## Abstract

A series of in situ corrosion measurements on the wreck City of Launceston (1865) have confirmed that the vessel is close to collapse. If the long-term corrosion rate of 0.119±0.014 mm/ year continues until 2005, the average hull plate thickness will have fallen to less than 1 mm of steel. In this condition it is unlikely that the vessel will be able to withstand the impact of the strong storms that periodically dominate the weather patterns in Port Phillip Bay. The local surface pH of the corroding metal was used to establish the most likely sites for disintegration of the hull. Corrosion data have provided evidence of the detrimental impact of weed clearing.

# Keywords

conservation, corrosion, iron shipwrecks, corrosion potentials, surface pH, metal thickness, seawater

# In situ corrosion monitoring of the iron shipwreck City of Launceston (1865)

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# Introduction

On the evening of November 19, 1865, while steaming down Port Phillip Bay, the *City of Launceston* was accidentally rammed by the steam-powered ship *Penola*, which rescued all crew and passengers. Salvage attempts in the 1860s used patented cast iron drums (Macquay devices), which used chemically generated hydrogen from the reaction of metallic zinc and sulfuric acid to provide the lift. This raised the ship a few metres, but it remains 21 m below the surface in the middle of Port Phillip Bay. Divers removed the masts and funnel for safety reasons and the wreck remained essentially intact until snagged scallop dredges damaged the stern superstructure in the 1970s. Pre-disturbance measurements in 1991 preceded a detailed examination in 1997. Measurements in 1998, 1999 and 2001 established the nature of the decay process.

# Physical oceanography

The wreck lies on a flat bottom of shingle and silt, which mounds to within 2 m of the starboard and 1 m of the port side deck and fills the interior, along with shell debris. When the site is disturbed the visibility falls to zero. 'The Bay is at various times unstratified, stratified by temperature, stratified by salinity, or stratified by both temperature and salinity' (Cowdell et al. 1985). With average residence times of one year the site has a 'low energy' with an annual mean surface oxygen concentration is  $5.7 \pm 0.2$  ppm, temperature  $15.8 \pm 0.6^{\circ}$ C, pH values of the seawater were  $8.0 \pm 0.2$  and the salinity was  $34.8 \pm 1.2$  ‰. Bottom temperatures were  $14^{\circ}$ - $16^{\circ}$ C with stratification of one degree between water depths of 16.6 m and 19 m. Occasional currents of 0.5 knots improved visibility during *in situ* measurements. Visibility seemed to improve with repeated site visits.

# Marine biology of the site

In 1865 the wreck was clearly visible from the surface but major developments in the Port of Melbourne in the 1890s, 1920s and the 1960s made the site very silty, which inhibited marine growth and increased exposure to the corrosive effects of oxygen (North 1976, La Que 1975). The extent and maturity of colonization of the wreck was significantly different at the bow and the stern, compared with the middle section of the vessel. It was the cessation of scallop dredging after the predisturbance survey that resulted in a marked increase in the level of colonization and not the natural cycles in turbidity that would favour biological growth in April and May (Cowdell et al. 1985). The W-SW to E-NE orientation creates a natural barrier to the flow of sediment in the bay and causes scouring at the bow and the stern. Filter feeding marine organisms have a steady supply of nutrients and are free to grow to maturity, but the sedentary organisms in the midsections are subject to periodic burial in silt.

## **Corrosion studies**

The state of decay of an iron shipwreck can be determined through a series of measurements on the corrosion potentials,  $E_{corr}$ , the surface pH, residual metal thickness *t* of the hull plates, the depth of graphitization (i.e. corrosion of cast iron,  $d_{mm}$ ), and its annualized value,  $d_g$  in mm/year since the ship sank. This study on the *City of Launceston* involved more than 175 sets of pH and corrosion potential measurements. Hull plate thickness was conducted with a Cygnus 1 ultrasonic metal thickness meter. The  $E_{corr}$  measurements were made using a 2 mm diameter platinum electrode and a silver/silver chloride reference electrode (Ag/AgCl<sub>sed</sub>), which was calibrated against the Normal Hydrogen Electrode (NHE) using a pH 4 solution, saturated with quinhydrone, and corrected for the temperature of the seawater. The pH data are conservative, i.e. the reported values will tend to be less acidic than the actual values.

Poor visibility meant there were delays in getting the electrode into position and this allows penetration of normal seawater into the corroding interface. The lack of calcareous colonizing organisms meant that the concretion covering was only a few mm thick, which is not enough to facilitate the build up of a significantly different microenvironment (North 1976). The slow rate of re-colonization became apparent when, one year after taking the metal thickness measurements, the 8 cm diameter sections that had been cleaned were still discernible. Corrosion potential measurements made on large structures, such as hull plates attached to steel frames and ribs, tend to reflect the average environment but the pH of the corroding metal is generally a better indicator of the local corrosion activity in a complex site such as the *City of Launceston* (MacLeod, 1995).

# Periodic burial

A thin layer of the deep-blue copper sulfide covellite (CuS) on a copper pressure vessel on the engine is consistent with it having been buried in about 15 cm to 40 cm of sediment, since the same mineralization occurred on a bronze tallow pot and the main copper steam pipe from the SS *Xantho* (1872) engine, which had been periodically buried under 40 cm of sediment. Both objects had the same  $E_{corr}$  value at  $-0.137 \pm 0.005$  volts vs. Ag/AgCl<sub>sea</sub>. The pH was estimated to lie between 6.5 and 7.5. The sulfide ions come from the metabolites of sulfate reducing bacteria such as *desulfovibrio salixigens* (MacLeod et al. 1986, Macleod 1982).

# Depth of graphitization of cast iron

During the initial survey in 1991 and during a site inspection by Terry Arnott in 1994, a series of corrosion potential measurements were made on cast iron fittings on the vessel and a set of five depths of graphitization measurements were made. Based on the assumption that the wreck has been in a relatively constant environment since it sank in 1865, the mean depth of graphitization of  $15.4 \pm 1.85$  mm equates to a corrosion rate, or a  $d_g$  value, of  $0.119 \pm 0.014$  mm/yr<sup>-1</sup>. Using the values of the corrosion potentials (NHE) and associated  $d_g$  values of the individual cast iron objects, the following relationship describes the average corrosion environment on the *City of Launceston*:

$$\log d_{\rm c} = 3.25 \, \mathrm{E}_{\rm corr} + 0.202 \tag{1}$$

This linear relationship between the log of the corrosion rate and the corrosion potential has been previously described and provides a direct method for the interpretation of corrosion potential data (MacLeod 1988, 1989, 1996a, 1998). The primary rate determining step in the corrosion process is the flux of dissolved oxygen to the encrusted artefact, with  $E_{corr}$  values being more anodic, less negative, when there is an increased flux of dissolved oxygen to the marine encrusted surface of the object. The initial inspection voltage of the cast iron engine cylinder was – 0.289 volts vs. Ag/AgCl<sub>sea</sub>, which indicates that the metal is largely graphitized, which is consistent with the easy penetration of the drill bit into the internal cavities of the cylinders. The  $E_{corr}$  of the cast iron *Macquay* devices and the massive propeller

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Figure 1, Metal thickness of hull plates on port and starboard sides vs. distance from the bow

were 264 mV more negative at -0.553  $\pm$  0.004 volts and retained significant amounts of solid metal.

## Effects of alloy composition on corrosion potentials

In a cast iron with 3.5 wt% of carbon, the atomic concentration is almost 16%, thus carbon will have a major effect on the electrochemical reactivity of iron. The average carbon content of wrought iron plates is between 20 and 40 times less than that found in cast iron and the corrosion potentials are up to 70 mV more negative for the same corrosion rate but only 33 mV different on the *City of Launceston*. When determining average corrosion rates for the hull plates, the voltages are corrected for the effect of the carbon content when using equation 1 to estimate the corrosion rates of the wrought iron hull plates.

## Metal thickness

Reproducible measurements of metal thickness involved clearing areas typically 8 cm in diameter, owing to the roughness of the corroded plates. Eighteen surveyed locations from the bow to the stern on port and starboard sides were measured (Figure 1). There were several areas where the cleaning showed up perforated plates. The mean metal thickness was  $1.98\pm0.47$  mm after more than 130 years of corrosion but there is no systematic trend of metal thickness with distance from the bow, nor is there any direct relationship between the thickness and the present  $E_{corr}$ data. Although there is no real difference between the mean 1.9±0.5 mm thickness on the port side and  $2.0\pm0.6$  mm on the starboard side, there was a difference between the mean pH data. The higher silt mound on the portside gave lower corrosion rates, i.e. it was less acidic than the starboard side, with the mean values being  $pH_{nort}^{97} = 6.83 \pm 0.56$  and  $pH_{sthd}^{97} = 6.48 \pm 0.70$ . Two years later the same trend continued, but the lower pH values of  $pH_{port}^{99}$  7.22±0.23 and  $pH_{sbd}^{99}$  was 7.14±0.43 are due to the incomplete re-colonization. The surface pH of the corroding metal is normally a good indicator of localized corrosion since the hydrolysis of the primary corrosion product of iron (II) chlorides produces increased acidity, viz.,

Plots of the 1997 pH values from the bow to the stern (Figure 2) shows a number of points along the length of the vessel that have lower pH and these generally correlate with higher  $E_{corr}$  values, both of which indicate a higher corrosion rate. The starboard side of the *City of Launceston* has pH minima at 7 m from the bow and then at 36 m, 46 m and 52 m from the bow while the port side has pH minima at 3 m, 29 m, 46 m and 50 m from the bow.

When the pH data are plotted on the site plan there is a trend toward the port side minimum occurring several metres before a corresponding minimum on the starboard side. The mean angle of the lines joining the adjacent minima is  $32^{\circ} \pm 9^{\circ}$  from north, which is close to the angle at which the vessel lies with regard to



Figure 2. 1997 in-situ pH for port and starboard hull plates

the flow of the current across the site. Clearly there is a strong correlation between the localized corrosion rates and the current that brings the dissolved oxygen. Analysis of the comprehensive 1997 data indicates that the pH is dependent on the log of the thickness of the residual metal x, where x is in mm of metal. The starboard plates followed equation 3, and had a five-point correlation factor of 0.85.

$$pH_{stbd}^{97} = 4.76(0.55) + 0.89(0.27) x \tag{3}$$

The port side data were more scattered with correlation coefficient of 0.62 for equation 4

$$pH_{port}^{97} = 5.90(0.44) + 0.34(0.22) x \tag{4}$$

The values in parentheses are the standard deviations associated with the lines of best fit. Since the intercept and slope values of equations 3 and 4 differ by more than the sum of the errors the results appear to be significant which indicates that the starboard side is corroding at a faster rate than the port side. Given that the actual metal thickness is not greater than 2 mm, the error of  $\pm 0.1$  mm in any measurement equates to at least 5% so the correlation coefficients are not unreasonable.

Localized increases in corrosion rate (less negative  $E_{corr}$ ) were coincident with two of the pH minima on the starboard side at approximately 6 m and 35 m from the bow. The fact that low pH values at 46 m and 52 m were not mirrored by elevated  $E_{corr}$  values is probably due to the hull plates being in contact with more protected parts of the wreck. A diagrammatic representation of the corrosion environment in 1997 is shown in Figure 3, which highlights the lack of uniformity



Figure 3. 1997 season of E measurements for port and starboard hull plates

Table 1. Corrosion potentials vs. Ag/AgClsea and calculated corrosion rates for all field seasons

Date	E <sup>stbd</sup> corr	i stbd mm/year	Ecorr	i corr mm/year
April 1991	-0.585±0.006	0.149±0.006	-0.591±0.003	0.142±0.003
November 1997	-0.613±0.011	0.114±0.009	-0.612±0.012	0.113±0.010
November 1998	-0.596±0.026	0.134±0.023	-0.593±0.022	0.137±0.020
October 1999	-0.581±0.023	0.150±0.020	-0.583±0.011	0.147±0.011
November 2001	-0.599±0.013	0.130±0.013	-0.604±0.012	0.128±0.013

of the microenvironment. Comparison of the  $E_{oor}^{98}$  and  $E_{oor}^{97}$  values for solid metal plates showed that the mean  $E_{oor}^{98}$  value is 15 mV more anodic than in 1997, i.e. it has a 12% higher corrosion rate. Hull plates that are extensively corroded and have very little solid metal are characterized by potentials that are between 100 mV and 350 mV more anodic than the  $E_{corr}$  values of sound plates (MacLeod 1981, Pourbaix 1974). The *Penola* bow was 22 mV more anodic than the nearby hull plates (Figure 3), which is due to a mixture of the effects of increased localized turbulence and differences in alloy composition and residual stress associated with the ramming. The 32 mV elevation in the  $E_{corr}$  of the rudder is probably due to localized turbulence and the effects of non-annealed cold working.

#### Calculation of apparent corrosion rates

A convenient way of interpreting  $E_{corr}$  values is to use the corrosion equation,  $log i = 3.25 E_{corr} + 0.202$ , to work out the apparent corrosion rate, after corrections for the voltage differences between wrought and cast iron. The overall situation is summarized in Table 1, where the mean  $E_{corr}$  values are tabulated, along with the corresponding estimates of actual corrosion rates for the hull plates during the five visits to the wreck site. The cessation of scallop dredging and associated improved light penetration and marine growth probably accounts for the drop in corrosion rates between 1991 and 1997. Stripping of the weed growth from the deck after the 1997 measurements, to enable the site to be fully surveyed, seemingly increased the corrosion rate by 17.5% and by a further 12% almost one year later before the rates fell to nearly 5% below the 1998 value following two years of site stabilization. The marked changes in the corrosion potentials after site stripping shows that corrosion on iron wrecks is very sensitive to removal of marine encrustations. The overall impact of conducting a detailed site survey by traditional tapes and photogrammetry on iron wrecks is major.

During the 1997 survey five of the 58 hull plates were totally corroded but this number had increased to ten out of the 56 one year later. Using the mean 1997 corrosion rates, the calculated metal loss over 132 years was  $15\pm2$  mm, which matches the mean depth of graphitization of  $15.4\pm1.9$  mm. The original plate thickness was estimated by adding the residual and lost metal values, which gave a value of  $16.5\pm1$  mm. Since the construction specifications are unknown these data indicate an original 5/8" plate (15.9 mm) was used to build the vessel.

# Wreck location and localized corrosion

In moving from the bow to the stern, the starboard 1998 pH data indicate that there are zones of increased localized corrosion activity at 3m to 8 m, at 25 m, at 43 m and at 55 m from the bow. Apart from these hot spots the overall trend is towards a more uniform value of the pH, which is probably due to the lack of colonization only one year after stripping. The  $E_{corr}$  data, as the solid line in Figure 4, generally follow the trend of the pH data except between the 36-m and 52-m marks. Here the elevated voltages are reflecting the impending demise of the steel hull plates in that area.

Similar patterns of behaviour were observed for the port side, showing hot spots near the bow, at 5 m, 24 m and 36 m from the bow. Where there is a divergence of the  $E_{corr}$  data and the pH values, it is due to the loss of integrity of the hull plates. The site stabilization brought about with cessation of scallop dredging was destroyed by the 'de-weeding' operations. The re-colonization process took more than two years to begin to correct this impact (Figure 5). Without some form of



Figure 4. Starboard in-situ values of pH and  $E_{corr}$  for 1998 as a function of distance from the bow



Figure 5. Starboard corrosion potentials for hull plates from 1991-2001

stabilization, it can be estimated that the wreck will begin to collapse from areas about 4 m to 7 m from the bow and at from 46 m to 51 m from the bow, i.e., about 5 m to 10 m from the stern. This collapse will be dependent on the timing of a major storm and can be expected to occur within the next one to three years.

#### Conclusion

The use of *in situ* corrosion measurements has established that the City of Launceston is in the final stages of its existing configuration as a complete hull. Surface pH measurements appear to be good indicators of localized corrosion rates for continuous iron and steel hulls. Corrosion potentials and associated depths of graphitization of cast iron objects provide a quantitative tool for assessing the past and present corrosion environment. When the original conditions were compared with data obtained in 1997 and 1998, they showed that the wreck was undergoing a significant deterioration, partly due to the archaeological activities of site recording. This brought on an excavation program. Subsequent monitoring in 1999 confirmed the trend towards impending collapse of the wreck. Final measurements in 2001 show the site is moving back toward its long-term corrosion rate. While silt has protected the site from major storm damage, by acting as an effective transmission medium for shock waves, it is necessary to remove some for archaeological reasons. The upper works of the vessel are also significantly decayed with several ribs, frames, the capstan and a deck plate having no solid metal. Based on best estimates of the present corrosion rate and the residual metal thickness in 1997, the wreck can be expected to collapse within the next five years.

#### Metals

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