



AN IN-SITU STUDY OF THE CORRODED HULL OF HMVS *CERBERUS* (1926)

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SUMMARY: During massive gales in December 1993 the wreck of HMVS *Cerberus* collapsed two metres into the sea leaving only the superstructure and part of the decks above water. Because of the historic significance of this iron Monitor styled warship a corrosion survey was commissioned to establish the remaining life of the vessel. From a combination of in-situ corrosion potential, pH and metal thickness measurements it has been possible to quantify the present rate of deterioration. The impact of wind, wave action and local water movement within the site have been ascertained. From a combination of long-term corrosion profiles and present residual metal thickness, calculations of original dimensions of plating, ribs and frames have been made. Thus maritime archaeologists and heritage managers now have a new tool with which to investigate the nature of historic iron shipwrecks.

Keywords: in-situ corrosion, pH; marine corrosion, iron shipwrecks, corrosion potentials, conservation management

1. INTRODUCTION

The Monitor styled iron and steel warship *Cerberus* was built in England for the Royal Victorian Navy in 1867. After many years of service the 2107 ton vessel was stripped of its engines and towed to Half Moon Bay at Blackrock, Victoria and sunk as a breakwater in 1926 to protect the nearby yacht club from the prevailing seas that sweep across Port Phillip Bay. The upper works of the vessel were clad in 10"-8" of steel armour plate and the two swivel action gun turrets contained four muzzle loading rifled Armstrong guns with a 10" bore and a length of fifteen feet. Because of the constraints of the specific form of naval architecture the vessel was supported by a rather lightly built hull. The overall effect of nearly seventy years of marine corrosion was to leave an extensively degraded hull structure supporting a massive load of more than two thousand tonnes of steel in the upper decks and gun turrets. During a violent storm in December 1993 the gale force winds and high seas brought about a sudden a dramatic collapse of the structure. The upper deck fell by more than two metres leaving the teak deck timbers awash at each high tide. The civic and heritage authorities suddenly realised that a well loved and noted landmark was disappearing before their eyes. Before any recommendations could be made on the management of this resource it was essential to undertake a corrosion survey of the vessel and assess what were the chances of survival into the next century. Given that the only other vessel of this type lies in over 250 metres of water off Cape Hatteras in South Carolina, the wreck of HMVS *Cerberus* provides a unique opportunity for those wishing to study armaments and warship technology from the last quarter of the nineteenth century. A series of measurements of corrosion potentials (E_{corr}), surface pH and residual metal thickness d_r were performed over four days in October 1994 at the request of the Maritime Archaeological Unit of Heritage Victoria and this data forms the basis of the report.

2. CORROSION POTENTIAL MEASUREMENTS ON HISTORIC SHIPWRECKS

After a decade of immersion in sea water, the initially rapid iron corrosion rate falls to a pseudo steady state. Our *in-situ* measurements give quasi thermodynamic data that relate fundamentally to the kinetics of the processes of deterioration. After many years of immersion in sea water and with the presence of a fouling colony, an acidic and chloride-rich microenvironment is established around the corroding metal object (1). Prior to measuring the E_{corr} , a small area of the layer of concretion must be cleared to allow for direct electrical contact between the platinum electrode and the underlying metal. Because the influx of alkaline sea water will tend to neutralise the acidity arising from past hydrolysis of the metal corrosion products, the *in-situ* pH is recorded before the voltage by inserting the snugly fitting flat surface combination glass electrode into the 13 mm diameter hole. The determination of corrosion potentials is effected by reading the voltage recorded by a high impedance digital voltmeter housed in a waterproof case, along with a digital pH meter in the same box. The measured voltage refers to the difference in electrical potential of the silver chloride reference electrode in the sea water ($Ag/AgCl_{sea}$) and the platinum working electrode.

Once the E_{corr} and the pH were recorded, along with the water depth and temperature, a 25 mm diameter area was cleared of concretion and corrosion products in order to obtain a section of bright clean metal. The sensing head of the Cygnus 1 Underwater metal thickness probe was gently moved across the surface until reproducible readings of residual metal thickness (d_r) were obtained. In the waters close to the surface it was often very difficult to obtain reproducible data as the water movement made the task of obtaining a good ultrasound echo very difficult. The data from each location was recorded manually using a pencil on a plastic slate attached to the instrument case. Prior to each dive the pH and ultrasound sensor were calibrated and the voltage of the reference electrode was periodically checked against external standards to obtain a value of the voltage of the Ag/AgCl_{sat} electrode relative to the Normal Hydrogen Electrode (NHE) which was +0.240 volts. The values of E_{corr} in the text will be reported relative to the NHE unless otherwise stated.

Although sea water is naturally alkaline, owing to the presence of dissolved carbonate and bicarbonate ions, the metal surfaces are normally more acidic as a consequence of the hydrolysis of the iron(II) and iron(III) 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 (1,2). The concretion was penetrated with the aid of a compressed air-driven drill with a masonry bit but a shear force applied to a diving knife driven by a 1 kg hammer proved to be most effective in clearing the larger areas for obtaining the metal thickness measurement. Correct determination of the corrosion potential was indicated by the obtaining of a very steady voltage, i.e. a reading that varies by only 1 to 2 millivolts over several minutes and so differences in E_{corr} > 2mV are significant.

Previous studies have shown that the corrosion rate of marine iron is controlled by the diffusion of dissolved oxygen to the concreted interface (3) with a physical separation of the anodic and cathodic processes. Because of the overvoltages associated with this corrosion cell a Tafel type relationship exists between the annualised depth of corrosion and the corrosion potential. This linear relationship between the logarithm of the corrosion rate and the corrosion potential for the artefacts measured under aerobic conditions means that very small changes in corrosion rate are readily detected in changes in the value of 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 to produce ferrous chloride as the primary corrosion product,



Subsequent hydrolysis reactions of the primary corrosion product result in a wide range of iron(II) hydroxy chlorides existing close to the corroding metal surface. 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. In the absence of calcareous colonising organisms, a corroding iron wreck will generally be covered with a matrix of corrosion products and marine organisms such as algae, barnacles and tunicates. Wrecks such as the *City of Launceston* (1865) in Port Philip Bay are typical of historic iron vessels that are corroding in deep water (22 metres) in the absence of calcareous concreting organisms (4). In-situ corrosion measurements on this vessel and others in Port Philip Bay confirmed that the same corrosion mechanism operates for wrecks in this type of environment as for material that is concreted with a matrix of calcareous materials. The *Cerberus* has a relatively heavy calcareous layer in the upper works in the former intertidal zone which gives way to a relatively thin layer at 3 metres and below where secondary colonisers are similar to those found on the *City of Launceston*.

For metal that is totally buried in the sediment and is not electrically connected to iron that is exposed to oxygenated waters, the major cathodic reaction will be the reduction of water and the associated evolution of hydrogen. Under such circumstances; the corrosion process is often dominated by microbiological activity (5) since the presence of dehydrogenase enzymes will often control the rate of hydrogen evolution (6,7). Although electrical continuity measurements were not performed on the various sections of the *Cerberus* the construction of the vessel is such that most elements below the surface of the seabed are likely to be electrically in contact with iron that is exposed to oxygenated water.

3. RESULTS AND DISCUSSION

3.1 Overall site description

A total of 63 sets of corrosion potential, pH and metal thickness measurements were performed over the three days at 21 different locations ranging from the bow to the stern of the vessel, at intervals of between four and six metres across the seabed. At each location a series of measurements of E_{corr} , pH and d_r were made at typical water depths of 3.9 ± 0.3 metres (sea bed), 2.3 ± 0.5 metres (standing on the sea bed) and near the surface at a depth of 0.9 ± 0.3 metres. Data was collected from both the sheltered port side and the starboard side which is exposed to the prevailing weather and wave action from across Port Phillip Bay. The lower sections of the vessel are characterised by a series of bent and heavily distorted ribs and frames that have been subjected to extreme stress during the storm as the vessel collapsed. The amount of concretion cover over these recently torn members is small and offers little protection to the underlying metal. Metal plating sections have been bent over backwards upon themselves or bent over under themselves to create unusual "U" shaped sections which are either lying proud of the seabed or are still attached to sections of the vessel by the rivets attached to the more sound elements. The maximum water depth recorded on the site was 4.4 metres and the bottom was a mixture of sand and fine silt which reduced visibility during our measurements and when the wind came up. The problems of the silt obscuring our operations was greatest under the stern section when examining

the propeller shaft casings. The vessel has a list to the port side and there is evidence of new colonisation at a water depth of approximately 0.7 metres over material that was previously in the intertidal zone. The water temperature was 15°C and the sea water had a pH of 8.14 with a salinity of 32.5 ‰ which gives a dissolved oxygen content of 5.8 cm³/dm³, assuming 100% saturation (8).

3.2 Corrosion potential and pH measurements

The surface pH ranged from maximum values of 8.76 to a minimum of 6.04 with a mean value of 7.31 ± 0.60 . The most alkaline pH was associated with a calcareous matrix at the freshly colonised interface on the port side in an area that had previously been intertidal. The minimum pH was associated with a relatively thick black concretion matrix on the seabed where there was a reasonably dense matrix of calcareous deposits and corrosion products. The measurements on the plating and other fittings were generally taken close to the seabed, at a depth approximately 1.6 metres above the seabed and at a depth that varied between 0.9-0.6 metres below the surface.

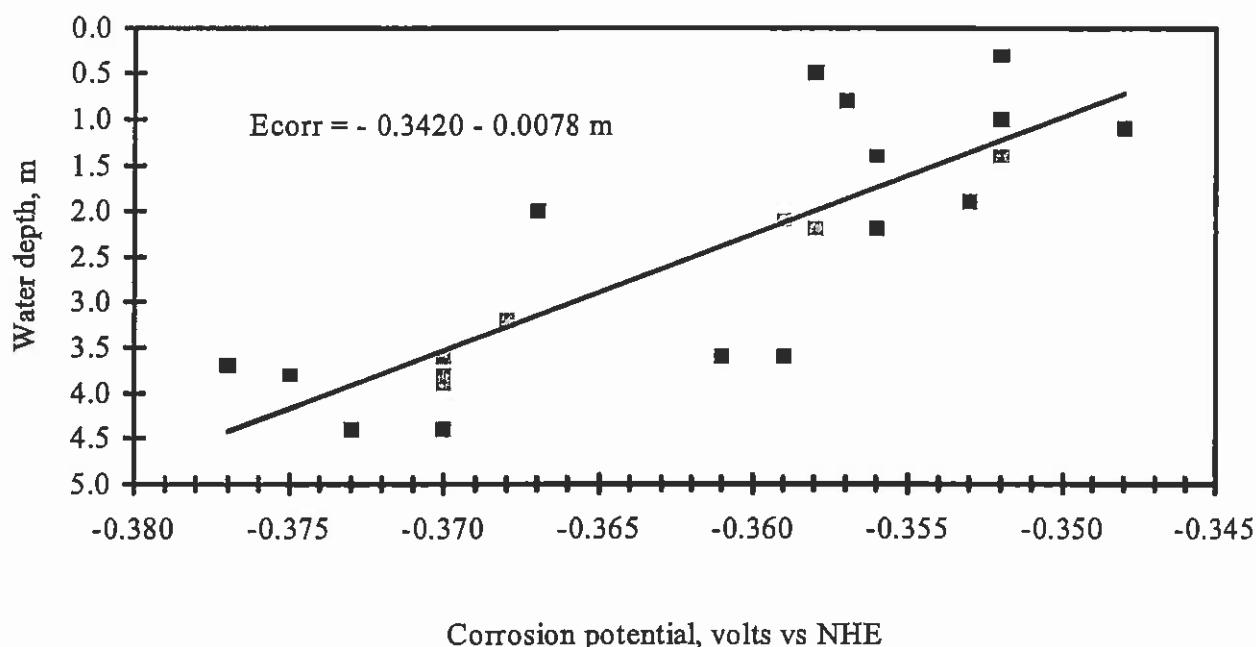


Figure I: Plot of the corrosion potential for the starboard side as a function of the water depth.

Inspection of the data shows that there are some systematic trends in the values with site parameters such as water depth and physical location on the site with regard to local water movement. The behaviour of the corrosion potentials ($E_{corr.}$) is summarised in table I where we see that on the seabed there is a small difference of 7mV between the port and starboard values which increases to a difference of between 15-16 mV in the waters closer to the surface. The more weather side (starboard) had a mean $E_{corr.}$ of -0.362 from twenty six measurements. The more sheltered port side had a mean $E_{corr.}$ of -0.376 volts which indicates a less corrosive microenvironment.

3.3 Effects of water depth on pH

The measurements of the surface pH were much more difficult on the starboard side of the wreck because of the greater amount of water movement which, along with the relatively thin layer of concretion, made it difficult to obtain an accurate value of the *in-situ* acidity. The average pH data is listed in table I where we see that there are indications of a trend towards more alkaline values as the water depth decreases on the starboard side and the reverse trend on the port side. This is consistent with a lower corrosion rate being observed in the deeper and inherently more sheltered deeper water. The scatter of the experimental data from both sides prevents any easy comparison of the different sides of the wreck, as the standard deviation of the mean data sets at each average water depth is too large to permit any statistically valid comparison.

Initial inspection of the pH versus water depth scatter diagram for the starboard side indicates a random collection of data. Once the location codes of varying water depth are considered it is seen that the data points can be joined in a series of parallel lines where the pH falls by 0.56 ± 0.03 per metre of increased water depth. An alternative way of viewing this trend is to use the reciprocal slope to note that an increase of 1.8 ± 0.1 metres is needed to bring about a fall of one pH unit in the measurement of surface acidity. The aggregation of the data points indicates that for each subset of measurements at a similar depth, the pH becomes more alkaline with increasing water depth, which is consistent with the average values listed in table I. Assuming that the data is free from any major systematic error, the trend to more alkaline values with increasing depth is consistent with the fall

off in corrosion rate with increasing water depth and concomitant water movement. The trends in the port side pH data with water depth are similar to those on the starboard side except that the slope is greater with an average of 0.7 ± 0.3 fall in pH per metre of water depth. This is consistent with the more sheltered nature of the port side compared with the more exposed starboard side of the vessel.

Table I: Effect of water depth and site location on the mean value of the surface pH

Location		Port	Starboard
Bottom	av. depth 3.9 m	6.97 ± 0.62	7.48 ± 0.46
Mid water	av. depth 2.3 m	7.35 ± 0.65	7.40 ± 0.74
Surface zone	av. depth 0.9 m	7.42 ± 0.54	7.39 ± 0.47

3.4 Effects of water depth on corrosion potential

The plot of the corrosion potentials, on the starboard side, as a function of water depth, as shown in figure I shows a general trend to less anodic values as the water depth increases. The linear relationship between the mean E_{corr} data at the different water depths had a correlation coefficient of 0.996

$$E_{corr}^{sbd} = -0.342 - 0.0078 m \dots\dots\dots 2$$

Thus the corrosion potential is seen to move to more negative values as the water depth increases at an average rate of 7.8 mV/metre. The fall in E_{corr} with water depth is less than the 18.9 ± 1.5 mV/metre observed on heavily concreted wreck material that was in higher energy zones associated with open ocean and shallow reef strewn waters (3). A similar dependence of E_{corr} with water depth, to that observed on concreted open ocean sites, of 21 ± 3 mV/metre was noted for iron wrecks in the River Murray in South Australia (9). In this case a dense and adherent layer of mud and magnetite prevented direct access of the dissolved oxygen to the corroding metal surface. The physical barrier in the River Murray had a similar effect of separating the anodic and cathodic sites as the concretion has on open warm water marine sites. The general trends in E_{corr} with site location and water depth on the HMVS *Cerberus* site are summarised in table II.

Table II: Effect of water depth and site location on E_{corr} .

Location		Port	Starboard
Bottom	av. depth 3.9 m	-0.380 ± 0.008	-0.373 ± 0.004
Mid water	av. depth 2.3 m	-0.376 ± 0.008	-0.361 ± 0.004
Surface zone	av. depth 0.9 m	-0.369 ± 0.006	-0.353 ± 0.004

When the mean E_{corr} data from the port side is plotted as a function of water depth there is a linear relationship, with a correlation coefficient of -0.9966, for the fall in corrosion potential with increasing water depth. The data is given by equation 3,

$$E_{corr}^{port} = -0.368 - 0.0028 m \dots\dots\dots 3$$

and so the average E_{corr} for the sheltered port side falls by almost 3 mV per metre of increased water depth. The smaller dependence of E_{corr} on water depth on the port side is consistent with a lower energy zone characterising the water in this area. Inspection of the E_{corr} data from across the site also indicates that there is a general trend towards more negative values as we move from the bow or stern towards midships, as shown in figure II. The port side E_{corr} values are up to 20 mV more negative in the middle of the site than at the stern

These differences in E_{corr} can be equated to a numerical difference in corrosion rate by using the known relationship between the slope of the $\log d_g$ versus E_{corr} plots and the amount of dissolved oxygen in the sea water. This slope is effectively the inverse of the Tafel slope and has the units of V^{-1} and can be calculated from the equation $\delta \log d_g / \delta E_{corr} = 10.33 \log [O_2] - 3.47$ (10) where the dissolved oxygen concentration is given in $cm^3/litre$, which gives a value of 3.29 for the HMVS *Cerberus* site. The dissolved oxygen content of the site was obtained from the measured salinity and water temperature of the site and tables in the literature (8). A saturation level of 100% dissolved oxygen is reasonable given the shallow depth of the wreck site. The annualised depth of graphitisation, d_g of the cast iron propeller shaft casings was 0.118 mm/year; this was obtained by dividing the total depth of graphitisation d (8mm) by the 68 years of immersion on the site. With a corrosion potential of -0.370 volts vs NHE and the calculated slope, along with the d_g value, the intercept value of +0.286 can be determined. The corrosion equation for the HMVS *Cerberus* site is therefore given by the relationship,

$$\log d_g = 3.29 E_{corr.} + 0.286 \dots\dots\dots 4$$

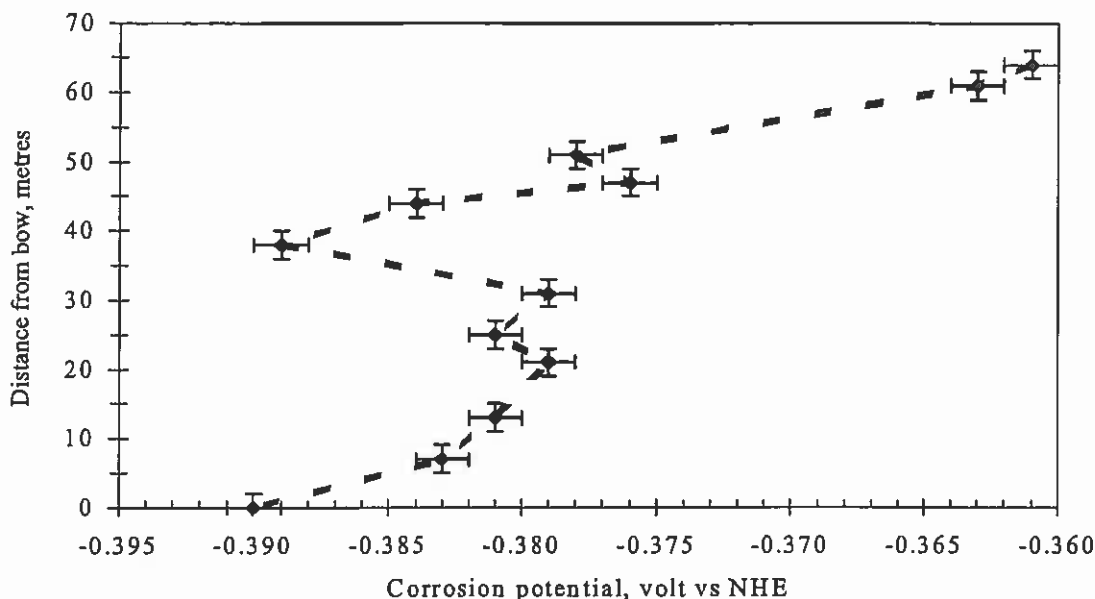


Figure II. Port side corrosion potentials at a depth of 4 metres as a function of distance from the bow.

This equation can then be used to show that the differences in corrosion potential between the bow and the midships of 20 mV equates to a difference of approximately 16% in corrosion rate. Plots of the $E_{corr.}$ and pH data on a Pourbaix or thermodynamic stability diagram (11) show that most of the readings of corrosion potential and pH are in the zone of active corrosion for iron in seawater with a mean $E_{corr.}$ of -0.370 ± 0.011 volts at a mean pH of 7.31. Data sets in this area generally described by equation 5



which gives a 29 mV fall in corrosion potential for each unit increase in the pH of the metal surface (12,13). The few data sets that lie outside this active corrosion zone are characterised by heavy calcareous deposits and are in a passive or diminished corrosion zone where Fe_3O_4 is the major observed corrosion product. For these samples the $E_{corr.}$ falls by 59 mV for each unit increase in the pH, according to equation 6,



This equation describes both the observed nature of the corrosion matrix as well as the dependence of $E_{corr.}$ on the pH (14,15). The corrosion potentials at the bow are significantly more negative than the nearby sections and the more cathodic values are probably due to the differences in composition of the stem (bow) compared with the frames and plates as noted in the original specifications (16).

3.5 Metal thickness and overall site corrosion

The data on the metal thicknesses observed on the vessel shows that there is a large spread in values from the order of 20-3mm as we move from the bow to the stern. A distribution diagram of the residual metal thickness is shown in figure III. Given that the original armour plating was between 8"-10" (203-254 mm) it is readily apparent that our experimental method has not picked up the massive plating. The absence of the expected metal thickness data is not due to experimental error or to operator ineptitude. Our data relates to a secondary cladding over the armour belt and the degraded values of plating and frames and ribs. Inspection of the starboard side of the wreck shows a clear line of extra plating that ceases about 3 metres below the original deck height. Although this extra layer of plating was not in the original specifications a refit in 1897 saw a strengthening of the armour plating by the addition of an extra "belt" as concerns had been expressed about the ability of the vessel to survive impact from the newer guns. When the data is separated into a number of subsets associated with plating and ribs we see that the mean thickness of materials in the middle of the site is greater than in the areas closer to both the bow and the stern. This trend in residual metal thickness is also consistent with the observed trends in $E_{corr.}$ which are lower in the middle of the site and so reflect a lowered corrosion rate.

When the thickness data is plotted in order of increasing residual material there appears to be four subsets of varying thicknesses associated with the structure of the vessel. Statistical analysis for the data is listed in table IV along with estimations of the original dimensions which were based on the average corrosion rate of 8mm in 68 years on the partly buried propeller shaft

casings. The aggregation of the data is partly subjective and it is possible to interpret corrosion rates as being widely dissimilar if different initial thicknesses are assumed.

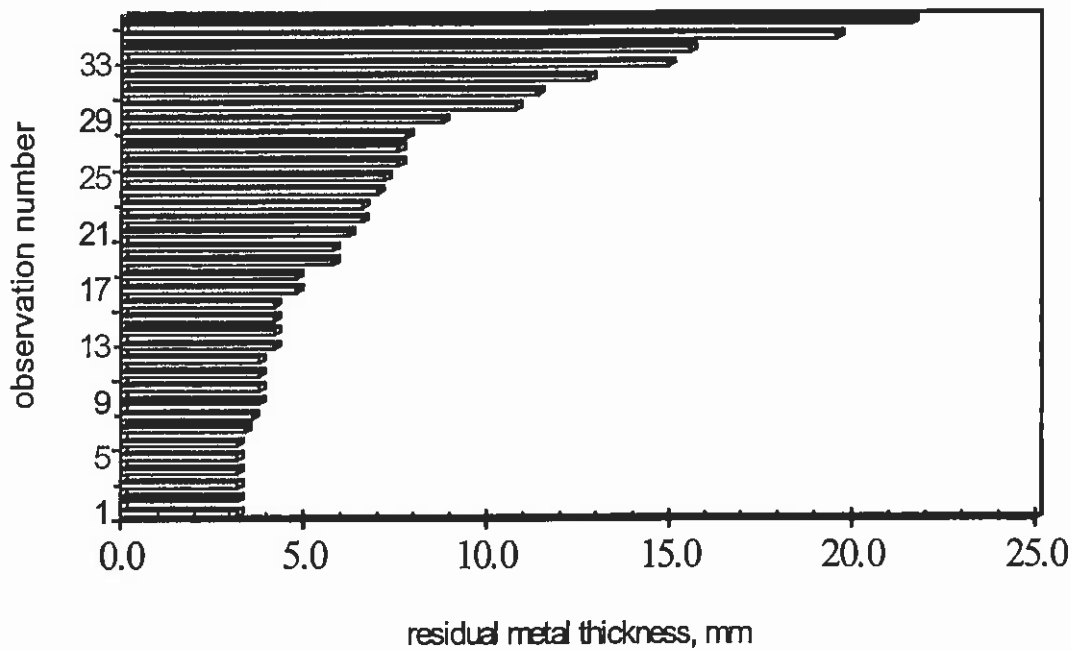


Figure III: Plot of residual metal thickness as a function of frequency of observation

This scenario is unreasonable since the data obtained on the depth of corrosion on the shaft housing has been used as a guide and the 42 mV range of E_{cor} values across the site indicates that the overall differences in corrosion rate are small. Given that so much of the original documentation of the specifications for the vessel is extant and that many of the structural members are seen to be in the order of thickness from ½"-19" the estimated original thicknesses are also realistic. The data summarised in table IV indicated that the *Cerberus* used a range of metal thicknesses which generally incremented by 7" and that the upper works have suffered greater corrosion than the middle of the vessel. The amount of corrosion of the upper section is similar to that of the frames and ribs at the interface between the sea bed and the vessel.

Table IV: Average metal thickness for iron on the HMVS *Cerberus* site

Mean thickness mm	Calculated	Corrosion loss mm	Number of samples
3.77±0.46	12.7 mm ½"	8.9	23
7.60±0.79	15.9 mm 5/8"	8.3	16
11.7±0.95	19.1 mm ¾"	7.4	7
18.2±2.40	27.0 mm 19"	8.8	7

The implications of this study for underwater heritage managers are very significant in that field measurements of residual metal thickness in association with on-site data on the depth of corrosion on cast iron can provide a method of determining the original dimensions of the scantlings. Many wrecks contain only a series of iron ribs and frames and which could have come from a number of vessels known to have been lost in the general vicinity. Given that most wrecks at the same site came from different sized vessels and from different periods of history, this new approach of using the corrosion measurements as a diagnostic tool has major implications for maritime archaeology and the management of iron shipwrecks.

3.6 Conservation management of the site

All the measurements of corrosion potentials, pH and metal thickness tell the same story that the wreck of HMVS *Cerberus* is degrading at a fairly steady rate of 0.122±0.009 mm/year. Given that the mean thickness for 23 plates, ribs and frames was only 3.77±0.46 mm it will be only a matter of five to ten years before these structural members will no longer be able to support the massive loading of the armour belting, the two turrets and the four guns. Unless urgent action is taken to stabilise the site it will continue to collapse owing to the load on the degraded hull structure. The primary force controlling the rate of deterioration of

the metal is the flux of dissolved oxygen from the surrounding sea water to the concreted metal surfaces. Factors such as a rock infill or a breakwater will slow down the rate of deterioration. **There is essentially no long-term future for the site unless some form of active site management is undertaken.** Issues to be considered must include the need to prevent unauthorised access to the interior of the vessel which is very dangerous as the corroded structure can readily snag a diver. Penetration diving carries a significant risk of having a large and heavy section of the degraded material fall on a diver.

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