via the relationship

$$R = 3610 \ d_g^2 \ -0.110 \quad \ldots \ldots \quad 9$$

where R is the chloride ion release rate in mg.cm^{-2}.hr^{-1} and d_g^2 is the square of the annual average depth of graphitisation of the cannon (in mm.y^{-1}). Even though the more corroded cannon have a significantly greater amount of chloride in the corroded matrix, the rate of release is dependent on the tortuosity of the diffusion path with the more extensively corroded cannon allowing faster washing owing to the greater void space. With a knowledge of the depth of graphitisation and the time between when the vessel was wrecked and when the artefact was recovered, it is now possible, using equations 8 and 9, to calculate the amount of chloride that can be expected to be released into the treatment solutions and the rate at which the ions will diffuse into the wash solutions. The relationships allow estimation of electrolysis treatment times and to assess whether or not the physical set-up of the electrolysis is optimal.

When the concentration of chloride ions at the plateau levels are compared with the total amount extracted by the end of the treatment some common relationships are found. The expressions for the percentage of chloride removed at each of the washing stages is given by the following relationships:

$[Cl]_{ext}$ at first plateau = 65.8 ± 2.8%

$[Cl]_{ext}$ at second plateau = 21.5 ± 3.4%

$[Cl]_{ext}$ at third plateau = 10.6 ± 2.9%

Since the average of the total

Table 7 : Comparison of calculated and real times of immersion of corroded iron cannon, based on desalination kinetics.

Vessel	R mg.cm^{-2}hr^{-1}	d mm	t_w years	t_{actual} years
Trial 3207 (1622)	7.5	17.2	375	363
Batavia 80309 (1629)	11.1	18.0	323	347
HMS Sirius 49 (1790)	67.4	25.0	183	195
Rapid 4032 (1811)	14.6	10.0	157	167

amount of chloride released after the first three solutions changes is 97.9%, it can be seen that for some cannon a fourth electrolysis solution is required to complete the desalination.

In planning the treatment of cannon it is often useful to have an estimate of how long it will take before it is necessary to change the wash solutions. Analysis of the corrosion and washing data shows that there is a relationship between the extent of corrosion and the time it takes to reach the first and subsequent plateaus. The general form of the equation is

$$t_n = k_n / d_g \qquad \dots \dots \dots \dots \quad 10$$

where t_n is the number of days to reach the nth plateau, d_g is the annual depth of graphitisation of the cannon (in mm.y^{-1}) and k_n is a constant for the nth plateau. The values for the plateau constants are $k_1 = 33.9 \pm 5.6$, $k_2 = 68.5 \pm 20$ and $k_3 = 103 \pm 45$ days.y.mm^{-1} . The increasing standard deviations associated with the time taken to reach the subsequent plateaus is due to the natural errors associated with the variability of the depth of corrosion over the surface of the cannon and also due to the non-standard conditions associated with the electrolysis of the cannon. All the above relationships apply to deconcreted cannon that are undergoing electrolysis in sodium hydroxide. The chloride extraction kinetics of the Zuytdorp cannon did

not follow the same relationships as the others because the tompion had effectively sealed the bore of the cannon(MacLeod,1988).

DATING

If the date of the wreck is unknown it may be possible to use the depth of graphitisation and the chloride ion extraction rates to calculate the age of the vessel. Since the average annual depth of graphitisation d_g is obtained by dividing d by the time between sinking and recovery(t_w) equation 9 can be rearranged to give

$$d_g = d/t_w = \{(R+0.11)/3610\}^{\frac{1}{2}}$$

The calculation of the immersion time is made according to

$$t_w = 60.08 \ d/(R+0.11)^{\frac{1}{2}} \quad \dots \dots \quad 11$$

The applicability of equation 11 as a dating method has been used on a number of wrecks of known dates, chloride release rates and depths of graphitisation. The results are shown in table 7 where the calculated t_w dates agree with actual dates within the error range of -3.9 $\pm$ 4.8%. When consideration is given to all the variables associated with dating an object from kinetic data, the agreement is very good and promises to be of value to conservators and archaeologists.

COMPOSITION AND CORROSION

The composition of eight cannon from

Table 8 : Analysis of cast iron cannon from historic shipwrecks.

Artefact	C	S	Si	Mn	P	Ni	Cu	Cl	Carbon Eq./
Rapid 4032	4.0	0.18	1.93	0.475	0.37	0.22	0.023	0.005	4.8
Batavia 8720	4.45	0.12	1.45	0.330	0.32	0.019	0.007	1.95	5.0
Cumberland 52	2.90	0.075	1.57	0.275	0.30	0.013	0.016	< 0.005	4.7
Trial 3207	9.4*	0.30	2.54	0.315	0.74	0.019	0.013	1.31	n.a.
Fairy Queen 3516	2.80	0.015	3.13	1.30	1.04	0.021	0.011	0.0002	4.2
Vergulde Draeck 2435	6.85*	0.070	1.33	0.76	0.40	0.012	0.006	< 0.0002	n.a.
Zuytdorp 3926	4.30	0.055	0.80	0.115	0.46	<0.005	0.065	0.29	4.7
Sirius 49	3.5	0.08	0.10	0.48	0.51	0.015	0.015	0.19	3.7

/ The carbon equivalent is defined by $C_{eq} = C + 1/3(Si+P)$; n.a. Values for these cannon were not calculated.

different wreck sites dating from the seventeenth to the nineteenth century have been determined by chemical analysis of core samples taken when the connections were being made for the attachment of the cathodic current cable. The data is summarised below in table 8. In general the composition of the cannon varies remarkably little from the earliest guns of the Trial (1622) to the wreck of the Rapid (1811), with typical carbon contents of 3.66±0.7 %.

The asterisked values in table 8 for the Vergulde Draeck and the Trial relate to a corroded sample rather than parent metal and so the carbon content is anomalously high and is not a reflection of the basic core composition. There are two sets of typical sulphur impurity levels; one set of five cannon has average values of 0.059± 0.026 % and the other three 0.20 ± 0.09%. The lower values are typical of material that was produced in a charcoal fuelled furnace (Samuels,1980). There is sufficient manganese in all the cannon to form manganese sulphide inclusions and so effectively remove the sulphur from the metallurgy of the metal. Normally, higher sulphur

levels tend to promote formation of coarser graphite flakes.

The amount of silicon for the Sirius (1790) carronade is very low at a value of 0.10 wt.% compared with the average value for four of the other cannon of 1.57±0.26%. Higher silicon levels promote graphite formation and suppress carbide formation; this may account in part for the extensive corrosion of the carronade. High levels of phosphorus and low levels of silicon are both associated with a low temperature of blast furnace operation(Samuels,1992). The Rapid cannon bears the cipher of GⅢR and so it is unmistakably an English cannon - the high nickel impurity is probably associated with a specific nickel mineral deposit that was mined with the iron ore.

The only cannon with an atypical composition is that of the Fairy Queen(1875); the 3.13% silicon content is very high and in a similar way the manganese level of 1.30 % and 1.04% phosphorus are indicators of poor foundry practice or just a low quality ore. One of the apparent consequences of the composition is that the corroded

zone of the cannon spalls away from the bulk of the object once it has been placed in alkaline solutions.

It was originally thought that accidental drying of the first *Fairy Queen* cannon prior to electrolysis treatment had caused the later exfoliation. Given the past record the second cannon of the matched pair was transported to the laboratory in a wet state and soaked in sodium hydroxide solutions without electrolysis and it was never allowed to dry. It also exfoliated. The small cannon have apparently suffered from the high manganese content which favours formation of cementite, Fe_3C, and the high phosphorus content would have made the metal brittle. The lower carbon content may have also contributed to the outer zone of the cannon having a different metallographic microstructure to the bulk of the material.

CONCLUSION

The measurements of in-situ corrosion parameters on a wide variety of shipwreck sites ranging from turbulent open ocean waters to sheltered fresh water rivers has provided a unique insight into the mechanisms of deterioration. From a combination of chemical and metallographic analysis and from data obtained during the conservation treatment of the artefacts, it has been possible to develop a range of equations that describe the basic phenomena that control the rates of desalination of the objects. The insights obtained on the long-term interactions of materials in a marine environment has applications to the management of iron and non-ferrous materials in a hostile marine environment.

Having been immersed in sea water for many centuries the materials found on shipwrecks provide corrosion scientists with a unique set of deterioration experiments. The results of this work has

application to the management of offshore structures associated with the petroleum industry and to the performance of metals in a chloride rich environment often associated with mine sites.

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