# The Electrochemistry and Conservation of Iron in Sea Water

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**About the author**

*After completing his PhD on the electrochemistry of fluorides in HF at the University of Melbourne Ian Mac-Leod went to Glasgow for two years to study organophosphine co-ordination chemistry. A job offer from the late Jim Parker brought him to Murdoch University in 1976 where he studied the behaviour of copper and its minerals in aqueous acetonitrile. Since 1978 his research activities at the W.A. Museum have centred on the corrosion and conservation of metals recovered from historic shipwrecks.*

## Introduction

Rusting iron is synonymous with the marine environment owing to the combined effects of salts, moisture and oxygen which rapidly corrode uncoated metal. Iron recovered from historic shipwrecks corrodes at an elevated rate once it has been removed from the sea-bed unless preventative conservation measures are applied.[1] The corrosion mechanism for iron and its alloys has been the subject of great controversy owing to the problems associated with delays between excavation and subsequent analysis.[2]

Thanks to the pioneering work of Neil North at the WA Museum, the nature of marine iron trapped under the protective calcareous concretion layer has been determined.[3] Further work on a variety of shipwrecks has shown that on-site underwater measurements of corrosion potentials and the pH of the interfacial regions can provide a remarkable insight into how microbial and marine biological activity and alloy composition affect corrosion rates.

Recent work on the wreck of HMS Sirius on Norfolk Island has led to the development of a corrosion model that has major implications for the management of our maritime archaeological heritage.

## Concretion Formation and Iron Corrosion

The formation of marine concretions on iron objects refers to the complex series of physical and chemical changes that ensue following the placement of an uncoated iron object in the sea.[3] As iron begins to corrode the metal has anodic and cathodic areas on the one surface, but this situation soon changes.

Dependent on the water depth, temperature and the season of the year, marine organisms will rapidly colonise the surface of the object and cause physical separation of the anodic and cathodic reactions. Within the space of a few years the hard calcareous layers of coralline algae, bryozoa and foraminifera will have reduced the corrosion rate of iron by virtue of the physical barrier it provides to dissolved oxygen.

The concretion also acts like a semipermeable membrane which results in the increased concentrations of chloride and hydrogen ions at the surface adjacent to the corroding metal (see figure 1). The major primary corrosion product is iron (II) chloride (up to $0.6\,M\,FeCl_2$)[4] and the pH falls to typical values of 4.8, though sometimes as low as 4.2, as a result of hydrolysis reactions such as

$$2FeCl_2 + 2H_2O \rightarrow$$
$$FeCl_2.Fe(OH)_2 + 2H^+ + 2Cl^- \qquad (1)$$
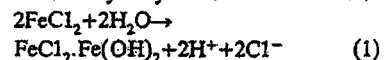
Outside the concretion, the pH of sea water is $8.2 \pm 0.2$ and the dissolved oxygen level is typically 7-8 ppm.

Measurements of the conductivity of iron concretions show that freshly excavated material will have resistance of the order of $4,000\,\Omega$ across 2cm of marine growth while dry concretions have very low conductance. In the wet condition the current is predominantly carried by ionic species whereas in the dry state the semi-conducting properties of secondary corrosion products such as magnetic and iron-oxy hydroxides result in resistances as high as $15M\Omega$ across the same sample.

The thickness of the concretion layer has a major influence on the corrosion rate. On-site measurements of the corrosion potentials under the concretion show that the iron is often in strongly reducing conditions with Eh values at −0.30 volts at pH 4.8, ie, just below the hydrogen evolution potential for the same pH. Hydrogen has been identified as a major component of the gases released when concretions are penetrated for the first time in centuries.[4]



*The author measuring pH and corrosion potentials of ballast at the Sirius wreck site.*
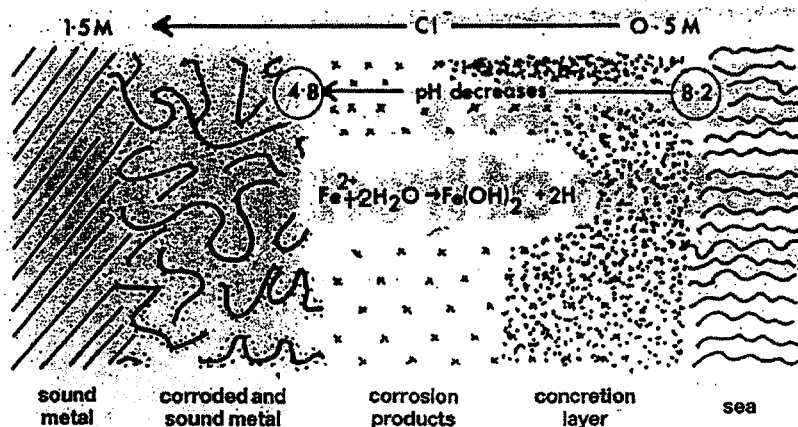*Photo: Pat Baker.*

Figure 1: *Schematic cross-section of a concreted corroded iron object in sea water.*

The labels in figure 1: 1·5M ← Cl⁻ → 0·5M; 4·8 ← pH decreases → 8·2; $Fe+2H_2O \rightarrow Fe(OH)_2 +2H^+$; sound metal / corroded and sound metal / corrosion products / concretion layer / sea

Since the concretion provides a mechanical and electrochemical barrier to dissolved oxygen it is not surprising that the ballast with reduced overall concretion cover will corrode at a faster rate.

The differences are significant since the ballast with an on-site $E_{corr}$ of −0.140 volts was graphitised to 61mm while the most stable $E_{corr}$ value corresponded to a graphitisation depth of 25mm. The difference of 150mV in corrosion potential reflects an increase of 143 per cent in corrosion rate.

## Development of Corrosion Model

Measurements of dissolved oxygen on wreck sites[7,9] around the Australian coastline show little difference between surface levels and those found at depths up to 30 metres. There is a slight increase in oxygen concentration up to depths of approximately 50 metres which is due to the pressure increase of one atmosphere for every ten metres of depth.

The major factors affecting solubility of oxygen in sea water are the water temperature and salinity. Since these factors were constant over the period of measurements the differences in corrosion potential cannot be directly due to dissolved oxygen levels. The lower corrosion potentials found in deeper waters are apparently a reflection of a lower oxygen flux to the corroding concreted iron objects.

Factors affecting water movement on a wreck site are going to include the height and period of the waves, the water depth, prevailing currents and the turbulent motion associated with the rush of water as waves break and respond to the profile of the sea bed and the objects scattered across it.

George Creswell[7] showed that because of the way in which the reef platform falls away to deeper water, the "Sirius" site is subject to the full force of waves breaking over the inner part of the wreck site. With water moving at speeds

Other gases included carbon dioxide from $CaCO_3$ dissolution, and methane.

Since methanogenic bacteria are often active in strongly reducing conditions it was essential to determine if the $CH_4$ was of inorganic or biological origin. Since bacteria effectively fractionate carbon isotopes in favour of $^{12}C$ the isotope shift (delta $^{13}C$) has values −55 to −75 ppt[5] (relative to the standard limestone, PDB) for bacterially produced methane. The observed isotope shift was −4.7 ppt which showed that the methane was inorganically derived via reactions such as

$$CO_2+4H_2 \rightarrow CH_4+2H_2O \qquad (2)$$
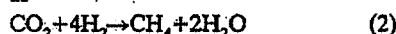
Inspection of the carbon Pourbaix diagram[6] shows that methane is the thermodynamically stable form of carbon under the lower portion of the range of Eh and pH.

### Corrosion and HMS Sirius

A recent expedition to Norfolk Island located and accurately surveyed the positions of 220 concreted lumps of iron ballast from the wreck of HMS Sirius. The flagship of the First Fleet struck a reef close to the shore and was wrecked while unloading convicts and stores in 1790.

Since the pig iron ballast was scattered over the site it provided the opportunity to carry out a corrosion survey where any differences in parameters would be due to local conditions. Our measurements of the iron corrosion potential ($E_{corr}$) showed a considerable variation with the range being $-0.290 \leqslant E_{corr} \leqslant -0.130$ volts vs NHE at water temperatures of 22±1°C. The salinity of the site was 35.7 parts per thousand.[7]

The ballast pigs with the most corrosive $E_{corr}$ values also had significantly lower pH values of $4.2 \leqslant pH \leqslant 4.6$ than those normally encountered, ie, most iron concretions have 4.8 as the minimum value of pH. The results of all the measurements are shown on the iron Pourbaix diagram for sea water (figure 2).

Inspection of the archaeological site plan showed that wrought iron anchors and cast iron pigs in the shallower part of the site (1-2 metres) generally had higher $E_{corr}$ values than those found in the deeper part of the site at depths of 2-3

metres. The pig with the lowest $E_{corr}$ value of −0.290 volt was recorded in the lagoon area off the main wreck site where it had been covered with half a metre of sand.

By way of contrast the ballast (No. 21) with the highest $E_{corr}$ at −0.130 volts was in 1.25 metres of water lying on top of several other pigs where it was exposed to maximum turbulence as the two metre waves broke above the inner part of the wreck site during our measurements.

The next most aggressive environment was recorded by an isolated lump of ballast lying proud of the hard calcareous rock at a depth of between one and two metres. Closer inspection of the surface showed that pits approximately 5cm in diameter were found along the vertical faces of the concretion.

Subsequent excavation showed that the 50kg cast iron block (initial weight)[8] had been more extensively corroded than the pig recovered from the lagoon. The depressions were made by Wunna's, the black long-spined sea urchins *Heliocidaris tuberculata* (Lamarck, 1816) which create a protective niche for themselves by burrowing into the concretions which are approximately 20mm thick.
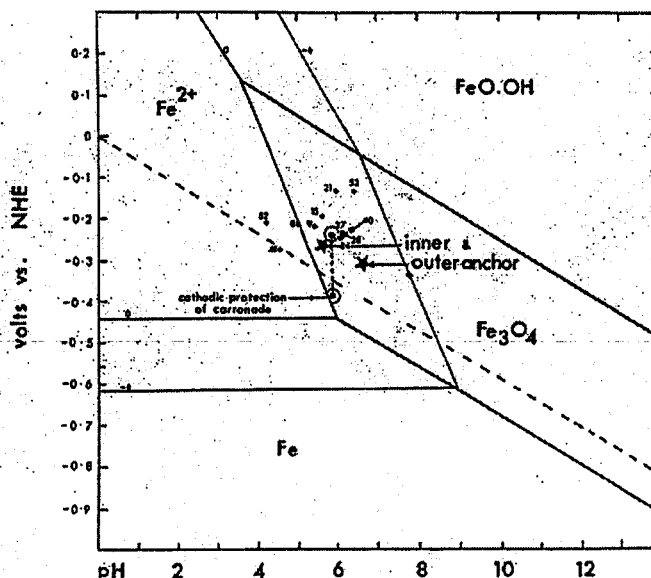


Figure 2: *Pourbaix diagram for iron showing pH and corrosion potentials of iron artefacts on the HMS Sirius wreck site.*

of greater than $5ms^{-1}$ (10 knots) it is not surprising that the inner ballast blocks reflected a very corrosive environment with high $E_{corr}$ and record low pH values. It also explains why every object was not measured — a typical wave shoves a diver back and forwards a total distance of 11 metres![7]

Calculations of the formal reduction potential for oxygen at pH 8.2 and 7 ppm for the equation

$$O_2+2H_2O+4e^-\rightarrow4OH^- \qquad (3)$$
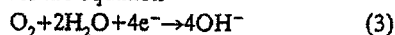
gives a potential of 0.546 volts. Since the average $E_{corr}$ for the "Sirius" site is −0.217 volts this represents an overvoltage of 763mV for the cathodic reaction and 230mV for the anodic oxidation of pure iron to $Fe^{2+}$. Under diffusion controlled conditions the limiting current is inversely proportional[10] to the thickness of the diffusion layer delta.

Increased water movement characterises the site conditions in the shallower part of the "Sirius" site and so the greater corrosion rate and higher $E_{corr}$ values are largely due to an increased oxygen flux and lower delta values. Ritchie et al also found that the corrosion of iron in reduced ilmenite in 0.1M $NH_4Cl$ is also limited by the oxygen flux to the corroding surface.[11]

The effect of water depth on corrosion potentials can best be demonstrated by comparing the $E_{corr}$ values for cast and wrought iron objects from a variety of shipwreck sites. Although the data is confined at present to those sites off the Western Australian coast they do show some interesting trends, as shown in figure 3. Inspection of the data shows a linear dependence of $E_{corr}$ on water depth for both types of concreted iron, namely that $E_{corr}$ becomes increasingly negative with increased water depth. This supports the model that the corrosion rate is largely determined by the flux of dissolved oxygen. The relationship between corrosion potentials and depth are given by the equations for cast iron (4) and wrought iron (5)

$$E_{corr}=-0.0203d-0.167 \qquad (4)$$
$$E_{corr}=-0.0174d-0.237 \qquad (5)$$

where $d$ is the water depth in metres and $E_{corr}$ is the corrosion potential in volts vs NHE. The error associated with the slopes of the graphs (±0.0065) means that the $E_{corr}$ for cast and wrought iron objects show the same depth dependance of 18.9±1.5mV per metre.

The more positive corrosion potentials for cast iron is a reflection of the "enobling" effect of the carbon. Typical values of 4 wt% (16.24 mole %) carbon in cast iron will result in large proportions of phases such as graphite and cementite ($Fe_3C$) in the alloy. The difference in E°s for oxidation of cementite and iron to $Fe^{2+}$ is 50mV which is very similar to the difference in corrosion potentials of wrought and cast iron artefacts at the various water depths shown in figure 3. It should be noted that wrought iron is composed principally of pure ferrite with strips of slag incorpo-

rated into the structure during the blacksmithing (hot working) manufacturing process.

Corrosion of cast iron results in gradual removal of the iron-rich phases from the surface layers which finally leaves only graphite. The depth of corrosion or graphitisation is a measure of the mean corrosion rate.[4] With the passage of decades and centuries the enhanced corrosion rates due to warmer summer sea temperatures and the lowered rates in winter will tend to be averaged out.

The objects measured for depth of corrosion came from similar temperature regimes with mean annual temperatures ranging from 22 to 25°C.[12] There is insufficient data at present to precisely determine the effects of temperature on long-term corrosion rate but one compensating factor for lowered water temperature is an increase in oxygen solubility.

For example, at constant salinity of 36 ppt the solubility of oxygen increases from 4.70 to 5.65 $cm^3/l$ as the temperature falls from 25°C to 15°C.[13] In order to gain an average long-term corrosion rate the depth of graphitisation is divided by the number of years of immersion. There is a linear relationship between the logarithm of the annual mean depth of graphitisation and on-site corrosion potentials, viz.

$$\log C=3.05\,E_{corr}-0.210 \qquad (6)$$

Where $E_{corr}$ is the corrosion potential in volts (vs NHE) and C is the corrosion rate measured in mm/year of immersion. One mm/year is eqivalent to a corrosion current density of $86.1\mu A\,cm^{-2}$. Owing to limited data base there is a significant error associated with the slope of equation 6. Using the relationship between $E_{corr}$ and the corrosion rate in mm/year, a knowledge of the total depth of corrosion and the on-site corrosion potential will enable estimation of the time since the vessel was wrecked, ie, a potentially new dating method for archaeological iron objects!

### Site Management

When an archaeologist is conducting a site survey a knowledge of corrosion potentials, water depth and wave action can help in deciding which objects to raise. For example, a cannon with a lower $E_{corr}$ raised from a deeper part of the site will be less corroded and as a result it will take less time and money to properly conserve and place on display. If it is planned to raise an object in the future it is possible to attach sacrificial anodes to prevent further corrosion and to begin conserving the object in situ. Chloride ions diffuse away from the degraded surface and the pH increases under the influence of the current from the anode, viz.

$$FeCl_2+2FeO.OH+2e^-\rightarrow$$
$$Fe_3O_4+2Cl^-+H_2\uparrow \qquad (7)$$
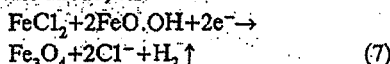
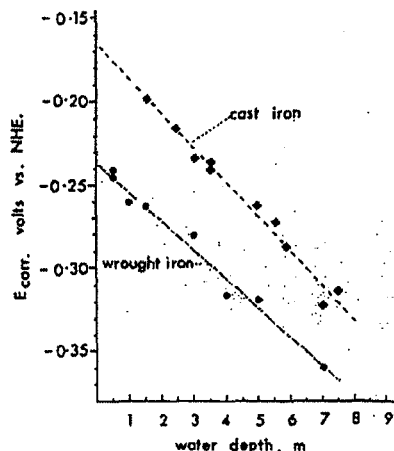One year of pretreatment on the sea bed helped stabilise the normally amorphous corrosion products on an



Figure 3: *Water depth dependence of $E_{corr}$ for wrought and cast iron objects on wreck sites.*

anchor from the "Sirius" so that when the concretion layer was removed large sections of the original wrought surface were still attached. To date this treatment has produced the best preserved anchor from a shipwreck — other anchors from the same site that were not pretreated had much greater surface loss. This method of stabilising corroding iron can be applied to the common problem of "concrete cancer" in reinforced concrete structures.

### Acknowledgements

References

1. N. A. North, in "Conservation of Marine Archaeological Objects", ed C. Pearson, Butterworths, London, 1987, pp 207-232.
2. S. Turgoose, *Studies in Conservation*, 1982, 27, 97.
3. N. A. North, *Int. J. Naut. Arch.*, 1976, 5, 253.
4. I. D. MacLeod, Proceedings of Conference 28, Australasian Corrosion Association, Perth, 1988, paper 2-6-1.
5. J. M. Hunt, in "Petroleum Geochemistry and Geology", W. H. Freeman, San Francisco, 1979, p 178.
6. M. Pourbaix, in "Atlas of Electrochemical Equilibria in Aqueous Solutions", 2nd Ed., NACE, Houston, 1974, p 449.
7. G. Creswell, in "The Oceanography of Norfolk Island and the HMS Sirius Wreck Site", 1989, unpublished report.
8. G. Henderson and M. Stanbury, in "The Sirius — Past and Present", Collins, Sydney, 1988, p 62.
9. I. D. MacLeod, Unpublished Observations.
10. R. N. Adams, "Electrochemistry at Solid Electrodes", Marcel Dekker, New York, 1969.
11. J. B. Farrow, I. M. Ritchie and P. Mangano, *Hydrometallurgy*, 1987, 18, 21.
12. I. D. MacLeod, *Corrosion Australasia*, 1985, 10, 10.
13. "Chemical Oceanography", Vol. 1, 2nd Ed. Eds J. P. Riley and G. Skirrow, Academic Press, New York, 1975, pp 561-2.