

CONSERVATION OF CORRODED CONCRETED IRON

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ABSTRACT Analysis of corrosion phenomena observed on iron objects recovered from historic shipwrecks provides a special insight into the problems of materials performance. Metallographic and chemical analysis of wrought and cast iron has shown that the level of impurities and their non-uniform distribution has marked effects on the corrosion mechanism. Isotopic analysis of the methane formed under marine concretions indicates an inorganic rather than a microbiological pathway. The thickness of marine growth on iron has been shown to be linearly dependent on the amount of phosphorus in the alloy. Sacrificial anodes have been used to effectively stabilize heavily corroded iron covered by dense concretion.

1 INTRODUCTION

Banner headlines announcing a catastrophic failure in materials performance is the living nightmare of many concerned with the erection and maintenance of structures incorporating iron and its alloys. A study of past performance can often provide solutions to contemporary problems. Although a plethora of electrochemical data on corrosion of iron exists, a psychological barrier of inherent suspicion on the side of the novice must be overcome before the results can be accepted and usefully interpreted. Once the problems of equating laboratory experiments with field experience have been reconciled the practitioner needs to consider a range of other parameters before writing a final specification. Factors such as the in-service micro-environment and the level of microbial activity can dramatically affect performance.

The shipwrecks off the Australian coast date back to the *Trial* in 1622 and analysis of iron artefacts can provide invaluable data on the effects of long-term corrosion in natural seawater. Observations on the effects of micro-structure (MacLeod, et al., 1986,88), elemental composition (MacLeod, et al., 1980) and concretion formation (North, 1976; MacLeod, 1982,85) on the corrosion mechanisms on both ferrous and non-ferrous metals have previously been reported. This paper is concerned with three interrelated issues of the effects of impurities on corrosion of wrought and cast iron, the extent of marine colonisation by encrusting organisms and how to stabilize corroded iron in an acidic calcareous micro-environment.

2 WROUGHT IRON METALLOGRAPHY

During excavation of the American China Trader *Rapid* (1811) many hundreds of concreted iron artefacts were recovered. On fracturing the dense semi-permeable marine growth (North, 1976) there were many cases when little or nothing remained of the iron fittings. Typical radii of the round sections were 12.7 ± 3.2 mm and given average long-term corrosion rates of 0.1 mm/year (MacLeod, 1981) the total loss of iron is not surprising. In some cases hooks and chain-plate from the rigging were recovered with very little corrosion having occurred. Whilst it was realised that effects of galvanic corrosion (MacLeod, et al., 1980) may have exacerbated corrosion on some parts of the wreck, the deliberate burning of the vessel after it had foundered (Henderson,

1983) may have caused metallographic changes to occur in parts of the rigging that could have been subjected to several hours of heat treatment at temperatures in the range 700-800°C. Samples of untreated iron from a hook and chain-plate were embedded in polyester casting resins and polished with wet and dry carborundum papers to 1200 grit followed by a series of diamond laps to $\frac{1}{2}$ micron. The principal etchant for revealing microstructure was 5% Nital.

3 CHAIN PLATE

Corrosion during 168 years of immersion in seawater had removed only 30% of the original material (measured by loss in transverse section from original diameter of 25.4mm). This corresponds to a corrosion rate of only 0.013mm/year. The microstructure is built up with angular grains of ferrite which are roughly the same size (approx. 50-60 microns) and there are no traces of cold deformation. There are occasional oxide films at ferritic grain boundaries. There were a large number of inclusions in the metal including some large slag inclusions showing the two-phase structure of FeO dendrites in a $2\text{FeO}\cdot\text{SiO}_2$ matrix. Their shape depends on the direction of working. Since the composition is uniform in transverse and longitudinal sections and there was no trace of plastic deformation, the object was made by hot-working (forging): ingress of salts close to the surface shows up lines of welded joints that have been produced by hot forging. Microhardness measurements (Tukon Model 300 with 500g load) showed uniform values of HV 207 ± 8 for the ferritic grains with values of ranging from 340-370 HV in the inclusions.

4 IRON HOOK

The average depth of corrosion on the wrought metal was 7.2mm or 0.042mm/year. The hook is composed of two different microstructures the compositions of which are listed in table 1. The 0.166 wt% carbon content of the inner zone is reflected in the observed ferrite and pearlite structure. The very low carbon, 0.005 wt%, of the outer zone is consistent with the ferritic surface structure. The metal has a very high purity since there are very few oxide inclusions - those present are more common in the ferritic part of the sample. There are also sporadic two-phase slag inclusions of FeO in the $2\text{FeO}\cdot\text{SiO}_2$ matrix which was probably incorporated during forging. Microhardness measurements on transverse and longitudinal sections show a marked change in going from the ferritic to the ferrite and pearlite microstructure with values increasing from 181 ± 4 HV to a mean value of 258 ± 28 HV - the large scatter of values depends on the precise location of the indenter. Maximum HV values were obtained in areas dominated by pearlite grains. The ferritic zone extended up to 4.5mm into the solid metal. The original structure of the metal was probably formed of ferrite and pearlite and decarburization probably took place during the production of the hook at the shaping stage. Another possible explanation of the loss of carbon could lie in the archaeological evidence of the intense heat resulting from the firing of the oak timbers. The character of the original structure corresponds to the present form of ferritic-pearlitic steel. When the concretion was removed a significant area of both objects was covered with the ferrous phosphate vivienite, $\text{Fe}_3(\text{PO}_4)_2\cdot 8\text{H}_2\text{O}$. The same mineral was found on Roman iron nails recovered from a bog where there was sulphate reducing bacterial activity (Booth, et al., 1962). Heat from the fire may have assisted in the conversion of the 0.13 wt% phosphorous into a form that provided the passivating film.

5 CORROSION MECHANISM

Chemists working underwater can measure the corrosion parameters of iron objects on the seabed several centuries after their inadvertent deposition thereby obtaining invaluable data on long-term corrosion. Potential measurements were made at a number of wreck sites using a high impedance digital multimeter

Table 1
Composition of iron objects recovered from historic shipwrecks (%)

	C	S	Si	Ni	Cu	Mn	P	Cl
<i>Batavia</i> (1629)								
cannon - outer	4.74	0.11	1.52	0.021	0.014	0.335	0.31	1.35
cannon - inner	4.45	0.12	1.45	0.019	0.007	0.330	0.32	1.95
<i>Zuytdorp</i> (1712)								
cannon -	4.3	0.055	0.80	<0.005	0.065	0.115	0.46	0.29
anchor - outer	0.24	0.025	0.25	0.060	0.015	0.10	0.12	0.023
anchor - high	0.08	0.05	0.45	0.125	0.030	0.46	0.50	0.046
anchor - low	0.10	0.05	0.30	0.120	0.030	0.43	0.46	0.051
<i>Sirius</i> (1790)								
cannon - outer	13.4	0.16	3.35	0.040	0.025	0.15	1.20	2.19
cannon - inner	3.5	0.08	0.10	0.015	0.015	0.48	0.57	0.192
anchor - outer	0.25	0.05	0.20	<0.005	0.015	0.090	0.035	1.12
anchor - inner	0.10	0.04	0.10	<0.005	0.015	0.015	0.15	0.612
<i>Rapid</i> (1811)								
hook - outer	0.005	0.004	<0.10	0.011	-	-	0.138	-
hook - inner	0.166	0.004	<0.10	0.012	-	-	0.127	-
<i>Xancho</i> (1872)								
plate -	0.165	0.050	0.36	0.053	0.022	0.022	0.33	0.02
bolt -	0.030	0.010	0.38	0.035	0.048	0.045	0.25	0.02
<i>Europa</i> (1897)								
ball -	4.2	0.20	4.10	0.065	0.010	0.27	1.05	0.066
anchor -	1.15	0.07	2.30	0.020	0.010	0.015	0.22	0.113

Analyses were performed by ANALABS except for the *Rapid* samples which were handled by Resource Development Laboratories.

(Fluke 8010A or 8020A) housed in a perspex box with a robust platinum electrode using Ag/AgCl-seawater as a reference. Measurements of pH were effected with an Orion 91-36 flat surface combination glass electrode after adapting it for pressure equalization across the reference junction. The Crison 506 pH/mV meter was housed in a waterproof box. The results of several hundred measurements (North, 1982; MacLeod, 1981) can be summarised as follows: in the presence of residual metal the pH values underneath the protective concretion layers ranged from 4.8 adjacent to the metal to 8.2 of normal seawater as one traversed the corrosion product-concretion matrix (North, 1976). Corrosion potentials covered the range -0.375 to -0.170 volt vs NHE depending on the degree of oxygenation and the extent of marine growth; the temperature effects have not been directly measured owing to insurmountable practical problems but repeated measurements of the *Xantho* boiler at Port Gregory (MacLeod, et al., 1986) over a period of four years gave an Ecorr of -0.274 ± 0.003 with the temperature at 4 metres depth ranging from 18.5 to 25.0°C. The small variation in Ecorr values indicates that after more than 100 years immersion the objects are not as sensitive to temperature effects as objects at 30 days exposure (Lee, et al., 1984).

The main cathodic reaction in corrosion of iron in oxygenated seawater is the reduction of oxygen. For concreted iron the cathodic oxygen reaction is physically removed from the anodic reaction occurring under the calcareous sheath (North, 1982). Once the acidic micro-environment has been established the alternative cathodic reaction of water reduction becomes increasingly significant. If this reaction is of major importance one would anticipate that hydrogen would be formed and be amongst the gases released when the concretion layer was penetrated by a drill during corrosion potential surveys. With corrosion potentials as low as -0.375 volts at pH 4.8 there is an over-potential of 91mV beyond the standard reduction potential of water at one atmosphere of hydrogen (Pourbaix, 1974). Despite the above data disputes about the nature of the entrapped gas continued (Turgoose, 1985). In an attempt to clarify these issues gas samples were collected from a concreted wrought iron anchor (late nineteenth century) in Bathers' Bay in Fremantle and from a similarly covered cast iron cannon from the *Batavia* (1629). The results of the analyses are shown in Table 2. Apart from the presence of hydrogen the major gas identified was methane.

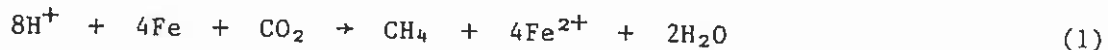
Table 2
Gas and isotope analysis from concreted iron objects

	H ₂	CO ₂	N ₂	CH ₄	δ ¹³ C _{PDB} (‰)*
19th Century anchor	10-15%	20%	balance	50%	-4.7
1629 <i>Batavia</i> cannon	3.9%	-	39.1	57%	-4.7

*The carbon isotope analyses refer to the methane fraction and are calculated from $\delta^{13}\text{C}(\text{‰}) = \frac{(\text{Rs} - \text{Rr})}{\text{Rr}} \times 1000$ where Rr is the ¹³C/¹²C isotope ratio in the PDB limestone standard and Rs is the isotope ratio of the sample (Aharon, 1982).

Since sulphate reducing bacteria (SRB) such as *desulfovibrio salixigens* have recently been positively identified (Barton, 1988) in marine sediments on the wreck of the *Cervantes* (1844) it is essential to establish whether the methane is the result of bacterial activity. The influence of SRB's on anaerobic iron corrosion has been recently reviewed by Pankhania (1988) and their utilisation of cathodic hydrogen by Hardy (1983). A recent report by Daniels, et al., (1987)

discusses the effects of methanogenic bacteria on the corrosion of iron through reactions such as



Their work indicated that the bacteria cause cathodic depolarization with the bacteria consuming adsorbed hydrogen on the surface or the free hydrogen gas. During biological production of methane the bacteria preferentially use ^{12}C and isotope shifts are typically -55 to -75‰ relative to PDB (Hunt, 1979).

Inspection of the data in table 2 shows that the $\delta^{13}\text{C}$ value of the methane trapped under the concretion was -4.7 ppt and so it was not derived from a bacterial source (Aharon, 1982). Methanogenic bacteria are strict anaerobes requiring Eh values less than -0.330 volts vs hydrogen (Winfrey, 1984). The most commonly encountered values of iron corrosion potentials have a mean of -0.290 ± 0.015 V which is not sufficiently reducing for the methanogenic species. Very low values of Ecorr at -375 mV vs NHE are generally found when there is virtually no interstitial water left in the corrosion zone.

The recent recovery of a cast iron cannon from the wreck of the *Zuytdorp* (1712) has provided large volumes of liquid representing the concreted micro-environment. On removing the tampion (the wooden plug sealing the loaded cannon) a large volume of gas escaped and 2.5 litres of a pale green solution was recovered. The dissolved oxygen levels read 0.0ppm and the redox potential was -0.193 volt at a pH of 5.5. The chloride concentration was 54,179ppm (1.54 M) which is 2.7 times higher than the chlorinity at the site. For the oxidation of ferrous ions to magnetite,



the observed voltage corresponds to a ferrous ion activity of 0.26 M. Given that the chloride concentration is sufficient for a 0.77 M FeCl_2 solution an apparent activity of 0.26 M is not unexpected. The tampion effectively sealed the 15 litre volume of the cannon bore since the 2.5 litres of liquid relates to the compression factor due to the height of the water column above the cannon on the wreck site. The touch-hole was sealed with corrosion products and concretion which in effect gave a very large crevice, some 2.5 metres long! These observations confirm that the major corrosion product under such concretions is ferrous chloride.

Inspection of the Pourbaix diagram for carbon (Pourbaix, 1974) shows that the range of Eh and pH found under marine concretions on corroding iron objects covers the thermodynamic stability range of carbon dioxide, carbon and methane which is consistent with our $\delta^{13}\text{C}$ values for methane. As the ferrous ions hydrolyse and are oxidized (equation 2) the hydrogen ions will dissolve some of the calcareous matrix and liberate CO_2 which can react with the cathodic hydrogen to form methane.

6 MARINE GROWTH: EFFECTS OF PHOSPHORUS

As part of our programme of assessing materials performance, the composition of a number of iron objects ranging from 1629 to 1897 was determined to see what effect the varying levels of impurities had on corrosion phenomena. In their classic study of wrought iron corrosion, Chilton and Evans (1955) showed that marked differences in the corrosion rates could be understood in terms of the distribution of sulphur, copper and nickel in the "bands" of wrought iron. The lower level of phosphorus, nickel and sulphur in the remaining "original surface" on the *Zuytdorp* anchor (see Table 1) is an example of these "zoning" reactions. Cannon from *Batavia* and *Sirius* with very high silica levels have been shown to be very prone to being chipped during service and on the seabed before the

protective concretion layer is formed. The well preserved iron rigging from the *Rapid* was found with a passivating film of vivianite $[\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}]$ under the layers of marine growth. Although phosphorus is known to have a deleterious effect on the corrosion of iron in environments ranging from acidic sulphide to sulphate and synthetic seawater, the effects are dependent on the oxidation state, i.e., aggressive as iron phosphide (Fe_2P) but can be passivating as a phosphate film (Riecke, et al., 1987). Kupper, et al., (1981) showed that regardless of whether phosphorus is present in solid solution or at grain boundaries, it will prevent passivation of iron if its local concentration is higher than 2-3 at. %.

Given that the pungent odour of corroded iron is reminiscent of organophosphines and organosulphur compounds (apart from the H_2S) it was decided to see if there was any correlation between phosphorus content and the amount of concretion. The average thickness of marine growth on the objects listed in table 1 was measured either directly from samples or from accurate photographs. Once rapid growth of the initial colonization period has covered the object it was reasoned that a "steady state" of growth could describe the build-up of the dense calcareous matrix. The total thickness was divided by the number of years of immersion and plotted against the phosphorus content and the results are shown in figure 1. The ten data points have a linear correlation coefficient of 0.9966 and it conforms to the equation

$$T = 0.0639 P + 0.076 \quad (3)$$

where T is the thickness in mm/year and P the wt% phosphorus. The non-zero intercept shows that apart from phosphorus promoting marine growth, iron itself stimulates the colonizing organisms.

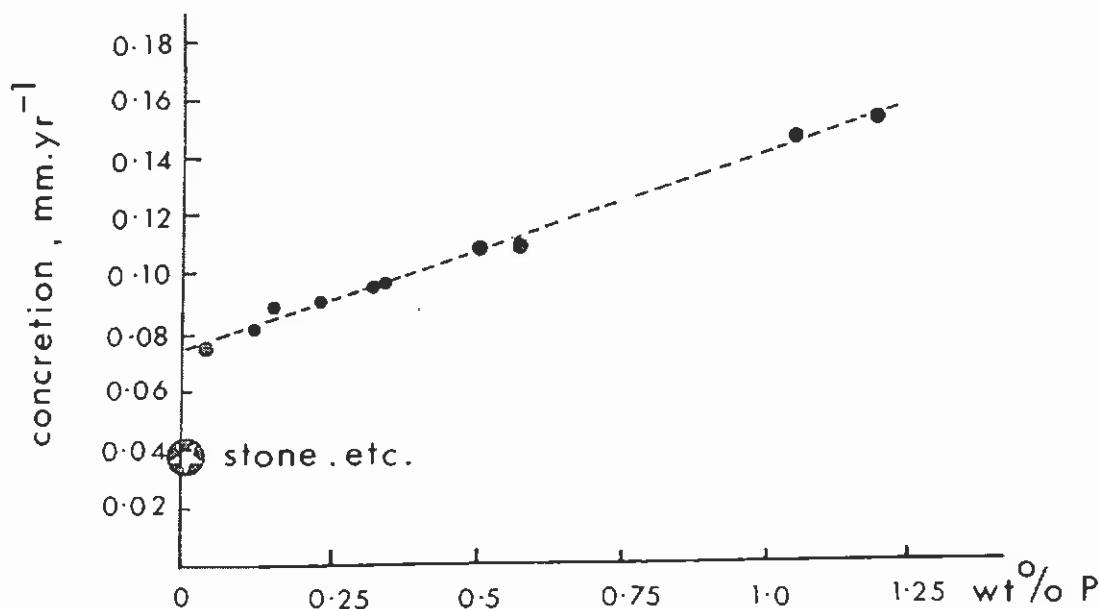


Fig. 1: Effect of phosphorus on the rate of concretion formation on marine growth.

Since both iron and phosphorus are essential nutrients the results are not totally unexpected. At the zero phosphorus level the values of maximum concretion thickness on stone, ceramic and other inert shipwreck materials has a mean value of 0.038 ± 0.005 mm/year. In other words, the presence of iron in the seawater environment effectively doubles the standard growth rate of 2-6.6

encrusting organisms. Recent work by Iverson, et al. (1983) has shown the presence of a volatile highly reactive phosphorus compound during anaerobic corrosion enhanced by sulphate reducing bacteria. This work also confirmed the presence of methyl mercaptan and dimethyldisulphide in such environments. Although we have not yet established the nature of the volatile phosphorus compound it apparently exerts a major influence on marine growth. Apart from phosphorus making steel prone to intergranular stress cracking (Krautschick, et al., 1988) the increased strain on offshore structures is perhaps even of greater design significance.

7 CONSERVATION OF CONCRETED IRON

The micro-environment existing under the concretion permits corrosion to proceed at a steady rate. We have applied sacrificial anodes in-situ to the wreck of the *Xantho* and to the *Batavia* iron cannon in a fresh water tank. After nine months protection of the stern by two 20kg zinc anodes, the surface pH under the concretion has been increased from 4.8 to values ranging from 6.4 to 6.8. Apart from reducing the acidity level the corrosion potential was lowered by 120 mV - outward migration of the chlorides under the influence of the cathodic current will assist in the overall stabilization of the stern section prior to excavation. The *Batavia* cannon was placed in a concrete tank and connected to a 20kg A3 aluminium anode via a copper cable welded to a modified insulated G clamp. The anode provided a current density between 50 and 35 mA/m² which is normally sufficient to protect marine iron (Fischer, 1983) from corrosion. The corrosion potential of the cannon was -0.420 ± 0.020 volt compared with -0.260 volt (NHE) before connecting the anode.

After 100 days the tank was drained and a pH profile taken after 826 grams of chloride had diffused out through the 34mm thick concretion layer. The results showed a change in pH from 4.9 to 7.45, i.e., the cannon micro-environment was shifting from an aggressive to a more benign/passivating regime. During seven-teen months of treatment the 3.5m long cannon released a total of 1.93kg of chloride into the wash solution. Having demonstrated that a highly reactive iron object could be stabilized by cathodic protection without resource to soaking in caustic solutions, the concretion was removed. The depth of graphitization in areas exposed on the site fourteen years ago was 42.3mm or an average rate of 0.118mm/year. The main point to be noted is that the anode was able to cause chlorides to diffuse away at the rate of approximately $0.87 \text{mg.cm}^{-2}.\text{hr}^{-\frac{1}{2}}$ or 8.7 grams of chloride for every square metre per hour^{1/2}. These quantitative results show that iron corroding in a high chloride environment (up to 2 wt%) under a very dense and thick calcareous matrix, can be stabilized with relative ease.

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