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In situ corrosion studies on iron shipwrecks and cannon

The impact of water depth and archaeological activities on corrosion rates

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Abstract

Twenty years of measurements on iron shipwrecks and on iron fittings from wooden and composite wood-iron wrecks have been analysed. This paper presents a summary of the findings with special emphasis on new understandings of how *in-situ* corrosion measurements have enabled a model to be established that allows prediction of corrosion rates of iron shipwrecks based simply on the oceanography and the water depth of the site. These relationships have enabled calculation of the impact of activities such as scallop dredging and the use of explosives in salvaging operations on the rate of loss of our iron shipwreck heritage. The effect of water depth on the corrosion rate of cast iron cannon from the seventeenth to the nineteenth centuries has been determined. Armed with this knowledge a conservator can now advise the maritime archaeologist on the best conservation management strategy to preserve the materials *in-situ* or on how passive interventions such as sand-bagging the site can be used to slow down the rate of decay.

Keywords

Corrosion, conservation, iron shipwrecks, cannon, seawater, excavation, site conditions, calculating, corrosion rates

Introduction

Conservators of shipwreck materials are more and more frequently being called upon to provide conservation and site management advice to maritime archaeologists and heritage managers who are charged with the responsibility of preserving our shipwreck heritage. Whilst some countries provide a legislative framework under which guidelines for effective management of site is possible, many more offer little or no protection for the wrecks and their contents.[1] Regardless of the circumstances of any particular nation, there remains the essential dilemma of how best to preserve the artefacts. Over the past twenty years a series of measurements of corrosion potentials and *in-situ* pH measurements have been performed on a number of shipwreck sites off the Australian coast and in several sites in Scotland, Denmark, the USA and in Canada. One of the problems associated with the compilation of the data is the simple issue of interpretation. Corrosion of metals on shipwreck sites is subject to a number of changing environmental parameters which can often mask the relationships between site variables, such as salinity, temperature, dissolved oxygen and marine growth.

The purpose of this paper is to provide a guide to conservators on how to interpret data obtained from the wreck sites. Having had the advantage of working on a number of sites it has now become possible for the author to establish some general relationships. A number of repeated measurements on the same wreck site at different times of the year shows how the changes in conditions are determining the corrosion rate. The interpretation of the changes will also illustrate the effectiveness of archaeological intervention. Prior to engaging in this exercise it is important to illustrate the basic factors affecting iron corrosion in open seawater. After an initially rapid rate of deterioration in the first few years of immersion, most iron artifacts on wreck sites develop some form of protective coating over their surfaces.[2] This limits the availability of dissolved oxygen to the corroding surface and the rate of corrosion falls to a pseudo steady state. In sea water this protective layer is normally calcareous in origin and in warm waters the growth of encrusting organisms can lead to iron artifacts being covered with a thick layer of encrustation after several centuries.[3–5] Objects such as cannon and anchors exhibit characteristic voltages and acidities that are indicative of the rate of deterioration.[6]

In the production of iron used in the construction of cannon and iron ships the metal has a common origin in that the material has been produced by a chemical reduction process at temperatures of the order of 1400°C. Under these conditions iron oxides had electrons 'forced' into them – thus the electrons are 'playing a waiting game' until they sense some dissolved oxygen in the local environment and can be released.[7] For corrosion to occur, electrons must flow from the iron alloy through the concreted metal surface to the dissolved oxygen in the surrounding seawater. Any factor that change the nature of the concretion, such as burial or re-exposure with concomitant changes in site conditions, will affect the corrosion rate. Seasonal changes in seawater temperature and salinity can also affect the rate at which the corrosion process occurs since these factors determine, amongst other things, the amount of dissolved oxygen in the waters surrounding the concreted artefact.[8]

When considering the interpretation of the E_{corr} data it is important to remember that it is a kinetic and not a thermodynamic property. Since the measured voltage of the corroding piece of concreted iron is due to a combination of the half cell voltages for the oxidation of iron and the reduction of dissolved oxygen, the E_{corr} values will respond to changes in either reaction rate.[9] Repeated measurements on the SS *Xantho* (1872) have shown that the removal of the engine from behind the boiler has had no detrimental effect on the corrosion of the boiler. This is seen in the fact that the E_{corr} values remained constant to within a few millivolts.[10] Previous studies[3] have shown that there is a relationship between the a logarithm of the corrosion rate and the E_{corr}. Thus small changes in E_{corr} result in a very small change in corrosion rate and so simple monitoring of this variable provides a sensitive indicator of the environment.[6]

Just as the standard reduction potential of a metal and its ions in solution depends on the activity of the element, so too the voltage of the oxidation half cell will depend on the alloy composition of the metal.[11] Thus addition of carbon to iron will elevate the voltage of the alloy to less cathodic, or more anodic values. It is therefore normal to expect that corroded cast iron artifacts will have a more positive (less negative) E_{corr} than corroded wrought iron or steel which is corroding at the same rate. In the experience to date, it is found that a less negative E_{corr} value relates to an increased rate of corrosion, unless some change has taken place which has involved the formation of a passive film or if some other form of corrosion inhibition has taken place.

Effects of engine removal and subsequent *in-situ* conservation of the SS *Xantho* (1872)

Analysis of the corrosion data collected in the pre-disturbance survey of the *Xantho* site led to the installation of aluminium sacrificial anodes on the engine and on the propeller shaft.[12] The plan was to minimise any further damage from corrosion and to begin *in-situ* conservation treatment. During the recovery operations in 1985, which saw the 7.5 tonne concreted mass of the engine recovered from the seabed, corrosion potential measurements were used to gauge the impact of the excavation on the remaining parts of the stern. Since the temperature, salinity and level of dissolved oxygen are known for the site, the equation for calculating the slope of the $\log d_g$ vs E_{corr} relationship viz.

$$\partial \log d_g / \partial E_{corr} = 10.33 \log [O_2] - 4.57 \qquad [1]$$

can be used to find the theoretical slope for the *Xantho* site. The calculated slope is 2.70 volts^{-1}, which equates to a Tafel slope of $^1/_{2.70}$ or 370 mV per decade change in corrosion rate. Using this relationship, the changes in the values of the E_{corr} for stern plates and the propeller shaft of the *Xantho* can be expressed in terms of the reduction/increase in the corrosion rate. Inspection of the E_{corr} values in Table I show that, whilst the application of the anodes to the propeller shaft, after the initial site inspection, has not stopped the corrosion, it caused a 37% reduction in the corrosion rate of the drive train. Because the anode remained attached during the engine recovery process, we cannot ascertain the impact of the excavation on this part of the wreck, except to note that, at the end of the anode life in May of 1986, the corrosion rate had increased by 14% above the pre-disturbance level. The attachment of new anodes in 1986 saw the initial corrosion rate cut in half.

Although the propeller shaft remained protected by the anode, the stern iron plating saw an increase in the E_{corr} of 48mV, which indicated an increased degree of turbulence as the current eddying was changed by the removal of the engine. Thus, the immediate impact of the excavation, recorded just four days after removal of the engine, was a 35% increase in corrosion rate. Although the relative corrosion rate for the stern section fell by 12% after a year, as the site conditions of increased sand coverage began to correct the effects of the engine removal, it was not until new anodes were directly attached to the stern section that the initial impact of the archaeological intervention was corrected. The present condition of the stern section is that the corrosion rate has been reduced by 91% compared with the pre-disturbance values. Although current archaeological practice precludes the original plan to recover the stern section for exhibition purposes, the regular replacement of the sacrificial anodes will ensure that the metal is actively conserved on the seabed. During *in-situ* treatment with anodes, the iron remaining on the seabed is effectively undergoing a form of electrolysis. One result of the cathodic current flowing into the object is that the acidity from the original hydrolysis reactions of the Fe^{2+} ions is reduced as hydrogen gas is evolved and the high concentration of chlorides is reduced.[13]

Table I: Effect of site disturbance and conservation measures on the stern of the SS *Xantho* (1872).

Condition	E_{corr}	% change in i_{corr}	Date
Pre-disturbance propeller shaft	-0.269	initial	15/03/83
Propeller shaft with anode	-0.319	37 ↓	18/04/85
Propeller shaft, spent anode	-0.246	14 ↑	15/05/86
Propeller shaft, new anode	-0.380	100 ↓	15/05/86
Pre-disturbance stern plate	-0.280	initial	15/03/83
Iron plates not protected	-0.232	35 ↑	24/04/85
Iron plates on the stern	-0.261	12 ↑	15/05/86
All stern sections	-0.384	91 ↓	19/02/88

Impact of sandbagging on cannon corrosion at the *Swan* (1653), Isle of Mull, Scotland

The *Swan* is a Cromwellian frigate which was wrecked off Duart Point on the Isle of Mull as a result of a violent storm[14]. Observations by the site director, Colin Martin from the Scottish Institute for Maritime Studies in St Andrews University, had noted that the site seemed to be subject to scouring and a marked increase in corrosion activity. The author was contacted and asked to carry out a pre-disturbance survey of the vessel. Long-term corrosion rates can be gauged by drilling into the graphitised cast iron cannon and measuring the depth of penetration. This distance is determined by drilling until the bit reaches the residual, very hard, cast iron. Since the date of the wreck is known, an average or annualised corrosion rate of *x* mm/year can be obtained. This data is listed in Table II and shows that three of the cannon were corroding at a high rate whilst two others were significantly protected by the nature of the topography of the site.[6] The *in-situ* corrosion potential data were measured and from the study it was possible to calculate the present (1994) corrosion rate and to compare it with the long-term data obtained from the depths of graphitisation For cannon 1 there had been a marked increase in rate of deterioration, but for cannon 2 and 3 there was little difference between the long-term data and the present rate. For cannon 4 there was a marked increase and for cannon 5 it was essentially catastrophic. Prior to the second set of measurements on the cannon in September 1995, part of the site near cannon 1 was sandbagged. This archaeological intervention was in response to the observation of significant scouring of the marine debris, which was tending to expose delicate organic remains. The 1995 measurements showed that the E_{corr} of the cannon had changed.

One complicating factor in the interpretation of the data is that the site conditions had changed. The first set of measurements were done in July when the water temperature was 11°C, while the second set was taken in September when the water temperature was 14°C. The difference of 3°C in water temperature means that the saturation level of dissolved oxygen has fallen from 6.32 to 5.90 cm^3/dm^3, which changes the slope of the relationship between $\log i_{corr}$ and E_{corr} from 3.70 to 3.39. Once this had been taken into account, the data in Table II shows that the sandbagging resulted in a 20% reduction in the corrosion rate of cannon 1, while for cannon 2 the amount of water movement over the area remained essentially the same. Given the experimental error in determining the corrosion potentials is ± 0.002 volts, it is sufficient to say that the corrosion rate for cannon 2 was kept constant and so, compared with the increased corrosion rates of other cannon, which were not close to the sandbagged area, the constancy of the corrosion rate can be regarded as a positive sign of the direct benefits of the sandbagging activities. The changed conditions around cannon 3 resulted in an 11% increase. Cannon 4, which is closer to the bay from which the massive volumes of water pour on the ebb tide, has suffered a 43% increase in corrosion rate. Cannon 5 lies in the lee of an underwater cliff and so the impact of the changed site conditions is less than for cannon 4.

This data clearly demonstrates that it is possible to quantify the impact of changed archaeological practices on the rates of deterioration of iron cannon on a wreck site. Since these measurements were done, a set of sacrificial anodes have been placed on the cannon and they are being regularly monitored. One of the reasons why these cannon are corroding at a rapid rate, compared with ordnance of a similar age and in a similar depth of 11–12 m, is that the extent of the marine growth on the surface is much less in the cold and less saline waters of the west coast of Scotland than in the warm tropical to sub-tropical waters of Western Australia. Since one of the primary factors affecting the corrosion rate of marine iron is the effectiveness of the diffusion barrier between the corroding object and the dissolved oxygen in the surrounding sea water, it is clear that the thickness of the concretion plays a major role. Typical thickness of the calcareous deposit on the Duart Point cannon was 2 mm, whilst that on the *Batavia* (1629) and the *Vergulde Draeck* (1656) is more typically 25–35 mm. Assuming a similar efficiency of pre-treatment to that found for the *in-situ* electrolysis of the *Sirius* (1790) carronade on Norfolk Island,[13] it is anticipated that the cannon from the *Swan* (1653) will be completed by the end of the year 2000.

Impact of anomalous tides on the corrosion of the SS *Clan Ranald* (1909)

Normal tides

The waters of Investigator Strait are found in the lower reaches of Gulf St Vincent in South Australia; so named after the vessel of explorer captain Matthew Flinders, who charted the treacherous waters in the nineteenth century. The land elements that set the boundary are the lower reaches of the Yorke peninsular and the 4350 km^2 of Kangaroo Island.[15] It was the original intention of the site inspection to determine how fast the wreck of the turret ship *Clan Ranald* was corroding, since it was planned to open up the dramatic wreck site to cultural tourism in the form of escorted diving tours. The wreck is also famous for the number of persons who were lost and for the subsequent enquiry, which exposed the evils of the White Australia Policy.[16] A secondary aim of the project was to see if it was possible to combine measurements of residual metal thickness with corrosion meas-

Table II. Effects of changed site conditions on the *Swan* (1653) site on the cannon corrosion rates.

Cannon no	1994 E_{corr} volt vs NHE	1995 E_{corr} volt vs NHE	*long term* i_{corr} mm/year	1994 i_{corr} mm/year mm/year	1995 i_{corr} mm/year	% change i_{corr}
1	-0.182	-0.255	0.180	0.290	0.231	20 ↓
2	-0.235	-0.281	0.183	0.185	0.189	2 ↑
3	-0.233	-0.266	0.189	0.188	0.212	11 ↑
4	-0.262	-0.267	0.066	0.147	0.210	43 ↑
5	-0.242	-0.271	0.019	0.174	0.204	17 ↑

urements to see if the original dimensions of the steel sections could be calculated. The data would also be used to estimate the remaining life span of the wreck.[16]

The wrecksite lies some 700 m offshore from Troubridge Point in 18 m of water. A considerable amount of material is scattered along the 108 m of the site. The *Clan Ranald* has been subjected to explosive charges being detonated as part of the recovery operations which removed the bulk of the non-ferrous metals. A series of 12 measurements were made on the steel plates of the boilers, hull plating and on the wrought iron of the stern post as well as cast iron fittings on winches and windlasses. The results of the measurements are summarised in Table III and the average of the 11 E_{corr} measurements (one object was totally corroded) was -0.344 ± 0.018 volts vs. NHE at a pH of 6.74 ± 0.44.

When the mean E_{corr} and pH data are plotted on a Pourbaix diagram we see that it lies within the zone of active corrosion where the primary corrosion product is ferrous chloride.[17] Metal thickness measurements were made on the most significant artifacts, which included the massive 15 ft (4.57 m) diameter main boiler and sections of the double bottom of the hull, which was lying proud of the sea bed. The site corrosion rates were determined using data generated from the depth of corrosion of the cast iron fittings. Prior to using equation 2 to calculate the corrosion rate for wrought iron and steel sections, the corrosion potentials were corrected for the ennobling effect of the carbon content in the cast iron. Typically this correction amounted to 20 mV.

$$\log d_g = 2.92\, E_{corr} + 0.0878 \qquad [2]$$

The statistical analysis of the fit of the linear regression showed that the calculated value of the slope (2.92) had an error of ± 0.35 or some 12%. The largest part of the error is due to measurements on the depth of graphitisation, which at the best has an error of ± 0.5 mm. The mean of the actual and calculated corrosion rates is 0.122 ± 0.015 mm/yr. The scatter of results is 12% around the mean value and this shows a good set of agreement given that the nature of the site is relatively homogeneous, in an oceanographic sense.

When the estimated present corrosion rate, or the long-term corrosion rate, is multiplied by the length of immersion (86 years), we can then calculate how much metal has corroded away and then add in the present data on remaining solid metal to gain an estimate of the original thickness. The estimates of original dimensions were shown to provide valuable data on factors such as boilers and hull plate thickness which could not be found from extant documents. The plating measured at station 12 was apparently a part of the original double hull. Thus the calculated plating thicknesses for the *Clan Ranald* are consistent with that required under the Lloyds specifications for a turret class vessel. No estimates were done on four of the cast iron fittings as it was not possible to obtain a good reading on these surfaces as the surface profile prohibited reproducible measurements being taken by the ultrasonic probe.

The main and donkey boilers and the nearby plating had the lowest corrosion rate while the cast iron mast fitting, only some 10 m distant, has a significantly higher rate of decay. The higher average thickness of concretion over the cast iron fittings of 19.5±4 mm, compared with 4–7 mm on the metal plating, would normally provide better protection from the effects of the flowing sea water. The cause of the differences in corrosion rate may well lie in their metallurgical microstructure.[18]

'Dodge tides'

In October 1996 the site was re-assessed to see what impact a major storm had on the stability of the wreck. The local dive-tourism manager reported recent damage that had been associated with a 'one in twenty years storm'. Although there was some mechanical damage to the site, such as the partial collapse of formerly free standing structures and loss of some of the concretion surfaces, the overall impression of the site was that it seemed to be in a less corrosive environment. 'Astronomical tides are cancelled out near the equinox and the water level remains constant for a whole day, the so-called *dodge tide*. The tides can vary the water level between two or three metres, reaching the upper figure near Port Wakefield, and tidal currents are associated with the tidal elevations'.[19] The corrosion potential measurements were generally at less anodic voltages(i.e. more negative) than they were for the normal tidal situation. One factor to consider was that the water temperature of 17°C for the second visit was much cooler than the 22°C of the first visit. As previously noted for the cannon at the Duart Point wreck in Scotland, the main effect of this is to increase the dissolved

Table III. Corrosion data from the wreck of the *Clan Ranald*.: normal tide.

Location and description	E_{corr} volts vs. NHE	pH	Corrosion mm	Solid metal (mm)	Corrosion (mm/yr)	Original (calculated)	
1: Cast iron mast fitting	-0.320	6.33	n.a.	9	0.142_{calc}	21.2-19.5 mm	¾"
2: Main boiler	-0.350	6.56	10.0	23.2	0.109	32.6-33.7 mm	$1^{5}/_{16}$"
3: Donkey boiler	-0.363	7.34	9.0	17.8	0.107	27.0-27.3 mm	$1^{1}/_{16}$"
4: Hull plate	-0.367	6.78	n.a.	3.6	0.104_{calc}	13.1-14.7 mm	$^{11}/_{20}$"
6: Rudder post	-0.340	6.57	n.a.	3.6	0.124_{calc}	14.1-14.3 mm	$^{11}/_{20}$"
7: Stern plate	-0.338	7.16	n.a.	4.6	0.126_{calc}	15.1-15.4 mm	$^{12}/_{20}$"
8: Stern winch	-0.340	6.29	11.0	19.4	0.124	29.9-30.1 mm	$1^{3}/_{16}$"
12: Elevated plating	-0.354	7.52	n.a.	4.2	0.113_{calc}	13.5-14.7 mm	$^{11}/_{20}$"
5: Prop shaft casing	-0.309	6.36	13.0	na	na	na	
9: Middle of fwd. winch	-0.355	6.94	n.a.	67	na	na	
10: Port side of fwd. winch	-0.336	6.33	11.0	27	na	na	
11: Windlass	-0.237	8.04	n.a.	18.6	na	na	

Table IV. Comparison of corrosion *Clan Ranald* data with normal and 'dodge' tides.

Object	normal E_{corr}	'dodge tide' E_{corr}	normal tide (mm/yr)	'dodge tide' (mm/yr)	% change
boiler B2	-0.350	-0.356	0.116	0.103	11 ↓
donkey	-0.363	-0.391	0.107	0.081	24 ↓
hull over donkey	-0.367	-0.398	0.104	0.077	26 ↓
propeller shaft casing	-0.309	-0.357	0.153	0.102	33 ↓
rudder post	-0.340	-0.370	0.124	0.093	25 ↓
stern plate	-0.338	-0.369	0.126	0.094	25 ↓

oxygen content of the colder water. Oceanographic data from Bye[19] shows that the slope of corrosion equation no 2 will change from 2.92 to 3.02. In effect this means that it takes 331 mV for a ten fold corrosion rate change compared with a previous value of 342 mV. Whilst this 3% change in 'sensitivity' to the electrochemical environment may not seem much, it is important to be aware of these changes as it is the only way in which to be sure that the same values of E_{corr} mean the same thing in each condition.

An indication of the net effect of the 'dodge tide' on the rate of decay of the vessel is seen in the data listed in Table IV, which shows the E_{corr} data and the calculated corrosion rates for the matching points on the wreck during the two seasons of measurements. The average corrosion rates falls from 0.1220 mm/year to 0.0924 mm/year or a fall of 24.6%.. Since the underlying acidity is due to hydrolysis reactions, such as shown in equation 3,

$$2Fe + 2H_2O + 2Cl^- \rightarrow \{FeCl_2.Fe(OH)_2\} + 2H^+ + 4e^- \quad [3]$$

the change in corrosion rates is also reflected in the changes in the average pH of the corroding iron ship. Thus the decrease in corrosion rates is seen in the mean 'dodge tide' pH of 7.06 being more alkaline than the mean value of 6.89 for the normal tides. Since the 4.6 m diameter boiler B2 profile has not changed with the effects of the storm, the net effect of the 'dodge tide' can be seen in terms of the 11% reduction in the rate of deterioration of this boiler. When a direct comparison of specific locations on the wreck is made we see that the partial collapse of decking round the donkey boiler has caused the corrosion rate to fall by 24% and the propeller shaft has fallen by 33%.

The larger drops in corrosion rate are therefore due to other changes that have taken place during or after the massive storm. This is in fact a more reasonable indication of the net effect of the 'dodge tide' and the overall change in conditions associated with the changes in site profile accounts for the greater part and so the storm could be seen to have caused a lowering of 13.6% in the corrosion rate. A more detailed analysis of the data can be found in the site reports.[20]

Differences in the corrosion rates across the site are largely associated with differences in the profile of the wreckage on the sea bed and the co-location of massive sections of the remaining structure, which either protect the other item or cause a series of eddies to form around it. Bartels' current meter measurements[16] during the 'dodge tide' season indicated a very complex pattern of water movement across the site. Average water flow across the site ranged between only 20–35 cm/sec or some 0.4–0.7 knots, whereas the average currents associated with normal tide flow in Investigator Strait are of the order 30cm/sec or 0.6 knots. Because of the complex way in which water flows are affected by salinity changes, the average currents vary by a factor of 4.4 times so it is not unexpected that there are significant decreases in the corrosion rate at 'dodge tides'.

The high long-term corrosion rates are also likely to have been affected by the use of explosives on the site. As the shock waves from the detonation apply their force to the concreted metal surfaces, the concretion spalls. The sudden exposure of the corroded metal to the direct electrical contact with dissolved oxygen in the sea water will cause an immediate massive increase in the corrosion rate. After a few years of re-colonisation by the marine encrusting organisms the corrosion rate would decline towards its pre-disturbance value. A more detailed discussion of this effect is found in the following section.

Effects of water depth, embayment and explosives on the corrosion of iron shipwrecks

In attempting to find some order amongst the data that has been collected from a number of shipwreck sites around the Australian coast, it became apparent that it was important to directly compare the corrosion phenomena on iron shipwrecks with each other. The data that forms the basis of the survey comes from a number of wreck sites which range in depth from zero to 22 m. The shallowest vessel is that of the breastwork monitor HMVS *Cerberus* (1926) in Port Phillip Bay in Victoria, which was sunk as a breakwater. The deepest vessel is the *City of* Launceston (1865), which is also located in Port Phillip Bay but in the middle of the west shipping channel. The corrosion measurements on the *Cerberus* related to zero water depth for the former splash zone to 4 m. The annual corrosion rate of 0.242 mm/year at zero water depth relates to the armour plating on the outerdecks of the vessel.[21] Composite vessels such as the *Zanoni* (1867) in Gulf St Vincent in South Australia were found to have apparently anomalously low corrosion rates, when compared with iron wrecks in a similar physical environment.[22] Further studies on the *Zanoni* and other composite vessels are needed before any conclusions can be drawn. The lower apparent corrosion rates may be due to the fact that the wood extractives gave some *in-situ* protection to the wrought iron and steel frames. There appears to have been no marked effect of the copper alloy sheathing on the overall corrosion rate of the iron frames on this vessel.

Since previous studies[3] had shown that the E_{corr} steadily decreased with water depth the corrosion rates from

Table V. Iron shipwrecks and their average corrosion rates as a function of water depth.

Vessel	Date	Depth (m)	Corrosion (mm)	Actual corr rate (mm/year)	Calculated corr rate	% increased rate
City of Launceston	1865	19.7	15.4	0.117	0.072	39
Clan Ranald	1909	17.8	10.8	0.126	0.085	33
SS Pareora	1919	10.1	11.8	0.156	0.146	6
Songvaar	1912	7.7	11.0	0.129	0.167	-30
Cerberus$^{\text{prop shaft}}$	1926	4.4	8.0	0.118	0.199	-68
SS Investigator	1918	3.6	16.5	0.209	0.207	1
SS Willyama	1907	3.6	5.9	0.193	0.207	-7
Omeo	1905	1.5	19.0	0.230	0.228	1
Cerberus$^{\text{splash zone}}$	1926	0.0	16.5	0.242	0.244	-1

the iron shipwrecks were ranged according to the average water depth. The primary indicators of the corrosion rate was determined from the annualised depth of graphitisation, expressed in terms of mm of iron corrosion per year of immersion. A number of regression analyses were tested and the best fit was in the form of a quadratic equation with the square of the correlation coefficient being 0. 9985. Such a high correlation coefficient is a strong indicator that the relationship has a high degree of validity. Thus the long-term corrosion rate of an iron shipwreck in the open ocean waters of southern Australian latitudes is given by equation 4, viz.,

$$i_{corr} = 0.2438 - 0.0107\,m + 0.0002\,m^2 \qquad [4]$$

where i_{corr} is in units of mm/year and the water depth m is in metres. The benefit of this relationship is that it can be used by any person to calculate the expected corrosion rate for vessels when the only archaeological information known is their date of wrecking and the water depth. If the original thickness of the metal ribs, frames and plates are known then equation 4 can be used to estimate how much of the materials is likely to be remaining on site. Corrosion data from wreck sites such as the *Songvaar* (1912), which lies in the lee of Wardang Island in Spencer Gulf in South Australia, can now be assessed to gauge the impact of being protected from the full brunt of the ocean waves. The results are shown below in Table V.

The data from the calculations indicates that the observed rate of corrosion on the iron clipper *Songvaar* is some 30% less than would be anticipated on the basis of the water depth. In a similar fashion, the wreck of the steam ship *Willyama* (1907) is 7% lower than anticipated. The *Willyama* lies in the shallow waters of Marion Bay in Investigator Strait but the amount of shelter it receives is less than that of the *Songvaar* in the nearby Spencer Gulf. Another possible factor that may have lowered the historical corrosion rate of the iron clipper *Songvaar* is that, when it sank on its own anchor, the vessel was fully laden with wheat. As the wheat swelled it would have begun to undergo marked biodeterioration, which would have rendered the waters on the inside of the vessel anaerobic and so reduced the initial corrosion rate.

The increased rate of corrosion of the *Clan Ranald* of some 33% is probably due to the impact of it having been extensively blasted during a series of salvage operations. Shock waves from the exploding charges tend to strip the protective concretion from the hull and other fittings and so give direct access by the dissolved oxygen to the degraded metal. Observations of the rapid increase in corrosion potential of several hundred millivolts when an iron artifact has its protective concretion accidentally removed during archaeological excavations testifies to the impact of such activities.[21] The wreck of the *Pareora* shows an elevation of some 6% and this site was also affected, but to a lesser extent, by charges being let off during the initial salvage operations, whereas the main blasting on the *Clan Ranald* took place some fifty years after the vessel had foundered. Clearly the effect of stripping of the protective concretion has a much larger impact on the vessel after the iron has been subjected to decades of corrosion activity.

A fine example of the effect of embayment is seen in the difference of observed and calculated corrosion on

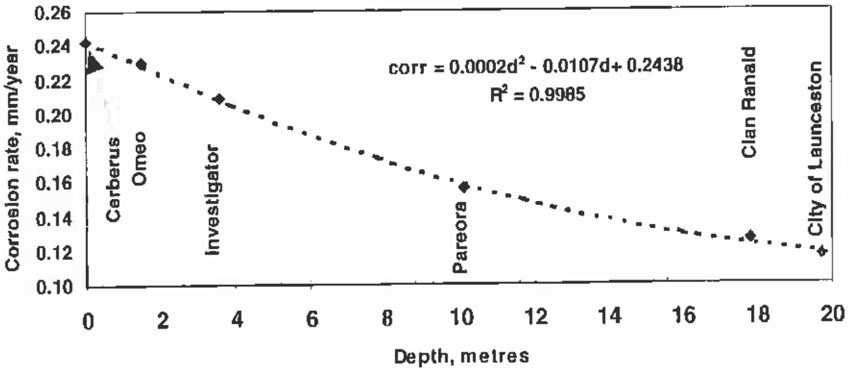

Figure 1. Effect of water depth on the corrosion rate of iron shipwrecks in Australian waters.

the cast iron propeller shaft of HMVS *Cerberus*. When the corrosion data was collected in 1994 the shaft was just lying proud of the seabed in a very fine silty deposit. Clearly the 68% lower corrosion rate is simply due to the fact that for long periods the propeller shaft has been either buried or largely sheltered by the rest of the vessel from the brunt of the wave action.[21] This observation clearly indicates that the equation for calculating the rate of degradation of the iron wrecks should only be used for vessels in open waters. The effect of water depth on the annualised corrosion rate can be seen below in Figure 1.

In the case of the *City of Launceston* the equation anticipates a 39% lower corrosion rate than that which has been observed on the site. During a recent site visit in November 1997, it was noted that the E_{corr} values for several repeated points of measurement on the hull had fallen to more cathodic levels. The water clarity was much better than in 1991 when it was first examined and the extent of marine growth was much greater. The wreck site is littered with the remains of a dozen scallop dredges as the area was actively trawled for nearly thirty years. The higher corrosion rate may well be due in a large proportion to the impact of scallop dredging and in part due to cyclical changes in the amount of protective marine growth over the shipwreck. With the dredging causing a large decrease in the amount of sunlight penetrating, the amount of protective marine growth covering the wreck would be decreased. This is due to the fact that the primary colonising organisms are tunicates, algae and sponges.

One implication of the quadratic nature of equation 4 for calculating the corrosion rate of the iron wrecks is that, with the negative value of the constant for the m term being of greater numerical value than the positive constant associated with the m^2 term, there will be a minimum value for i_{corr} at a particular water depth. This minimum can be determined by simple differential calculus. Thus differentiation of the equation

$$i_{corr} = 0.2438 - 0.0107\,m + 0.0002\,m^2 \qquad [4]$$

with regard to the water depth m will result in the slope of the relationship being given by equation 5, viz

$$\partial_i / \partial_m = 0.0004m - 0.0107 \qquad [5]$$

and the minimum value is reached when the slope is equal to zero, which occurs at a water depth of 26.8 m. This observation has profound implications since it implies that once an iron wreck is in water of greater depth than 26.8 m, the overall effect of the increased water depth is limited. It must be stated that these observations are limited to the data that has been collected and that the deepest site measured was 22 m. The other implication is that the minimum corrosion rate of iron shipwrecks is 0.100 mm/year, which is the average long-term corrosion rate of marine iron in an exposed location.[5]

Effect of water depth on the corrosion rate of 17–19th century cast iron cannon

The conservation laboratories of the Western Australian Museum have treated more than twenty cannon from a number of shipwrecks and the analysis of the data resulted in a series of relationships that enabled prediction of treatment times, the total amount of extractable chloride ions and the rate at which the chlorides would be released during the first stages of treatment. It was also demonstrated that it was possible to use the kinetic data from chloride release rates under electrolysis in caustic solutions to form the basis of a method for calculating the age of the shipwreck.[24] This section of the work reports on a new relationship that has emerged between corrosion and water depth. Part of the role of the modern conservator is to provide the maritime archaeologist with advice on whether or not it is wise to recover cast iron artifacts from historic shipwrecks. Massive objects such as ship's stoves and marine steam engines can look very stable on the seabed but they are often totally graphitised and readily disintegrate during recovery or transport procedures in the journey back to the laboratory. A case in point was the recovery of the stove from the wreck of the *Rapid* (1811), which had corroded for 170 years on the seabed. The stove was excavated successfully but it disintegrated by the time it reached the laboratory some 1200 km south of the wreck location near the North West Cape of Western Australia.

As part of the study of the desalination of cast iron cannon, one important parameter was the depth of graphitisation of the iron. Since the cannon all have a similar composition and a similar microstructure, it was decided to see if there was any general correlation of the extent of degradation with the site conditions. Since many of the cannon that have been treated in the conservation laboratories of the Western Australian Museum are from sheltered or periodically buried sites,

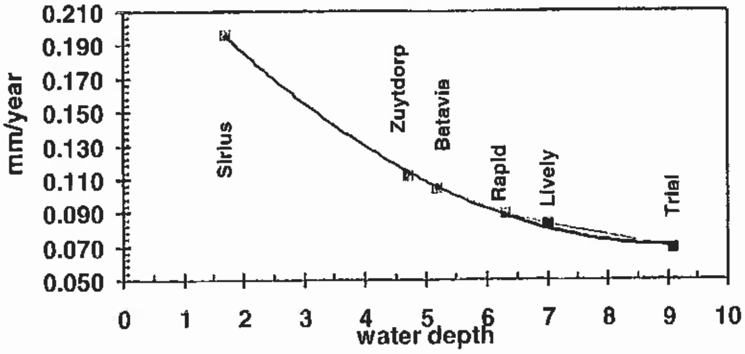

Figure 2. Effect of water depth on the rate of corrosion of cast iron cannon.

it was important to look only at data from cannon which had apparently been continuously exposed to open sea water. This reduced the data set to only six cannon, which ranged from the wreck of the English Eastindiaman *Trial* (1622) to the American China Trader *Rapid* (1811). The effect of increasing water depth on the rate of corrosion, as measured by the annualised depth of corrosion, is shown below in Figure 2.

Analysis of the data shown in the figure shows that the six points can be represented by equation 6, viz.,

$$i_{corr} = 0.259 - 0.0414\ m + 0.0023\ m^2 \qquad [6]$$

where i_{corr} is the corrosion rate of the cannon expressed in mm/year of immersion and m is the water depth in metres. The correlation coefficient for the data points was R^2 equal to 0.9981, which is again an extremely good fit. By the nature of the quadratic equation shown above (6), there will be a minimum corrosion rate which can be determined by differential calculus. Applying the same process as for equation 4, we find that the slope of the graph is given by

$$\partial_i / \partial_m = 0.00046\ m - 0.0414 \qquad [7]$$

which gives a minimum in the corrosion rate at 9 m, which is close to the depth from which the *Trial* cannon was recovered. It is interesting to note that the iron cannon corrosion rate predicted by equation 6 at zero water depth gives a rate of 0.259 mm/year, which is, within experimental error, the same rate as predicted for iron shipwrecks at zero water depth. This corrosion rate was observed for the iron at the splash zone of HMVS *Cerberus*. The other implication of these relationships of corrosion rate and water depth is that equation 6 predicts a minimum corrosion rate of 0.073 mm/year. This compares with the rate observed on the *Trial* cannon of 0.069 mm/year. Recent data from the tropical waters of Torres Strait off the Cape York peninsular in Queensland on the wreck of HMS *Pandora* (1791) relates to material recovered from a water depth of 30 m. The one cannon which had been found buried in the debris of the coral in 1983 was corroded to a depth of 9.5 mm or some 0.050 mm/year. The carronade for which measurements are available was corroded to a depth of 20 mm in 204 years or 0.098 mm/year. Although this carronade had corroded at a higher rate than equation 6 would have predicted, by some 35%, it should be noted that this piece of ordnance was associated with nearby copper artifacts, which would have exerted a significant galvanic effect and so increased the corrosion rate of the gun. The apparent elevation of the carronade corrosion rate on the wreck of the *Rapid* due to long-range galvanic coupling (proximity corrosion)[4,24] is an increase from 0.072 to 0.096 mm/year or some 33%, which is the same as the values observed on the *Pandora* carronade.

Conclusion

The routine measurement of corrosion potentials and pH values of corroding metals on historic shipwreck sites has been demonstrated to be an invaluable tool for the applied maritime conservator. Having established a corrosion model for iron artifacts and for iron shipwrecks in their own right, it is now possible to move from an individualistic assessment mode to a predictive mode of estimating the corrosion rates of historic iron shipwrecks and cannon. This new information will be of great assistance to all those who are charged with the responsibility of managing the heritage resource of our shipwrecks. Through the use of *in-situ* corrosion measurements of the pH and the corrosion potentials of iron fittings and structural members, it is now possible to quantify the effects of activities such as sandbagging a site and excavating sections of a wreck and not backfilling the spaces that are created as a result of the archaeological intervention on the site. From an analysis of the data obtained on an individual site it is possible to determine which sections of the wreck are most susceptible to accelerated degradation and so initiate protective measures.

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Résumé

Les mesures accumulées depuis 20 ans sur des épaves de bateaux en fer ou sur des morceaux ferreux provenant des épaves en bois ou composite bois/fer ont été analysées. Cet article présente un résumé des conclusions en mettant l'accent sur les résultats permettant de comprendre comment les mesures de corrosion **in-situ** ***ont permis d'établir un modèle de prédiction du taux de corrosion des épaves en fer, basé sur les données océanographiques et la profondeur du site. Les relations entre ce type de données et le taux de corrosion permettent de quantifier l'impact, sur le taux de perte de notre héritage, d'activités telles que la pêche et l'utilisation d'explosifs lors d'opération de sauvetage des épaves. L'effet de la profondeur d'eau sur le taux de corrosion des canons en fonte datant des 17ème, 18ème et 19ème siècles a été determinée. Armé de ces résultats, le conservateur peut maintenant conseiller le spécialiste en archéologie sous-marine sur la stratégie de conservation à adopter pour obtenir le meilleur moyen de préserver les matériaux*** **in-situ** ***ou comment des interventions passives comme conditionner les matériaux et le sable qui les entourent peut ralentir la dégradation de ceux-ci.***