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IN SITU CONSERVATION OF CANNON AND ANCHORS ON SHIPWRECK SITES

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ABSTRACT

A wrought iron anchor and a cast iron carronade from the wreck of HMS *Sirius* (1790) received *in situ* electrolysis treatment using sacrificial anodes in the shallow waters off Norfolk Island in the South Pacific Ocean. This pre-treatment stabilizes the artifacts and ensures that they can be safely recovered and transported. Monitoring on the seabed and in the laboratory showed that approximately 80% of the chlorides had been removed from the carronade before excavation. The cathodic pre-treatment results in a significant improvement in the quality of the surface of the metals. It is possible to maintain artifacts on the seabed by continued use of sacrificial anodes.

INTRODUCTION

Twenty years ago the normal maritime archaeological practice was to excavate a site totally and treat all the artifacts, and restore some of them for exhibition purposes. This practice prevented looting but resulted in thousands of objects requiring extensive and expensive conservation treatments [1]. Currently the emphasis is on minimum intervention, site stabilization, documentation and limited excavation to provide characterization of the wreck. Electrochemical surveys have become an essential part of characterization and documentation of the nature of the site. The data obtained on corrosion rates can be used to quantify the energy state [2, 3].

Metal artifacts and their corrosion products can provide a unique record of the physical history of the site. From analysis of the varying depths of corrosion on the 13 cannon recovered from the wrecks of the *Rapid* (1811) and the *Lively* (c. 1820), it is clear that the extent of corrosion can easily vary by one order of magnitude across the site [4]. Part of the reasoning behind total recovery of the ordnance was that conclusive evidence of the nature of the wreck would be provided by ciphers on the guns. Only one cannon, on the American China Trader *Rapid*, bore a cipher: that of GIIIR of England!

Since corrosion is an electrochemical process, the rate of decay of a concreted iron artifact [5] is dependent on the voltage of the metal, the amount of dissolved oxygen, the salinity of the water and the amount of water movement. The voltage of the corrosion cell is a mixture of the potentials associated with the rates of the oxidation reaction (corrosion of iron) and the reduction of oxygen on the surface of the object. The voltage of the corrosion cell of the concreted iron object resting in seawater is called the corrosion potential (E_{corr}). Direct measurements of the corrosion potentials and the *in situ* pH of concreted iron objects have shown that the two factors are interrelated [6]. The net effect of hundreds of years of corrosion on cast iron artifacts can be measured from the depth of graphitization (d) of the metal. This measurement can easily be made in conjunction with the routine measurement of E_{corr} and pH by drilling directly into the corroded metal until solid hard cast iron is reached and correcting the penetration depth for the concretion thickness. Based on our current understanding of the way in which E_{corr} and the corrosion rates are related, it would now be possible to use the *in situ* data from the *Lively* cannon to determine which object(s) should be raised.

In situ studies on the Cromwellian wreck *Swan* (1653) off the west coast of Scotland have quantified the effect of recent site disturbances on the deterioration of the artifacts [6]. The electrochemical data have provided the maritime archaeologist with a clear picture of which objects are most degraded and which are most at risk of deterioration. Despite all these advances, the problem of transporting massive, extensively corroded, chemically

reactive and fragile artifacts thousands of kilometres to the laboratory demanded a solution. The solution has been found by using *in situ* cathodic protection from sacrificial anodes to treat the object prior to excavation.

CORROSION MECHANISMS FOR CONCRETED MARINE IRON OBJECTS

Within a decade of immersion, the microenvironment adjacent to iron artifacts becomes significantly more acidic and chloride-rich than the surrounding seawater [5]. The increased acidity is due to hydrolysis of metal ions which reaches a quasi-equilibrium state that is commensurate with the average long-term corrosion rate [6]. The inherent stability of iron artifacts on a site can be gauged from the location of the pH and E_{corr} data on a Pourbaix diagram [7, 8]. These diagrams place the artifact in either an active corrosion zone, a region of immunity from corrosion or a zone where the material is still corroding but in a 'passive' state. Measurements of iron fittings over several seasons on the SS *Xantho* (1872) site have shown that the E_{corr} data are surprisingly reproducible. In the absence of changes in site conditions, the value of the corrosion potential is within 3mV of the previous reading [9].

In the warm sub-tropical waters of Australia, the corrosion potential of an iron artifact is related to the long-term rate of deterioration via the relationship:

$$\log_{10} d_g = 3.05 E_{\text{corr}} - 0.210 \quad (1)$$

where d_g is the annualized corrosion rate in mm.yr⁻¹. The value of d_g is obtained by dividing the depth of graphitization (d) by the number of years of immersion [10]. The slope of equation (1) is dependent on the logarithm of the dissolved oxygen concentration which is interdependent on the temperature and salinity [6, 11]. The dominance of dissolved oxygen in the corrosion process is supported by laboratory experiments on a concreted diving knife, which had been lost 10 years ago on the *Xantho* site. The slope of plots of \log_i against E_{corr} in normal seawater was $3.06 \pm 0.05 \text{ volt}^{-1}$ which is the same as that observed on the aerated shipwreck sites. The physical protrusion of an object on a wreck site is of major importance in determining the flux of dissolved oxygen and hence the corrosion rate.

SACRIFICIAL ANODES AND *IN SITU* TREATMENT OF IRON ARTIFACTS

The HMS Sirius bower anchor

The excavation of the best bower anchor (SI 57) from HMS *Sirius* resulted in the loss of a section of concretion from the shank. The increased corrosion rate was monitored via measurement of the E_{corr} for four days. Within two hours of excavation the exposed part of the shank was covered with a lepidocrocite (γFeOOH) film, despite being kept underwater. Owing to the lack of any suitable treatment facility on Norfolk Island, it was decided to attach a sacrificial anode to the anchor in order minimize further damage. The problem of increased oxygen access to the corroding metal was overcome within minutes of attaching the anode, as shown by the corrosion potential falling to typical pre-disturbance values. After a year of receiving cathodic current from the corroding anode, the area of concretion loss was covered by a calcareous scum [12]. A maximum current of 500 mA.m^{-2} , based on the 7kg loss of anode material, was provided to the anchor, which is more than twice the amount needed to provide complete cathodic protection [13]. The E_{corr} at the end

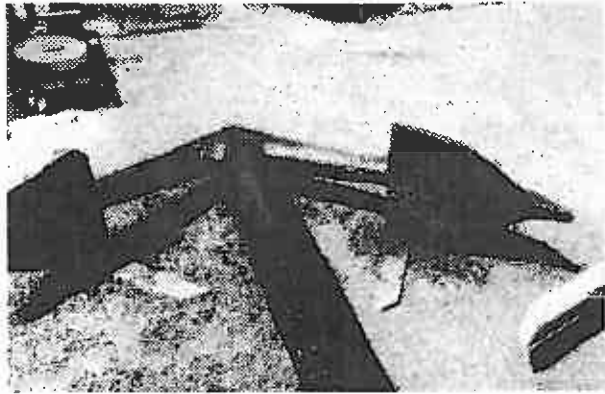
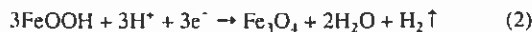


Fig. 1 HMS *Sirius* best bower anchor after completion of *in situ* and laboratory electrolysis.

of the treatment programme was -0.430 volts vs the normal hydrogen electrode (NHE), which equates to a pH of 7.43, assuming the surface is in equilibrium with hydrogen. This is supported by the fact that copious amounts of hydrogen escaped when the concrete was cracked at the end of the treatment programme. Unfortunately no pre-disturbance measurements of pH were possible, owing to extremely rough conditions, so the final pH can only be compared with that of another anchor. The increase from pH 5.6 to 7.4 is indicative of a reduced rate of corrosion. The other principal effect of the cathodic current is that chloride ions will diffuse through the concrete into the surrounding seawater [14].

After traditional gentle electrolysis treatment in sodium hydroxide solutions for two and a half years, the anchor was seen to have retained large areas of the original surface [8, 15]. The normally encountered friable surface that characterizes the zonal corrosion of the wrought iron [16] was replaced by a solid but fragile matrix. The best-preserved surfaces were on the palms, the crown and the lower section of the shank. All these areas had suffered no damage to the concrete during the excavation process (Fig. 1). The electrochemical reduction of iron(III) corrosion products to form magnetite and hydrogen during the *in situ* electrolysis according to the equation:



may be one of the main reactions that takes place under the concrete layer. In the absence of corrosion and under the influence of the cathodic current, chloride ions will diffuse out of the matrix. Since acid from metal ion hydrolysis has dissolved some of the original layers of concreted calcium carbonate, the reduction in acidity will tend to promote redeposition of calcium/magnesium carbonates (magnesium calcites) and the deposition of the iron carbonate, siderite (FeCO_3). The net result of the treatment is that the original slag inclusions are retained in a complex matrix which results in replication of surface detail such as manufacturing stamps. The one year of pre-treatment was equivalent to one year of land-based treatment.

HMS *Sirius* carronade

After the success of the treatment of the anchor it was decided to see if a similar approach would work on the second *Sirius* car-

Table 1 Corrosion parameters for the carronade SI 626

Date	E_{corr} volts vs NHE	pH	Condition
15/10/88	-0.240	5.82	pre-disturbance
24/10/88	-0.379	—	anode attached
20/03/90	-0.300	7.16	anode lost
26/03/93	-0.485	8.19 _{calc}	anode attached

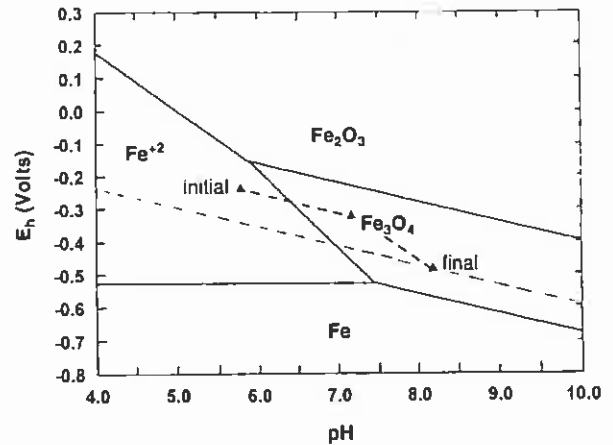


Fig. 2 Pourbaix diagram showing the corrosion potentials and pH values of the carronade during *in situ* treatment on Norfolk Island, for chloride concentration 2.5M and iron 1×10^{-4} M.

ronade (SI 626) [17]. Through a combination of pre-disturbance data and data obtained during three other visits, it was possible to monitor the treatment for three and a half years. This provided a much clearer understanding of the changes that occur during seabed electrolysis. The initial measurements showed that the gun was in a highly corrosive microenvironment; this was due to its location in 1.5m of water in the full surf zone on top of the reef platform. The changes in the values of E_{corr} and the pH of the carronade are listed in Table 1 and illustrated on the Pourbaix diagram in Figure 2. The shift of 140mV in the value of E_{corr} towards more negative potentials showed that good electrical contact had been made and that the cathodic current was flowing into the carronade. It was necessary to replace the first anode because a violent storm, which moved a 1.5-tonne concrete plinth several hundred metres across the seabed [18], ripped the first anode from the carronade.

The necessary fittings for the new anode bracket were fabricated at the Works Depot on Norfolk Island and attached in March 1990 (Fig. 3). The corrosion potential and pH data indicated that some lasting improvement had taken place during the six months that the first anode remained attached. The 60mV fall in E_{corr} is equivalent to a drop in corrosion rate of 34% but despite this the carronade was still in the active corrosion region of the Pourbaix diagram and further treatment was needed. After a further three years of cathodic protection the carronade was excavated from the depression in the reef and freed from the encapsulating coral. During the excavation process some of the concrete was accidentally dislodged from the breech end at the casable. Despite this direct exposure to oxygenated seawater



Fig. 3 HMS *Sirius* wreck site showing the bracket being bolted to the concreted carronade: the anode lies to the right of the gun.

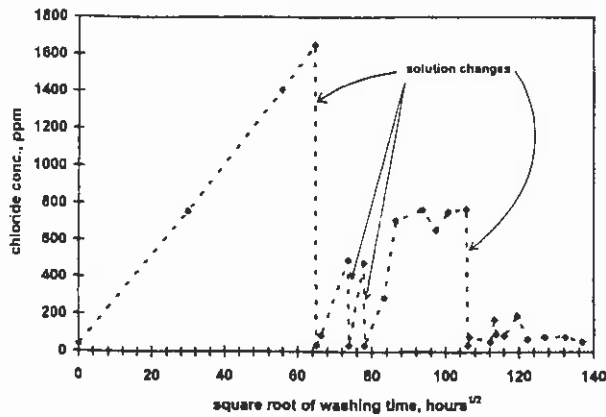


Fig. 4 Chloride concentration as a function of treatment time in sodium hydroxide solutions.

there was no sign of flash rusting during the final four days of excavation work. This indicated clearly that the carronade had undergone significant stabilization. Although the final E_{corr} was measured, a sudden deterioration in site conditions precluded recording of the pH. If the pH is in equilibrium with hydrogen at the same voltage as the corrosion potential, it can be seen that the calculated final pH of 8.2 is the same as that of the surrounding seawater. This indicates that the treatment was essentially complete. During the excavation, large volumes of gas evolved from small fissures in the concretion layer; this is consistent with the discussion regarding hydrogen evolution. Both the alkalinity and the lowered chloride content of the metal increase the degree of safety associated with the excavation.

During land-based treatment, the 1wt% caustic solutions were regularly analysed for chloride ions. Plots of the chloride concentration against the square root of time are linear, as expected for diffusion-controlled processes (Fig. 4). A small aluminium-alloy engine block provided the cathodic current for the first six months; typical data were a pH of 12.3 and an E_{corr} of -0.632 volts. Eight months after recovery the carronade was deconcreted. This revealed a wooden tompon which had kept the bore sealed for 200 years (Fig. 5). The inner surface of the tompon was covered with a brown waxy-oily layer that contained elemental sulphur which had probably come from gunpowder residues. A massive ball of wadding was attached by a rope to the tompon; the organic materials were quickly treated with neutral citrate solutions to prevent damage due to oxidation and precipitation of iron corrosion products [19].

The total amount of chloride removed from the carronade was 4.22kg and this small amount clearly indicates that a significant mass of chloride had been removed during the *in situ* treatment. Since it was impossible to determine directly the initial amount of chloride removed, it is necessary to resort to a series of comparative measurements in order to estimate the efficiency of the treatment. The first method involves a comparison of the composition of the *Sirius* bore solution and that from a similarly plugged gun from the wreck of the *Zuytdorp* (1712). The chloride ion concentration of the 1.25 litres of bore solution trapped by the tompon gave a concentration of 8366ppm, which is less than half the amount found in the local seawater. This indicates clearly that chloride ions had diffused through the concretion out into the sea. Given that the *Sirius* gun had corroded for only 200 years, compared with 275 years for the *Zuytdorp*, the initial chloride content of 54,593ppm found inside the bore may have been as high as $54,593 \times 200/275$, or some 39,704ppm. This indicates that the pre-treatment reduced the chloride levels in the bore solution by 78.9% during the time on the seabed.

A second way of estimating the amount of chloride released is

to compare the mass losses of the two *Sirius* carronades. The first carronade (SI 58) suffered a weight loss of 26.88% with a corrosion depth of 25mm while the second carronade lost only 20.7% but had a much greater depth of corrosion (39.5mm). Since the guns have the same shape it is reasonable to assume that, with an open bore, the mass loss from corrosion should be related directly to the depth of corrosion. After correcting for the five years longer immersion of the second gun, the calculated mass loss might have been expected to be $200/195 \times 39.5/25\text{mm} \times 26.8\text{wt}\%$, or 43.4%. This figure may seem extraordinarily high, but a cast-iron ballast pig, from the same part of the wreck site as the second carronade, lost 57.9% of its weight for a d value of 35.5mm. Another ballast pig with a corrosion depth of only 27.6mm lost 43.8% of its original weight. Given that the exposed surface area of the sealed carronade is two-thirds that of the open-ended SI 58, the actual weight loss represents a reduction by a factor of 2.12 from the calculated value for SI 626.

It is possible to use this same reduction factor to estimate the amount of chloride ions in the carronade before treatment began. From the known depth of graphitization, d , the number of kilograms of chloride that are expected to be released during electrolysis in caustic solutions [4] is given by equation (3):

$$\Sigma \text{Cl}_{\text{kg}} = 0.0367d^2 + 2.61 \quad (3)$$

The second carronade would have been expected to release 59.87kg if it had corroded with an open-ended muzzle. Application of the reduction factor of 2.12 reduces the expected amount to 28.24kg. Since the total amount of chloride extracted during the land-based treatment was 4.2kg, it can be estimated that the other 24kg or 85% had been released during seabed treatment. This value compares favourably with the figure of 78.9%



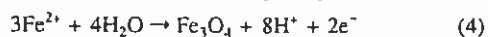
Fig. 5 Wooden tompon recovered from the muzzle of the *Sirius* carronade at the mouth of the gun.

which was based on the analysis of the trapped bore water. Given that the results from both methods of estimating the original chloride content of the carronade are in good agreement, it is reasonable to assume that something in the order of 80% of the chlorides were removed before excavation.

At the beginning of the laboratory electrolysis of the deconcreted carronade, the surface chloride concentration was measured using an Orion chloride ion electrode in conjunction with a Ag/AgCl double-junction reference electrode. Typical surface chloride activity measurements on freshly exposed marine iron artifacts are in the order of 40,000ppm chloride [20] whereas the value for the surface under the concretion layer was 4,100ppm. This value fell to only 0.4ppm at the end of the two years of electrolysis. This low level of chloride activity indicated that the treatment was finished. The low chloride ion activity and the stability of the carronade all pointed to the fact that significant stabilization had occurred on the seabed. The cathodic pre-treatment left behind a very clean graphitized metal surface which was very porous. A total of 13.9 litres of microcrystalline wax was absorbed by the gun during the two days in the molten wax tank. Based on a displacement volume of 51.05 litres and a mass of 350.8kg, the carronade had an average density of 6.87g.cm⁻³. The fall in density from 7.3g.cm⁻³ is commensurate with the porosity observed. The pre-treatment ensured that a finely engraved sight on the tiller was preserved. This area of the gun was lost during deconcretion of the first carronade (SI 67). The centreline of the sight is approximately 2° to the left of the midline of the gun. This deviation is apparently a small correction for accurate firing.

CORROSION PHENOMENA ON THE SIRIUS CARRONADE

The anaerobic nature of the liquid trapped behind the tompon was confirmed by the evolution of a mixture of hydrogen and methane when the touch-hole concretion was penetrated. Although the solution was analysed within a few minutes of excavating the tompon there had been some ingress of oxygen, since the E_h was -0.341 vs NHE. The slightly alkaline pH of 7.58 is consistent with some ingress of the caustic wash solution after the touch-hole was cleared. Analysis of the major solid phase in the rope attached to the tompon showed it was magnetite (Fe₃O₄) which would have been formed according to equation (4):



The presence of sea urchins (*Heliocidaris tuberculata*) played a significant part in accelerating the corrosion of the carronade. By burrowing through the concretion and into the metal the marine organisms had left semicircular depressions up to 12mm deep in the surface (Fig. 6). During the corrosion survey it was noted that this form of attack was relatively common; the worst

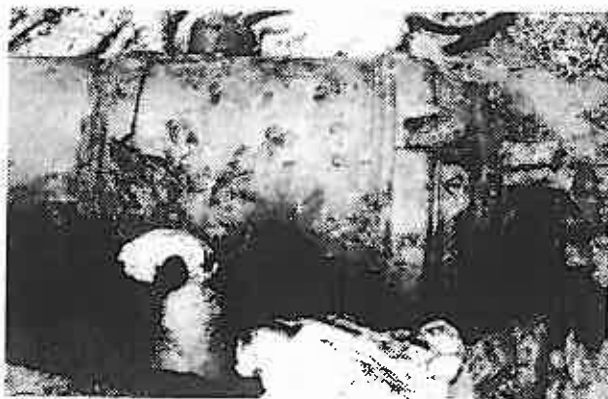


Fig. 6 The damage to the carronade from attack by sea urchins is the white depression just above the trunnion.

case was found with the pig SI 53. Plotting the E_{corr} and d_g values for these two objects places them above the average corrosion rates given by equation (1). The line joining these two data points has the same slope as equation (1) but the intercept value on the $\log d_g$ plot is 0.227 greater than the average. The difference is equivalent to an increased corrosion rate 70% above the normal levels. It is possible that the sea urchins are being attracted by the release of phosphines which are a by-product of anaerobic bacterial corrosion of iron phosphides [7, 21]. Chemical analysis of the second carronade showed a relatively high phosphorus content of 0.86%, which also explains the 32mm thickness of the concretion.

CONCLUSION

One year of pre-treatment by sacrificial anodes has resulted in the only recorded case of retention of parts of the original surface on a wrought iron anchor recovered from an historic shipwreck site. The second *Sirius* carronade was recovered in a remarkably fine state of preservation after more than three years of *in situ* treatment. At the time of excavation the cathodic current from the anodes had removed approximately 80% of the chloride ions. The use of sacrificial anodes not only improves the final quality of the object but also minimizes the risk of damage during recovery. The total desalination time is not diminished but the *in situ* treatment is equivalent to normal laboratory electrolysis. This results in greatly reduced intervals between excavation and exhibition.

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