# Managing a Monitor — the Case of HMVS *Cerberus* in Port Phillip Bay: Integration of Corrosion Measurements with Site Management Strategies

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The hull of the former HMVS *Cerberus* (1926) collapsed two metres during gales in December 1993, leaving the vessel half-submerged. Sunk as a breakwater in 1926, the vessel is one of the few remaining and accessible twin-turret Monitor-style warships from the 1870s. This paper presents the complex history of attempts to stabilize the site and to preserve the wreck. A series of in situ corrosion studies of corrosion potentials, pH, and residual metal thickness have provided a special insight into the processes of decay and have paved the way for future site stabilization. Removal of the four 16-tonne 10 inch Armstrong rifled muzzle loading guns and their in situ treatment alongside the wreck have assisted in relieving some of the stress on the remaining structure. The paper reports on correlations between the corrosion rate and the formation of concretions and how to determine the end point of an in situ treatment for cannon.

KEYWORDS Monitor-style warship, nineteenth-century iron wreck, in situ corrosion studies, anodes, conservation, concretion formation

# Introduction

## History of the ship

The 1860s was a period of rapid change and development in the construction and technology of warships. Experiments during the Crimean war indicated that low-profile, iron-clad rafts armed with powerful guns were more effective for coastal attack than traditional iron-clad ships-of-the-line (Herd, 1986: 8). The construction and battle between the American sailing iron-clads *Merrimac* and *Monitor* added further support for this new type of battleship. Two sailing monitors had been

commissioned for the British navy in the late 1860s when approval was given by the British Admiralty for the construction of Cerberus, for the coastal defence of Melbourne harbour. Cerberus was the first ship commissioned by the Victorian Colonial Navy, which until then had been composed of second-hand British Royal Navy vessels. Cerberus was designed by Sir Edward Reed to defend the rich commercial and manufacturing coastal settlements around Melbourne, in the British Colony of Victoria, from attack. As such, priority was given to heavy armament over the ability to travel large distances (Herd, 1986: 8), and Cerberus became the first British-built warship designed to operate solely on steam power. Cerberus was constructed by Palmers Shipbuilding and Iron Company at Jarrow, England, between 1867 and 1870 at a cost of £140,000 sterling. The hull of the vessel was clad in 8-inch thick armour-plating, whilst the two gun turrets located at either end of the breastwork were clad in 10 inches of armour plating (<http://www.cerberus.com.au/ specification.pdf>). The two gun turrets each contained two 10-inch guns that could be elevated and rotated for action. Details of the armaments and the construction of the vessel have been published elsewhere (Admiralty, 1867; Nicholls, 2001). For the voyage from England to Melbourne, temporary sides were constructed and a temporary sailing rig added. Cerberus encountered strong winds as it headed to the south coast of England to begin its voyage to Australia, and was eventually able to depart on 7 November 1870. Gales were encountered in the Bay of Biscay, and Cerberus rolled heavily and dangerously in the high seas. When the ship arrived at Malta, many of the crew chose desertion and the risk of jail over continuing the voyage to Australia. Cerberus departed, was towed through the Suez Canal in December, and finally reached Port Phillip in April 1871 to the great excitement of the Melbourne residents (Cahill, 1983: 9). It took five months to remove the temporary sailing rig and refit the vessel as a warship for its first trials in Port Phillip. Over the next fifty years Cerberus undertook numerous manoeuvres and mock battles with the coastal forts and its attendant torpedo boats; however, the guns proved to be too powerful to be fired close to shore, as the public protested to the resulting damage to windows. Cerberus underwent a number of refits, upgrades, and repairs, but spent most of its time at moorings off Williamstown in west Melbourne (Herd, 1986: 13). After the Federation of Australian States in 1901, Cerberus became a part of the Australian Commonwealth Naval Forces, remaining in commission as a tender to the Williamstown Navel Depot until 1911 (Cahill, 1983: 15), when the Commonwealth Naval Forces were given the title Australian Royal Navy. During World War I Cerberus was used as a port guard ship and a floating explosives store, and in 1921 was renamed Platypus II to act as the Submarine Depot ship for the six RAN J-class submarines. The submarine unit was disbanded in 1924 and Cerberus sold as scrap to the Melbourne Salvage Co. for  $\pounds_{409}$ . After everything of value was stripped from the ship it was sold on to Sandringham Local Council in 1926 for use as a breakwater at Half Moon Bay in the coastal south-east suburbs of Melbourne, outside Black Rock Yacht Club (Herd, 1986: 15). The ship was sunk in approximately 4 m of water with the gun turrets and guns still in place, creating a local landmark.

## Significance

The significance of *Cerberus* lies primarily in its historical and technological aspects, as an internationally unique example of an early stage in the development of modern

battleships, but it also has historical and social significance to the Australian State of Victoria and local Melbourne communities (Heritage Victoria, 2002: 6). The technological significance of *Cerberus* lies in the fact that it was an experimental vessel and represents many technological firsts, including being the first unrigged Britishbuilt iron breastwork Monitor, leading the way for the development of entirely steam-propelled turreted warships. *Cerberus*'s voyage from England to Australia via the Suez Canal was the longest ever undertaken by a Monitor-class vessel and is believed to be the first vessel destined for Australia to travel through the Suez (Heritage Victoria, 2002: 6). There are only seven known Monitor vessels surviving internationally, of which *Cerberus* is the only breastwork and only twin-turret example. At a national level, *Cerberus* is part of a small colonial naval shipwreck resource, numbering just three other sites. The full statement of significance can be found in the Conservation Management Plan for the site (Heritage Victoria, 2002).

*Cerberus* is recognized as a nationally significant heritage site (Figures 1 and 2) and listed on both national and State heritage registers. *Cerberus* was first recognized as a significant historic site in 1982 when it was registered as an 'historic building' by the Victorian Historic Buildings Council. It was listed on the Register of National Estate on 25 March 1986 (Record Number 005787). On 6 October 1994 it was gazetted as an historic shipwreck under the Historic Shipwrecks Act 1981. The Historic Shipwrecks Act 1981 was incorporated and replaced by the Heritage Act 1995, and the *Cerberus* is now listed on the National Trust of Australia Register (B2314) in 1997 and recognized as of 'outstanding national heritage value to the Australian nation' on



FIGURE 1 MacLeod at the stern of the *Cerberus* at high tide with decks awash, October 1994. *Reproduced with permission Heritage Victoria* 



FIGURE 2 Starboard view of the *Cerberus* at high tide in January 2005 with the lower deck awash.

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14 December 2005 when it was listed on the National Heritage List. The significance of the ship to the Royal Australian Navy is such that its shore training facility in nearby Westernport Bay was named after the vessel. There are seven known Monitor-class vessels available worldwide for comparison and study. Five of these are floating as museum ships, whilst a sixth lies in deep water off Cape Hatteras in South Carolina and has an associated Museum on land. The significance of *Cerberus* lies in that it is the only breastwork Monitor and the only twin-turret Monitor.

## Current protection and ownership

The wreck of *Cerberus* is currently owned by Bayside City Council, the successor to Sandringham Council, but is managed, due to its status as a protected historic shipwreck under the Victorian Heritage Act, by Heritage Victoria. A lobby group, Friends of the *Cerberus*, has been campaigning for many years for active conservation on the site, including investing in surveys and proposals for preservation works. In 2007 a joint funding agreement was made by the Commonwealth and State governments, with \$500,000 provided by the Commonwealth Department of Environment, Water, Heritage, and the Arts (DEWHA) in 2008 towards conservation and stabilization works. The National Trust of Australia (Victoria) holds this money as an independent non-government organization with an interest in the management of the site.

# **Current condition**

The *Cerberus* was a sea-going version of the gun batteries developed for coastal defences, and as such the armoured upper structure was supported by a relatively lightweight hull (Figures 3 and 4). Through a combination of weight increase associated with the marine atmosphere corrosion of the superstructure and reduction in integrity and strength of the hull frames and plates due to nearly seventy years of marine corrosion, the lower hull structure gave way in 1993 (Colquhuon, 1994). Corrosion rates for severe marine atmospheres are typically 12 per cent of the rates found in seawater itself (Cornet, 1970). The 1993 collapse, brought about by galeforce winds and high seas, lowered the upper deck by more than 2 metres, making the Danzig oak deck timbers awash at each high tide — see Figures 3 and 4. Following the collapse, Heritage Victoria introduced a 0.5 hectare protected zone around the wreck, preventing all access to the site without a permit (*Victoria Government Gazette*, 1994).

# Management approach

Heritage Victoria has been working to develop an appropriate management regime for *Cerberus* site since the collapse in 1993. This has involved commissioning corrosion surveys, structural survey, removal of the guns and their treatment in water close to the site, and the development of a conservation management plan for the site. Most



FIGURE 3 View of HMVS *Cerberus* in 1977 showing original profile and the relatively low free board.

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FIGURE 4 Detailed view of the stern of the *Cerberus* in 1977 before the collapse showing the rear turret and part of the conning tower. *Reproduced with permission Heritage Victoria* 

recently, Heritage Victoria have coordinated discussions with DEWHA (now Department of Sustainability, Environment, Water, Population, and Communities), National Trust, and Friends of the *Cerberus* to develop an active management regime to stabilize the site in its current condition, prevent the collapse of the turrets into the wreck, and slow the corrosion rate of the structure.

# Corrosion phenomena on the Cerberus wreck site

The rate of deterioration of metals on shipwreck sites is very dependent on the water depth and the flux of oxygenated seawater over the objects lying proud of the seabed. Corroding iron and steel in seawater rapidly becomes encapsulated by encrusting organisms (North, 1976). This encapsulation begins the process of separating the anodic and cathodic sites of the corrosion cell, with oxygen reduction generally occurring on the outer surface and oxidation of the metal occurring underneath the marine growth. The amount of solid concretion forming on wrecks in Port Phillip Bay is less than in warmer tropical to subtropical waters, but the thickness of the concretion layer does increase with time and the surface is dominated by tunicates and algae. The algae species are dependent on the amount of water movement and speciation differences can be seen between the upper and the bottom parts of the wrecksite (Borowitzka, 1989). The concretion consists of accumulated marine encrustation and the matrix of corrosion products, which together act as a semi-permeable membrane that sees chloride concentrations and acidity levels increase significantly above the ambient levels in the surrounding seawater. Chloride ions diffuse in to balance out the positive charges that result from increasing concentrations of  $Fe^{2+}$  ions at the metal-concretion interface. As the ferrous ions hydrolyse to produce a milieu of chloride and hydroxide containing species,

$$2 \operatorname{FeCl}_{2} + 2 \operatorname{H}_{2}O \rightarrow {\operatorname{Fe}(OH)_{2}\operatorname{FeCl}_{2}} + 2\operatorname{H}^{+} + 2\operatorname{Cl}^{-}$$
(1)

the acidity of the interfacial region increases. The dominant ionic species in equilibrium with solid phases is FeCl<sup>+</sup> with a small amount of un-dissociated FeCl<sub>2</sub> and an even smaller amount of FeOH<sup>+</sup> (Man-Seung, 2004). Higher concentration of soluble iron (II) species equates to higher corrosion rates and thus higher acid levels or a lower pH value. Thus the pH at the concretion metal interface provides an insight into the corrosion rate, providing that the concretion cover is thick enough to allow a truly representative pH to be developed (MacLeod et al., 2007; MacLeod and Richards, 2011).

The voltage measured at a piece of corroding iron on a shipwreck is a mixture of the two corrosion half-cells that make up the anodic (metal oxidation) and the cathodic or reduction reactions. For fully buried iron objects the reduction component of the corrosion potential ( $E_{corr}$ ) is the reduction of hydrogen ions and water. Under these conditions the corrosion process is dominated by microbiological activity since the presence of dehydrogenase enzymes will often control the rate of hydrogen evolution (Sequeira and Tiller, 1988; Fischer, 1983; Little and Ray, 2010). For iron objects lying proud of the seabed, the  $E_{corr}$  for concreted iron is controlled by the rate of reduction of dissolved oxygen at the concretion/seawater interface. Removal of the protective concretion layer provides direct access for the dissolved oxygen to the chloride-rich corroded and acidic metal surface, which will normally lead to the loss of archaeological values through accelerated corrosion and surface exfoliation (MacLeod, 1981; 1987).

Examples of such damage are readily seen at popular wreck dive locations where tying off to ship structure or dropping anchors onto wrecks breaks off the protective concretion. The tell-tale signs of recent damage are voluminous red-brown corrosion products on the abraded surfaces (MacLeod, 2006). In the case of *Cerberus*, when the initial inspection was undertaken in 1994 following the collapse, large areas of the submerged hull were festooned with active red-orange iron (III) corrosion products which were dominated by akaganeite, a chloride rich iron (III) oxyhydroxide. This is illustrated in Figure 5, where a whole sheet of plate has relocated to the sea floor after having all its lower rivets popped during the 'controlled collapse'. Owing to the wrought nature of the iron frame and knees its mode of deformation is one of elastic bending and stretching of the metal, rather like drawing out toffee when it is still in a semi-molten state. By way of contrast, the failure mode of cast iron is brittle fracture, rather than an elastic tearing, of the metal alloy which generally precedes rapid collapse of a structure.

Prior to scuttling at Half Moon Bay, *Cerberus* was stripped of all salvageable materials, all non-ferrous fittings on the engine and the twin propellers. As such, there has been no major corrosion due to galvanic coupling; however, the different reactivities of various components in the gun carriages, such as the elevation controls and the gun barrels themselves, will protect any non-ferrous materials that are in electrical contact or in close proximity (MacLeod and Garcia, 2009).



FIGURE 5 Diver inspecting the active corrosion on detached hull plates as shown by the red-brown colouration October 1994. *Reproduced with permission Heritage Victoria* 

The wreck of *Cerberus* is electrochemically more complex than fully submerged sites. The site encompasses areas that are fully exposed to a saturated salt aerial environment, others are immersed in the ocean, and the lowest sections of the vessel are buried in sand and fine silt. The above water part of the wreck, including guns, turrets, and upper bulwarks are subject to normal atmospheric corrosion in a marine environment; however, they will be interacting with other sections of the vessel that lie in the splash zone, a saturated salt microenvironment, and  $E_{corr}$  values need to be interpreted with caution. The sections of wreck in the splash zone will be in connection with the fully immersed structure, which is also connected to buried parts of the wreck. Despite this complexity, it is possible to interpret data from the same microenvironment, if there are a series of measurements of the same areas of the structure over a period of time. Under these conditions it is relatively easy to provide unequivocal interpretation of the degradation data. The bow of Cerberus points towards the Port Phillip Heads, the seaward opening of the Bay, exposing the starboard side of the wreck to the open water whilst the port side is relatively sheltered. The differences in wave movement on the port and starboard sides of the wreck mean they experience different fluxes of dissolved oxygen so they will corrode at somewhat dissimilar rates (MacLeod, 1989a).

# Data collection and methodology

To obtain reliable data on the in situ values of the corrosion potential, pH, depth of corrosion, and the combined corrosion and concretion cover, a compressed air drill

is used with a 12.5 mm masonry bit which matches the o.d. of the flat surface pH electrode. Some of the *Cerberus* concretion is very hard, particularly near the present and pre-collapse splash zones, and requires assistance from the buddy diver to penetrate through the matrix and expose the interfacial region. Assistance takes the form of acting as a brace to assist the drilling diver to obtain a better purchase on the concretion. Once the black cloud of magnetite ( $Fe_3O_4$ ) dwindles and the drill bit can go no farther, the flat surface pH electrode is readied for insertion into the hole as soon as the drill bit is removed. The pH reading falls as the electrode senses the acidic solution. When the minimum pH value has been reached, usually in 60–90 seconds, the drill hole is sealed with a finger whilst the data is recorded. Sealing the drill hole is vital as it can be extremely difficult to relocate the hole in poor visibility.

Corrosion potential is measured with a digital multimeter by using a 2 mm o.d. platinum wire electrode for contacting the underlying metal and a robust reference electrode. As the electrolyte is local seawater, the reference electrode requires calibration against a secondary standard since the voltage produced by the silver metal is dependent on the chlorinity (salinity) of the site. The practical details of the calibration process have previously been reported in this journal (MacLeod, 2006) and the authors are happy to provide practical guidelines for any persons wishing to conduct in situ measurements. The total depth of concretion and corrosion layers is measured with a plastic micrometer with a stainless steel extension probe. Determination of the corrosion profiles on cast iron objects is an essential step in obtaining a localized corrosion equation for the shipwreck. Graphitization depths d are determined by drilling with a 2 mm drill bit until no further penetration can be obtained and then recording the depth of the hole from the graphitized metal surface beneath to the concretion to the bottom of the drilled section with the micrometer. Dividing the d value by the number of years of immersion determines the value of  $d_e$ , which is a measure of the corrosion rate in mm.y<sup>-r</sup>. The measurement site is sealed through application of a kneaded sample of an underwater two-part epoxy resin.

Ideally, pre-disturbance measurements are taken after decades of immersion when the metals are corroding at a quasi-equilibrium state, but in the case of the *Cerberus* the first set of data was obtained after the 1993 collapse. Subsequent measurements have been used to monitor the site's condition. The minimal impact of such measurements on the integrity of an archaeological site is supported by the observation that repeated measurements on the boiler of the SS *Xantho* (1872) in coastal Western Australia over several years have shown that there has not been any measurable impact on the overall corrosion process since the corrosion potential was reproducible within two millivolts (MacLeod, 1992).

The development of the corrosion equation for the *Cerberus* site involved drilling into the propeller shaft which had corroded to a depth of 8 mm over the 68 years to provide a corrosion rate  $(d_g)$  of 0.118 mm.y<sup>-1</sup> at an E<sub>corr</sub> of -0.370 volts vs. NHE. The logarithm of the corrosion rate of iron is linearly dependent on the E<sub>corr</sub> value and the slope of this relationship is dependent on the salinity and the temperature, which in turn control the amount of dissolved oxygen on the site (MacLeod, 1995a). The slope was calculated according to the formula,

$$\frac{\partial \log d_g}{\partial E_{corr}} = 10.33 \log[O_2] - 3.47 \tag{2}$$

In equation 2 the concentration of the dissolved oxygen is given is in  $cm^3.dm^{-3}$  and thus the *Cerberus* site gave a slope of 3.29 which when combined with the d<sub>g</sub> and E<sub>corr</sub> data above gave equation 3,

$$Cerberus \log d_g = 3.29 E_{\text{corr.}} + 0.286 \tag{3}$$

Work in Chuuk Lagoon, Federated States of Micronesia, has shown that cast iron objects in the same chemical microenvironment with the same basic composition and physical location on a wreck site, the depths of graphitization has a reproducibility of  $\pm 0.1$  mm (MacLeod, 2006; 1989b). Since the corrosion rate is logarithmically dependent on the E<sub>corr</sub>, anodic shifts of 3 mV equate to an increase in corrosion rate of  $10^{\circ} \left(\frac{3}{304}\right)$  or some 2.3 % where the 304 is the reciprocal of the slope 3.29 V<sup>-1</sup> in millivolts. Similarly a 3 mV shift in E<sub>corr</sub> towards more negative values implies a reduction of 2.3% in the corrosion rate.

#### Baseline corrosion potential and pH measurements: October 1994

A total of sixty-three sets of corrosion potential, pH, and metal thickness measurements were performed over four days in October 1994 at twenty-one different locations ranging from the bow to the stern of the vessel, at intervals of between 4 m and 6 m along the exterior of the hull. Data was collected from both the sheltered port side and the more exposed starboard side. The December 1993 collapse resulted in a severely distorted structure below the water line which was characterized by a series of bent and twisted ribs and frames. The amount of concretion cover over these recently torn members was small and offered little protection to the underlying metal from the corrosive effects of the dissolved oxygen. Metal plating sections had been bent over backwards or bent under to create 'U'-shaped sections. In October 1994, some of these distorted elements were seen to have sprung free of the structure and were lying proud of the seabed while others were still attached to less corroded sections of the vessel by the original rivets. The maximum water depth recorded on the site was 4.4 m and the seabed consisted of fine silty sand, which was easily disturbed by divers and swells reducing visibility, and obscuring instrumentation. The low visibility problems were greatest under the stern section when examining the propeller shaft casings.

The water temperature was 15°C and the sea water had a pH of 8.14 with a salinity of 32.5‰, giving a dissolved oxygen content of 5.8 cm<sup>3</sup>/dm<sup>3</sup> assuming that the sea water is 100% saturated with dissolved oxygen (Riley and Skirrow, 1982). The surface pH ranged from maximum values of 8.76 to a minimum of 6.04 with a mean value of 7.31  $\pm$  0.60, which is not reflective of the high corrosion rate associated with this wreck site. The mean pH value is relatively alkaline because there is insufficient concretion coverage, following the collapse, to provide representative pH data commensurate with the present rate of corrosion. The most alkaline pH was associated with a calcareous matrix at the freshly colonized interface on the port side in an area that had previously been intertidal. The alkalinity is associated with the transition between soluble calcium bicarbonate and insoluble carbonate species and has been observed on an exposed J-class submarine  $J_7$  in the nearby sheltered location of the Sandringham Yacht Club in Port Phillip Bay (MacLeod and Steyne, 2011 in press).

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 (location **bottom**), at a depth approximately 1.6 m above the seabed (location **middle**) and at a depth that varied between 0.3–0.5 m below the surface (location **upper**). Copies of the 1994 survey data are available from the authors upon request.

Plots of the E<sub>corr</sub> values against the water depth for both sides of the vessel showed a series of parallel lines having the same slope but different intercepts. The most anodic values of the intercepts were associated with the upper parts of the wreck while the most cathodic, least reactive, were found for measurements made at the bottom of the site. This phenomenon has been reported on tropical historic iron shipwrecks in Chuuk Lagoon (Federated States of Micronesia) and on the Yongala in the Great Barrier Reef National Marine Park (MacLeod, 2006; MacLeod and Viduka, 2010). The median value of the slope for the  $E_{corr}$  vs depth plots for the more sheltered port side was  $-0.0100 \pm 0.0003$  V.m<sup>-1</sup> which was somewhat steeper than the better mixed waters on the starboard side which gave a median slope of  $-0.0088 \pm 0.0002$ V.m<sup>-I</sup>; the sensitivity of E<sub>corr</sub> to depth is similar to that reported for wrecks at a similar depth in Chuuk Lagoon (MacLeod, 2006). The upper data sets have the same intercept value of -0.577 V vs Ag/AgCl at zero depth which is consistent with wave chop providing the same microenvironment. However, the differences between the two sides of the wreck are more clearly seen in the bottom Ecorr intercept values which were -0.604 volts for the more sheltered port side compared with -0.590 volts for the starboard side. The differences in the intercept values are determined using equation 3 which equates the port as being 11% less corrosive than the starboard side.

The underlying acidity of the *Cerberus* iron, hence the corrosion rate, is seen to be very sensitive to water depth since when the pH data is plotted as a function of water depth the data presents itself as a series of parallel lines for both port and starboard sides but the slopes are different between port and starboard — see Table 1. For the sheltered port side the median slope of  $\frac{\partial pH}{\partial d}$  was  $0.41 \pm 0.03$  while the exposed starboard side the median value was  $0.66 \pm 0.02$  pH.m<sup>-1</sup> which demonstrates that the corrosion rate on the weather side is more sensitive to changes in water depth than on the port side. The fully submerged wreck of the *Hino Maru* in Chuuk Lagoon had  $\frac{\partial pH}{\partial d}$  of 0.39 at a depth of 7.5 m (MacLeod, 2006).

Port dpH	Port intercept	Starboard ∂pH / ∂d	Starboard intercept
0.38	7.69	0.63	7.03
0.40	6.73	0.65	6.16
0.42	6.40	0.67	5.40
0.46	5.78	0.66	4.80

TABLE 1 A SUMMARY OF THE DATA FROM THE PH ANALYSIS WITH DEPTH

The difference in the microenvironment of the port and starboard sides of the wreck is clearly seen in the values of the intercepts of the linear pH vs. depth plots shown in Table I where the port side is more alkaline by an average of  $0.79 \pm 0.18$  pH than the corresponding interval on the starboard side. There is insufficient data on residual metal thickness values at the splash zone (zero depth, intercept pH values) to provide an equation linking the corrosion rate with the pH for the *Cerberus* site.

#### Corrosion reaction mechanism

The electrochemical processes controlling the inter-relationship between the  $E_{corr}$  and the pH were determined through analysis of the voltage and acidity readings when plotted on a Pourbaix diagram (Pourbaix, 1974). Most of the readings of corrosion potential and pH are in the zone of active corrosion for iron in seawater with a mean  $^{NHE}E_{corr.}$  -0.370 ± 0.011 volts and a mean pH of 7.31 and a slope of -29 ± 2 mV for the voltage vs. pH graph as predicted by equation 4,

$$2Fe + 2H_2O + 2Cl^- \rightarrow \{Fe(OH)_2, FeCl_2\} + 2H^+ + 4e^-$$
(4)

which is the same as on most historic iron shipwrecks (MacLeod, 1981; 1986). The few data sets that lie outside this active corrosion zone are characterized by heavy calcareous deposits and are in a passive corrosion zone where  $Fe_3O_4$  is the major corrosion product and for these sites the  $E_{corr}$  becomes more cathodic by 59 mV.pH<sup>-1</sup> according to equation 5,

$$_{3}\text{Fe} + _{4}\text{H}_{2}\text{O} \rightarrow \text{Fe}_{3}\text{O}_{4} + 8\text{H}^{+} + 8\text{e}^{-}$$
 (5)

This equation accurately describes the corrosion matrix that was observed on many of the test site locations on the hull of *Cerberus* (North, 1982; MacLeod, 1989c; Selwyn, 2006). The seabed  $E_{corr}$  value at the bow is 12 mV lower than the average values observed in the general plating at the same depth and this may be due to differences in composition of the stem (bow) compared with the frames and plates as noted in the original specifications (Nicholls, 2001). The largest difference between the port and starboard  $E_{corr}$  values occurs in the forward areas of the vessel. Within 10 m of the counter stern there are few electrochemical differences between the port and starboard sides which have essentially the same range of  $E_{corr}$  and pH and this is due to the uniform mixing of waters around the stern zone. At a distance of  $45 \pm 10$  m from the bow there was a pronounced bump in the pH which had a median value of  $8.5 \pm 0.4$  and was characterized by some very thick concretion associated with the former splash zone before the collapse. This alkaline pH is most likely due to the drill bit failing to penetrate the dense inorganic calcium carbonate layer and to get contact with the underlying corroding metal.

#### Metal thickness and overall site corrosion

In order to determine what were the most likely original metal thicknesses associated with the scantlings for the float hull and outer sections of the *Cerberus*, it was necessary to determine the 1994 median values of water depth and  $E_{corr}$  then correct each data point to reflect either higher corrosion rates for shallower readings and vice versa. The results shown in Table 2, after corrections had been calculated according to the *Cerberus* corrosion equation — see equation number 3. The original thickness

Median thickness mm	Calculated thickness mm	Imperial equivalent, mm	Imperial value	Corrosion loss mm in 68 years	Number of samples
3.7 ± 0.5	$11.7\pm0.7$	12.7	1/2″	8.0	27
$7.2\pm1.0$	$15.2 \pm 1.3$	15.9	<sup>5</sup> / <sub>8</sub> ″	8.0	21
$11.8\pm1.8$	$20.5\pm1.6$	20.6	<sup>3</sup> / <sub>4</sub> ″	8.7	9
$19.6\pm1.6$	$26.7\pm1.6$	27.0	1 <sup>1</sup> / <sub>16</sub> "	8.7	5

 TABLE 2

 ACTUAL AND CALCULATED METAL THICKNESS FROM THE HULL OF HMVS CERBERUS

of the fitting or scantling was then determined by multiplying the present corrosion rate by 68 years and adding to it the actual metal thickness. When the calculated values were plotted as a distribution diagram the thickness fell into four categories which correspond with the following dimensions: frames and ribs originally  $\frac{1}{2}$  inch thick, plates being  $\frac{5}{8}$  inch and other elements at  $\frac{13}{16}$  inch with the outer plate on top of the armour belt being  $\frac{11}{16}$  inch thick. The calculated corrosion loss is 8.0 mm for the lower parts of the vessel where the majority of the measurements were made while in the upper parts of the site the corrosion loss was greater at 8.7 mm owing to the increased water movement.

Since the maximum calculated original metal thickness is  $I_{16}^{I}$  inch, it is clear that the ultrasonic Cygnus<sup>®</sup> gauge failed to detect the 8–10 inch (203–254 mm) underlying armour belting. This result was to be expected if the outer layer was that material which was added as an afterthought once the Cerberus had reached its destination of Melbourne as the ultrasonic pulse only penetrates to the first interface between solid metal and seawater. Concerns had been expressed that the as-built plating might prove to be insufficient to withstand newly developed gunnery. At the time of construction in the 1870s, the yard superintendent would have adjusted the use of various plate thicknesses and the three smaller thicknesses incrementally increase by  $\frac{1}{2}$  inch which is typical of steel vessels of that period. This method of assessing the original scantling thickness provides a useful archaeological guide since many of the details of a ship's construction were never properly recorded. It was common for the as-built construction to differ from the signed off construction plans. By using the calculated thickness measurements to determine the weight loss of metal, it is possible to link the pH of the site measurements with the calculated corrosion rate. A series of parallel lines were obtained for plots of log  $i_{corr}$  against pH with intercepts that were dependent on the water depth. The most aggressive corrosion rate was found for the shallower parts of the wreck site with  $o.5 \text{ metres} \log_{calc} d_g = 1.05 - 0.29 \text{ pH}$  and for the bottom measurements <sup>3.9 metres</sup>  $log_{calc} d_g = 0.80 - 0.28 pH$  which means that the upper sections of the Cerberus are corroding nearly 80% faster than the bottom of the site.

#### 1999 site inspection with recommendations and options from consultants

At the time the original report was presented to Heritage Victoria in 1995 it was estimated that at an average corrosion rate of  $0.119 \pm 0.010 \text{ mm.y}^{-1}$  it would only be a matter of 5–10 years before the ribs, frames, and plates would become too thin to

support the massive weight of the armour belt, turrets, and guns and the site would undergo additional collapse. In the period following the October 1994 measurements a number of reviews were conducted as the staff of Heritage Victoria sought to gain support to enact the recommendations made in the first detailed report (Strachan, 1995; MacLeod, 1995b). However, almost 4<sup>1</sup>/<sub>2</sub> years after the initial survey, the continuing impacts of corrosion lead to a further collapse. On hearing of the collapse, Heritage Victoria immediately conducted a site inspection on 13 April 1999 which showed the wreck in a deceptively stable condition on the surface (Maritime Heritage Unit, 1999). The situation under the water was anything but stable. The bow had split with the stem post rent in two, separated by almost 80 cm. The opening of the bow made the vessel more unstable, allowing turbulent water into the wreck, where previously waves were deflected by the bow. Along both sides of the vessel the frames, which previously supported the hull, had all collapsed and been flattened. The outermost layer of steel had been peeled off in large sections and lay alongside the wreck. The vessel had collapsed further on the seaward side due to the more rapid rate of corrosion, as previously noted.

The 1999 collapse had dramatically changed the water movement around the stern, which became scoured to a depth of 2 m, exposing the bedrock on which the keel lay. The scouring allowed a much clearer view of the remaining structural elements supporting the vessel, which looked very thin. No additional measurements were made on the residual metal thickness at this time due to the high risks associated with working under overhanging stressed iron plates. With continued lack of structural support around the stern, another major storm might see the vessel break its back amidships. With knowledge gained from the 1994 corrosion survey of how fragile the remaining structural elements (beams, frames, and ribs) were, it was determined that one possible way to relieve some of the stress on the remaining structural elements was to lighten the load and remove the four 10-inch Armstrong rifled gun barrels form the two turrets.

Since experience with the use of sacrificial anodes to stabilize artefacts ranging from the SS Xantho (1872) engine to the HMS Sirius best bower anchor had been positive (MacLeod, 1986; McCarthy, 1988), a tender for a cathodic protection solution for site stabilization for Cerberus was put out by Heritage Victoria in 2000 which attracted two responses. The consulting corrosion engineering firm AmaC<sup>®</sup>, who specialize in the use of anodes, felt that Cerberus was too decayed for effective use of a cathodic protection system. Additionally, it was considered that traditional marine coating systems would not be cost effective until a retaining wall was erected around the vessel to enable water to be pumped out and an island providing visitor access via a jetty to the site to be created. Only once the bund wall had been erected did they think it would be possible to start stabilization procedures. After the site was stabilized the hull could be infilled with either concrete or sand, which would support the heavy superstructure, as an alternative to using an extensive, and expensive, system of steel supports. AmaC<sup>®</sup> additionally advised against attempts to jack up section(s) of the vessel to restore the previous profile to public view, since it was felt that this would break the back of the Cerberus and so destroy the integrity of the site. AmaC<sup>®</sup> indicated they would consider sponsorship of the cathodic protection once the new wall and supporting structure had been set up. AmaC<sup>®</sup> also noted that the engineering issues would become prohibitively expensive once the structure had fallen below the present seawater level. It was agreed that there was a six-month window of opportunity before there would be significant further collapse and that it was imperative that action be taken as soon as practicable.

The second response to the tender was by Solomon Corrosion Control group (Solomon, 1999). Site assessments by their staff indicated that the amount of current which would be needed to apply effective cathodic protection would have been of the order of 200 amps, which is outside the scope of normal cathodic protection system. If such systems had been installed on the seabed adjacent to the wreck, the high level of current would cause dangers to local swimmers. Additionally, the Solomon proposal involved installation of supports for the wreck so that it could then be rebuilt to its original profile. While this was an appropriate solution from the perspective of a corrosion engineer, it was unacceptable on heritage grounds. They concluded that cathodic protection was not a cost-effective option and that it would be an irresponsible use of public funds.

In order to assess the possible engineering solutions, a feasibility study regarding the coffer dam option was conducted by the consulting group Gutteridge Haskins and Davey (GHD) in 2000. They found that the underlying rock substrate with 2 m depth of sand and silt was suited to the construction of a sheet piling structure around the perimeter of the wreck (Gutteridge Haskins and Davey, 2000). The report recommended an envelope of land around the wreck to enable an appropriate interpretation centre to be established. To keep the cofferdam dry for a long time would be a very expensive exercise, but it should be manageable for a limited period of time, sufficient to enable a support system to be installed. Once the structure had been established, the wreck could be jacked up to restore the sight lines from the shore. The option of removing the cofferdam once the vessel was stabilized and restored to the original sight line was also considered to be feasible. A full review of all the options was laid out in the *Cerberus* Conservation Management Plan produced by Heritage Victoria in 2002 (Anderson, 2002).

## Site management since the 1993 collapse

There has been a continuous review of the conservation management options available for *Cerberus* since its initial collapse in 1993. Throughout this time Heritage Victoria had continued to monitor the site, develop, and adapt potential options for conservation, based on changing site conditions, political priorities, and good heritage management practice. The community group Friends of the *Cerberus* has continued to raise the profile of the site at local and international levels through continued media and letter writing campaigns. As part of Heritage Victoria's continued monitoring programme, MacLeod has been engaged on a number of occasions to monitor the condition of the site through corrosion potential readings.

In 2008 the Commonwealth government provided \$500,000 seed funding for conservation works on *Cerberus*. The money was held in trust by the National Trust of Australia (Victoria). Discussions commenced in 2009 between Heritage Victoria, National Trust, and Friends of the *Cerberus* on the most suitable way to use the money. Agreement was reached that the funding should be used for medium term stabilization works and an associated programme of interpretation. The preservation of the turrets above water in situ was identified as a priority, particularly as these heavy features could potentially fall through into the water as the supporting structure corrodes and weakens. As stated above, the primary significance of *Cerberus* lies in its technological aspects, particularly the twin turrets and breastwork. Any heritage management work should, therefore, aim to preserve these aspects of the site. A number of previously suggested options were no longer considered appropriate heritage management approaches for such a significant site, as they would primarily 'reconstruct' the above-water profile of the site, and further damage the hull, but not necessarily conserve or preserve the significant aspects of the wreck.

The proposed conservation works included placement of anodes on the hull to slow the rate of corrosion, to be followed by archaeological recording of the two turrets, conning tower, and other aspects of superstructure. This would be followed by the placement of bracing structures, designed to take the weight of the two armoured turrets. The bracing would prevent the collapse of the turrets through the hull into the water. A programme of interpretation would be established at Black Rock to explain the significance of the site and the conservation works being undertaken. The works were approved by DEWHA, as required for all sites on the National Heritage List.

In January 2010, Heritage Victoria planned fieldwork to undertake investigations on the current site condition and potential for placement of anodes on the site, as part of Heritage Victoria's commitment to the proposed conservation works. As part of the routine documentation of the *Cerberus* site, salinity and dissolved oxygen measurements were taken at half metre intervals down the water column from surface to seabed. The data showed that the site was well mixed and fully saturated with dissolved oxygen with a small thermal gradient of  $1^{\circ}C$  between the surface and the bottom waters. In order to establish which parts of *Cerberus* were still electrically connected to each other, for the attachment points of the anodes, an electrical resistance study was conducted on the seaward side of *Cerberus*. Complimentary pH,  $E_{corr}$  and concretion thickness measurements were done at 5-m intervals and the resistance measured between successive points.

# 2010 fieldwork results — corrosion potentials as an indicator of site health

When the 2010 corrosion potential measurements are compared with those of previous years (see Figure 6) it can be seen that only <sup>3</sup>/<sub>4</sub> of the values lie in and around -0.325 volt vs NHE which is the average value for solid metal elements reported for that year. The remaining measurement points are characteristic of redox potentials for disconnected matrices of iron corrosion products (MacLeod, 2010). The other high  $E_{corr}$  in the region -0.200 to -0.250 volts is characteristic of iron that is largely degraded. Since all measurements in 1999 had all the characteristics of true corrosion potentials, it can be seen that the 2010 data represents a major change in the microenvironment of the wreck. The  $E_{corr}$  values on the starboard side of the vessel collected in 1994, 2005, 2009, and the present study in January 2010 are shown in Figure 7. There is a progressive shift to more anodic, less negative, values of  $E_{corr}$  which means that the wreck is corroding at an increasingly faster rate.



FIGURE 6 Plot of  $E_{corr}$  vs NHE of the starboard side of the *Cerberus* in January 2010 showing the loss of metal integrity in nearly a quarter of the tested regions.



FIGURE 7 Plot of starboard  $\mathsf{E}_{\mathsf{corr}}$  values in 1994, 2005, 2009, and in January 2010.

In reviewing the continuing degradation of the wreck of the *Cerberus*, it is useful to look at the way in which the  $E_{corr}$  values changed over time, between 1994 and 2010. The isolated point measurement taken in 2009 was during an assessment of the treatment of the gun barrels, however not much weight can be given to this single measurement as the data in Figure 7 shows a range of ±11 mV over a set of measurements. A summary of the increasing rate of deterioration of the vessel is seen in the trends towards more anodic values of the  $E_{corr}$  as seen in Table 3. These differences in voltage show that the average corrosion rate had increased by 28% between 1994 and 2005 and by an additional 12% between 2005 and 2010.

#### pH and concretion thickness sensitivity to water depth

The 2010 data on the corrosion potential, pH, and concretion thickness was collected at standing or kneeling depth close to the sea bed. The response of  $E_{corr}$ , pH, and concretion thickness with water depth is shown in Table 4. All the pH vs depth profiles had the same slope of +0.36 ± 0.01 pH.m<sup>-1</sup> which was much lower than the value of 0.66 ± 0.02 pH.m<sup>-1</sup> in 1994, but very close to the sheltered port side which had a median value of 0.42 ± 0.03 in 1994 which indicates that the amount of water movement on the lower starboard side has been significantly lowered with the second major collapse of the hull structure.

The slopes of the  $\frac{\partial E_{corr.}}{\partial d}$  plots were much steeper at  $-0.045 \pm 0.003$  than the -0.010 volts.m<sup>-1</sup> in 1994, and this is likely due to the fact that measurements were being taken directly on the armour belt and not on the additional plate and so the  $E_{corr}$  data is sensing a new post collapse environment — see Table 4. The intercept values of the  $E_{corr}$  vs depth plots reflect three different sub-sets of data; the most anodic relate to the redox potentials of heavily degraded sections of the wreck, the least reactive were associated with non-distorted hull plates, while the intermediate values relate to stressed elements. The 36 mV anodic shift of the stressed metal

	IN FOTENTIALS TOR CERBERG	JS SHE DOKING HIKEE W	AIN HELD SEASONS
<sup>1994</sup> E <sub>corr</sub> volt vs. Ag/AgCl	<sup>2005</sup> E <sub>corr</sub> volt vs. Ag/AgCl	<sup>2010</sup> E <sub>corr solid metal</sub> volt vs. Ag/AgCl	<sup>2010</sup> E <sub>corr all data</sub> volt vs. Ag/AgCl
-0.616 ± 0.007	$-0.583 \pm 0.004$	$-0.580 \pm 0.010$	-0.575 ± 0.006

TABLE 3 MEAN CORROSION POTENTIALS FOR *CERBERUS* SITE DURING THREE MAIN FIELD SEASONS

TABLE 4

DEPTH DEPENDENCE OF  $E_{CORR}$ , PH and CONCRETION THICKNESS T WITH WATER DEPTH: JANUARY 2010

$\partial E_{corr.}$ $\partial d$ slope volt.m <sup>-1</sup>	∂E <sub>corr.</sub> / int. ∂d volt vs. NHE	∂H∕∂d <sup>slope</sup> pH.m <sup>-1</sup>	∂ <i>H∕∂d</i> int. pH	$\frac{\partial t}{\partial d}$ slope mm.m <sup>-1</sup>	$\frac{\partial t}{\partial d}$ int.
-0.045	-0.093 <sub>redox</sub>	0.36	6.74 <sub>new concretion</sub>	$-14.0\pm2.0_{newer}$	48.7 ± 2.0
-0.045	-0.155 <sub>stressed</sub>	0.35	6.44 <sub>old concretion</sub>	$-13.6\pm1.2_{\rm older}$	$49.7\pm4.0$
-0.040	$-0.191_{\text{metal}}$	0.35	6.04 <sub>oldest concretion.</sub>	$-15.0\pm0.3_{\rm oldest}$	$62.5\pm1.0$

sections above the hull plates equates to a  $31 \pm 3\%$  increase in the corrosion rate as a result of the distortion of the structural members.

#### Concretion thickness as an indicator of corrosion rate

When the thickness of concretion profile t in millimetres was plotted as a function of water depth three subsets of parallel slopes of  $-14.0 \pm 0.7$  mm.m<sup>-1</sup> gave intercept values (zero depth) of 62.5 mm and 49.7 and 48.7 mm - see Table 4. The highest intercept value relates to original pre-disturbance concretion thickness and the values at 49.7 and 48.7 mm relate to essentially the same microenvironment of more recently re-concreted sections. The rate at which the concretion and corrosion matrix thickness fell with increasing water depth is a measure of the wave intensity bringing micronutrients to the marine organisms living on the surface of the wreck. If we assume that the Cerberus concretion has a similar nature to that on the USS Arizona (1941) in Pearl Harbour, then the rate at which the concretion thickness falls with water depth is a measure of how rapidly the corrosion rate falls. Their research had shown a direct correlation with the concretion thickness and corrosion rate and was based on the constant percentage of iron in the encrusting concretion (Johnson et al., 2006; Russell et al., 2006). Future monitoring measurements on the Cerberus site will include chemical analysis of the concretions to validate the above assumption. Thin and thus non-representative concretion layers on the Cerberus had a constant pH of  $8.03 \pm 0.05$ , but in areas of remnant or better developed concretion the pH fell by 0.6 per centimetre increase in concretion cover. The Cerberus data for the rate at which the concretion thickness falls as a function of depth fits the equation developed for the shallow water wrecks in Chuuk Lagoon which are of a similar age (MacLeod et al., in press). The rate at which the concretion thickness, and hence the corrosion rate, falls shows a logarithmic dependence on the water depth, as shown in equation 6,

$$\frac{\partial t}{\partial d_m} = 18.5 \log d_m - 23.7 \tag{6}$$

where  $d_m$  is the mean depth across the wreck site and the R<sup>2</sup> for the regression equation was 0.9836 with an error of ±0.6 for both the slope and the intercept of the equation. Previous studies on open ocean shipwrecks has shown that the corrosion rate conformed to the general expression,

$$\log dg = -0.630 - 0.016 d$$
 (7)

thus it is not surprising to find that the concretion profiles reflect a similar logarithmic dependence on water depth (MacLeod, 2006).

#### Electrical continuity of the starboard side

The electrical resistance between successive 5 m intervals on the starboard side were determined using a high impedance digital multimeter housed in a waterproofed stainless steel housing with a Perspex<sup>®</sup> viewing window (Figure 8). The resistance probes were connected to the meter through 'O' ring gland seals and the multimeter was set on the megohm (M $\Omega$ ) range. The measurements involved one diver operating the drill, one holding the far end of the resistivity metre probe, one taking pH, E<sub>corr</sub>, concretion thickness and resistivity measurements and the fourth member measuring



FIGURE 8 Diver measuring resistance between two 5 m separated points on the *Cerberus* hull.

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5 m intervals, holding extra equipment and taking photographs; the data collection took over two days. Resistance measurement sites and the location of the guns are shown in Figure 9. Corrections for the distortion of the linear dimensions along the outside of the starboard side facilitated location of data on the Admiralty plans of the vessel. The electrical survey data is found in Table 5 and the seabed on the starboard side is littered with broken frames, bits of hull plating, and other broken, deformed, and displaced parts of the lower buoyant hull.

The low resistance along the first eight 5-m sections shows that the first 40 m of outside edge are electrically connected. Sections between 40 and 50 m along the starboard side indicated poor connection, but there appears to be a total break for the interval between 40 and 45 m; that is, there is essentially no connection between the forward and aft parts of the vessel in the area between the turrets. The practical implications of the electrical discontinuity amidships means that any impressed current or sacrificial anode system would need to have separate connections at the bow and stern. More measurements in and around the midships would determine if the break in continuity is due to the disbondment of the additional  $r'_{16}$  inch layer armour plating or if it is due to a break in the more massive armour belting. Operational safety considerations prevented penetration diving and measurements of the



FIGURE 9 View of *Cerberus* showing approximate resistance measurement sites and gun locations, January 2010.

Image after Lindsay Stepanow 2006

TABLE 5

THE IN SITU DATA COLLECTION IN JANUARY 2010 ON THE STARBOARD SIDE OF THE CERBERUS

Distance from stern, m	рН	E <sub>corr</sub> vs. Ag/AgCl	$E_{corr}$ vs. NHE	Concretion thickness mm	Depth, metres	resistance $k\Omega$
0	8.07	-0.447	-0.188	21.5	2.1	
5	8.08	-0.582	-0.323	13.5	2.3	530
10	7.46	-0.575	-0.316	7.5	3.1	574
15	7.82	-0.573	-0.314	6.0	3.1	155
20	7.83	-0.585	-0.326	2.0	3.9	322
25	8.03	-0.583	-0.324	8.5	3.6	12
30	7.81	-0.580	-0.321	4.0	4.0	13
35	7.41	-0.579	-0.320	2.5	4.0	12
40	8.07	-0.506	-0.247	3.5	3.4	12
40	8.00	-0.563	-0.304	7.0	3.4	4800
45	8.02	-0.452	-0.193	4.0	3.2	4800
45	7.62	-0.557	-0.298	6.5	3.2	15600
50	7.12	-0.582	-0.323	2.0	3.3	5610
55	8.05	-0.374	-0.115	4.5	3.7	28
60	8.04	-0.558	-0.299	3.5	3.7	22
65	7.28	-0.586	-0.327	11.5	3.4	22
70	7.68	-0.582	-0.323	6.8	3.7	22

properties of the armour plating from inside the wreck. If corresponding measurements on the port side show the same discontinuity, then the implications for any proposed jacking of the vessel or other form of lifting is most serious and profound. The electrical resistance survey shows that *Cerberus* is more robust than previously thought and that the vessel is now relatively stable and resting on its armour belt. In May 2010, as part of the conservation approach agreed with DEWHA, National Trust (Vic), and Friends of *Cerberus*, a number of anodes were attached to the armour plating at sea bed level to begin in situ conservation works to the hull, internal structure, and turrets.

## In situ conservation of the four gun barrels

Four gun barrels were relocated from the wreck in January 2005 and placed adjacent to their original locations on the starboard side of the vessel and this removed  $4 \times 16$  tonnes from the structure (Figure 10). Since the *Cerberus* guns have been exposed to a saturated salt environment since 1926, it was decided to treat them in situ with anodes (Cornet, 1970). Prior to their relocation, the barrels were drilled and tapped to take 316 stainless steel bolts for securing the sacrificial anodes. After several years of cathodic treatment, the gun barrels have become heavily encrusted with concretion since the cathodic current makes the gun surface's alkaline and inorganic CaCO, deposits as a 1–2 mm thick protective film over the metal surface. The continuing



FIGURE 10 Removal of a 16 tonne gun barrel from the aft turret, January 2005, for placement on the seabed.

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alkalanization of the surface assists marine organisms in colonizing the gun barrels which lie in waters between 4.1 and 4.5 m.

The first in situ corrosion measurements on the guns took place 15 months after their placement on the seabed and at various intervals until the final measurements in January 2010 — see Table 6 and Figure 11 for details. It took several trials to determine the optimum configuration of anodes and cables as the fetch of the site

Objects	E <sub>corr</sub> 15/03/06 vs. Ag/AgCl	E <sub>corr</sub> 03/06/09 vs. Ag/AgCl	E <sub>corr</sub> 14/01/10 vs. Ag/AgCl	pH 15/03/2006	pH 03/06/09	pH 14/01/10
gun 1	-0.810	-0.863	-0.976	7.68	8.14	n.d.
gun 2	-0.808	-0.920	-0.820	7.87	8.15	n.d.
gun 3	-0.821	-0.633	-0.934	7.66	8.04	8.18
gun 4	-0.754	-0.933	-0.861	7.81	8.14	8.29
anode 1	-0.958	-0.946	-0.980	5.89	7.67	7.24
anode 2	-0.893	-0.960	-0.820	6.79	7.78	6.87
anode 3	-0.839	buried	-0.920	6.59	buried	6.43
anode 4	-0.724	buried	-0.912	5.98	buried	6.62

TABLE 6 IN SITU CORROSION PARAMETERS FOR *CERBERUS* GUNS DURING TREATMENT ON THE SEABED



FIGURE 11 Divers taking pH measurements on the anodes attached to one of the *Cerberus* guns.

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exposed the guns to strong wave action that led to work hardening and ultimately to snapping of the insulated copper cables. This led to times when the guns were unprotected other than through the accumulated dense concretions that had formed on them during cathodic treatment with the anodes — the  $E_{\rm corr}$  of gun 3 had a value of -0.621 volts in June 2009, indicating a disconnected anode, but this voltage dropped 200 mV within two hours of a new connection being made. This rapid fall indicated that there was little residual acidity to overcome and that the partially stabilized object quickly returned to a state of being actively treated for chloride ion removal. The deliberate burial of the anodes and cables precluded the direct measurement of data on some occasions.

The Ag/AgCl<sub>sea</sub> reference electrode was calibrated at +0.248 volts verses the Normal Hydrogen Electrode (NHE) at 21°C. *n.d. not determined*.

A graphical representation of the  $E_{corr}$  of the gun barrels is shown in Figure 12 which illustrates the way in which the treatment program has developed over the years. The initial in situ values for the gun barrels were estimated as being the same as the best preserved hull plates at the same depth on the starboard side of the vessel. Chloride ions in the guns undergo active diffusion resulting from the negative polarity of the metal that has been induced by the attachment of the anodes. The median voltage drop of the four guns 14 months after the anodes had been attached was  $201 \pm 30$  mV, and this increased to  $312 \pm 37$  mV after 28 months where it stabilized with the median voltage after 33 months of treatment at a combined drop of 290  $\pm 34$ mV. These voltage drops are indicative of effective cathodic protection (Morgan, 1993) and the attainment of a pH plateau after 28 months of treatment at 8.14  $\pm 0.05$ indicated that the treatment had finished.



FIGURE 12 Plot of  $E_{corr}$  of the four guns undergoing in-situ treatment on the *Cerberus* wreck site.

# Assessment of in-situ cathodic treatment and determining when the artefact is treated

Analysis of the E<sub>corr</sub> and pH data from a number of shipwrecks sites in different countries has shown that for aerobically corroded marine iron the arithmetic product of the pH and the corrosion potential is  $-3.6 \pm 0.4$  which is a pre-disturbance value, regardless of the site specifics of temperature, salinity or dissolved oxygen (MacLeod, 2011 in press). For the sake of convenient notation this arithmetic product is denoted as the CI or corrosion indicator. It is likely that the common value of the product of the pH and E<sub>corr</sub> is a due to several factors; a common microenvironment underneath concretion and the establishment of a dynamic equilibrium between acid-producing corrosion reactions and acid consumption by the encapsulating concretion. After anodes have been attached, the value of the CI becomes increasingly negative since the  $E_{corr}$  becomes more cathodic and the pH increases as the electrons consume the excess hydrogen. The plateau value for CI is  $-7.4 \pm 0.3$  at the end of the in situ treatment for this is the point at which hydrogen is being evolved from the entrapped water surrounding the artefact rather than from acid that was produced from its previous corrosion history. The CI value moves towards the plateau value faster on shallower wreck sites and is also dependent on the depth of graphitization  $(d_a)$  of the cast iron, with higher  $d_{e}$  values resulting in faster changes in the value of the corrosion indicator (MacLeod, in press). For the Cerberus gun barrels the March 2006 data showed that the CI value had decreased to  $-6.3 \pm 0.2$  and by June 2009 it had reached  $-7.5 \pm 0.3$  which saw no effective change with another 7 months' treatment which achieved a CI of  $-7.4 \pm 0.4$ ; in other words the treatment was over. The anodes had done their job of stabilizing 68 years of atmospheric corrosion on the Cerberus guns in only 2<sup>1</sup>/<sub>4</sub> years. Without the additional 15 years of experience with historic iron shipwrecks since the time of the initial report on the Cerberus in 1995, this present interpretation of historic and present data would not have been possible (MacLeod, 1996). The task of Heritage Victoria is to either keep the anodes in functional order on the seabed or recover the guns and place them in their stabilized condition in a land-based facility, with appropriate protective coatings on them.

# Conclusion

The experiment to remove the four massive 10 inch Armstrong rifled guns from the *Cerberus* to lighten the load on the remaining structural elements is likely to have slowed the rate of decay of the vessel, through the relief of some of the structural stress that is part of the nature of the stranded and collapsed shipwreck. The treatment of the guns on the seabed with sacrificial anodes can be deemed to be a very successful method of stabilizing the guns in the immediate vicinity of the wreck and so preserve significant elements of the original integrity of the site. Since the wreck is close to the shore and areas of significant boating activity and the exclusion zone is well policed, it is unlikely that the guns will suffer from any vandalism. It is recommended that a six-monthly monitoring site visit takes place to ensure that the anodes remain attached during the winter storms. The application of routine monitoring of the site through the use of in situ corrosion studies has been shown to be a powerful conservation heritage management tool that has enabled the discussions regarding the

fate of the only accessible Monitor-style twin turreted breastwork battleship to move forward. The development of the corrosion indicator product or *CI* from multiply the values of the  $E_{corr}$  and pH is a major step in the understanding the commonality of corrosion mechanisms on historic iron artefacts. By routinely monitoring these two core in situ parameters heritage managers, conservators, and maritime archaeologists will be able to provide informed comment on the anticipated time of treatment of artefacts undergoing treatment on the seabed.

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## Glossary

Chlorinity: The concentration of chloride ions in water, expressed as parts per thousand (ppt) or ‰

Concretion: The calcareous admixture of corrosion products and sedentary epifauna found on historic marine iron artefacts

- *Corrosion potential*: The voltage of a corrosion cell where the oxidation (anodic reaction or corrosion) and reduction (cathodic reaction) currents are equal and as such it is a kinetic parameter and not a thermodynamic value
- *Flux*: The amount of an electrochemically active component that is supplied to a corroding surface which is controlled by a combination of the water movement and the analytical concentration of the reactant

Interfacial: The region consisting of the surface of the corroding metal and the surrounding solution lying underneath the protective cover of the concretion

*pH*: The negative value of logarithm of the hydrogen ion activity (concentration) in an aqueous solution *Salinity*: The amount of soluble salts in an aqueous solution expressed as parts per thousand (ppt) or  $\infty$ 

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