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The application of corrosion science to the management of maritime archaeological sites

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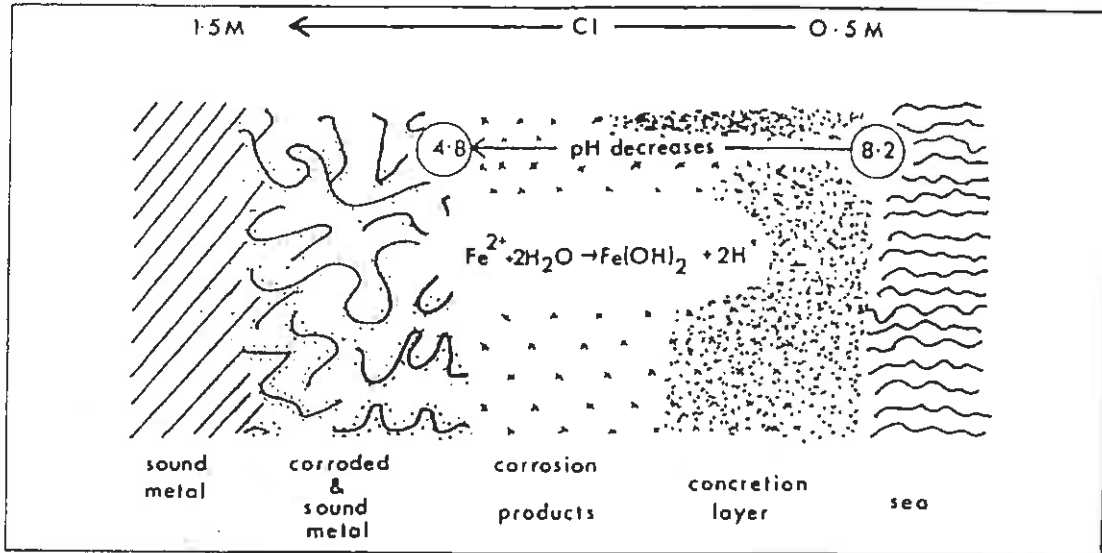


Figure 1. Schematic diagram showing the micro-environment that develops for an iron artefact covered by concretion after many years in the sea

Introduction

The routine measurement of electrochemical parameters such as the surface pH of degrading artefacts and the corrosion potential of metal objects on wreck sites has a very recent history. Following the early work on the *Rapid* (1811) conservators have found that the knowledge obtained through these on-site measurements is an invaluable aid in understanding the corrosion mechanisms and the modes of deterioration of materials on archaeological sites. The significance of this work has only recently been re-assessed and shown to be a very powerful tool not only in determining what has occurred over the past centuries on a maritime archaeological site but also by providing the practitioner with a rational and non-destructive form of assessment of the inherent archaeological potential of metal objects that are displayed on a wreck site.

Introduction to electrochemistry

The determination of corrosion potentials is effected by reading the voltage recorded by a digital voltmeter housed in its waterproof case. The measured voltage refers to the difference in electrical potential of a reference electrode, such as a silver chloride electrode in sea water, and a working electrode such as platinum. Platinum is used because it is electrochemically inert and it does not corrode in sea water and therefore the measured voltages refer to the object itself and are not part of the nature of the experimental apparatus.

When we look at the basic construction of a concreted artefact on the sea bed as shown in Figure 1, we see

that after many years of immersion, an acidic and chloride-rich micro-environment is established in which the corroding metal object is placed. The acidity results from hydrolysis of metal ions and as corrosion proceeds chloride ions from the surrounding sea water diffuse through the marine growth and corrosion products to the corroded metal interface to achieve electrical neutrality of the corrosion products. Corrosion potential measurements are made by drilling through the marine growth, more recently with the aid of a compressed air-driven drill with a masonry bit, and then placing the platinum electrode adjacent to the point of measurement, and reading the voltage. Correct determination of the corrosion potential is normally indicated by the obtaining of a very steady voltage, i.e. a reading that varies by only 1 to 2 millivolts over several minutes.

The significance of the corrosion potential (E_{corr}) can be seen in the diagram in Figure 2 which shows the relationship between the voltage of the oxidation/reduction processes and the logarithm of the rate of oxidation of the iron metal and the log of the rate of reduction of oxygen dissolved in the sea water. Most metals have a brief period of linear response of current with applied potential (Ohm's law), but gradually the corrosion current exhibits a linear logarithmic relationship with the applied potential as is seen in Figure 2. For an iron artefact covered with concretion and lying proud of the sea-bed the anodic current is due to the oxidation of iron to ferrous ions, i.e. $Fe \rightarrow Fe^{2+} + 2e^-$. The cathodic reaction is controlled by the rate at which oxygen will accept

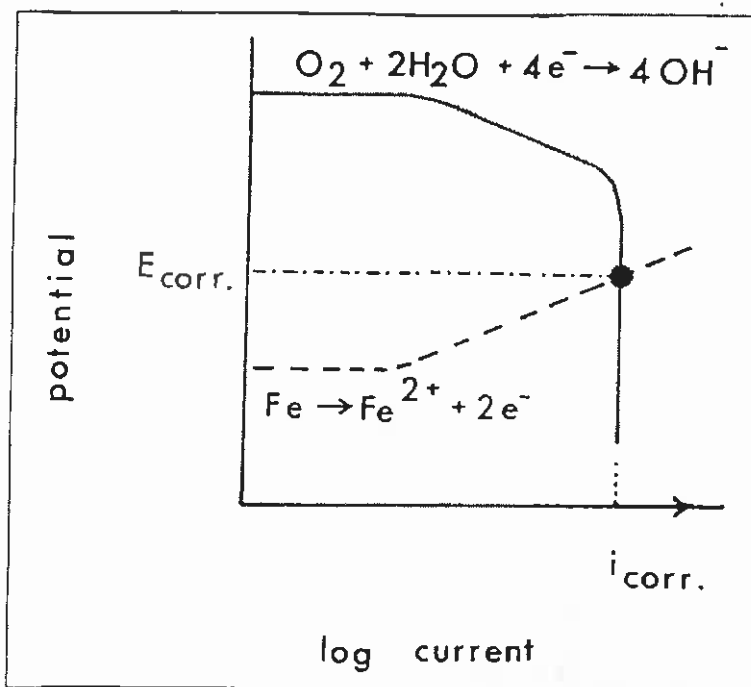


Figure 2. Diagram showing the relationship between the corrosion rate (i_{corr}), the voltage, the individual components of the oxidation and reduction reactions and the observed value of the corrosion potential, E_{corr} .

electrons to produce the hydroxide ion. The rate of this reaction is largely determined by the rate at which the oxygen dissolved in the solution can diffuse to the corroding interface.

The typical variation of corrosion potential and pH with depth of concretion is shown in the Pourbaix diagram in Figure 3. Pourbaix diagrams are thermodynamic stability maps which show whether a metal is in an active, passive (slow rate), or immune region with regard to corrosion. In the outer zones, where the corrosion products are typically red-brown, the potential is essentially a redox couple measuring the ratio of Fe^{3+} to Fe^{2+} ions whereas once we get electrical contact with the metal itself the voltage is the true corrosion potential.

The data for Figure 3 was obtained from a cannon on the wreck of the *Rapid*; it should be noted that the colour of the concretion which relates to the nature of the corrosion products also relates to thermodynamically observable and measurable parameters. It should be stressed, however, that the corrosion potential is not a true thermodynamic function in that it is essentially a kinetic one for it reflects a non-equilibrium situation, but one that is for our purposes a dynamic equilibrium. The primary corrosion product occurring underneath the concretion has, after many years of controversy and research, been established as ferrous chloride. Ferrous chloride subsequently undergoes hydrolysis to β ($\text{Fe}(\text{OH})_2 \cdot \text{FeCl}_2$). As the ferrous chloride solution diffuses out through the concretion matrix and undergoes hydrolysis the resultant increase in acidity causes the dissolution of the calcium carbonate in the marine organisms. Re-precipitation of iron carbonate follows with concomitant oxidation of the iron (II) corrosion products to iron (III).

Sacrificial anodes, corrosion potentials and conservation of artefacts

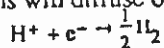
In March 1985 the best bower anchor of HMS *Sirius* was raised from the wreck site and brought alongside the Kingston jetty on Norfolk Island. A small section of concretion, approximately 50 cm x 10 cm, had come away as the anchor left the seabed. Within two hours the exposed part of the shank was covered with a red-brown iron (III) oxy-hydroxide film. Corrosion potential measurements on the anchor showed that the corrosion rate had increased significantly from its predisturbance value. Monitoring continued for 96 hours until the corrosion potential (E_{corr}) eventually plateaued at -0.340 volts vs AgCl. The positive shift of 240 mV in E_{corr} corresponds to a shift in corrosion rate from approximately 0.1 mm/year to 10 mm/year! Given that no commercial sacrificial anodes were available on Norfolk Island we improvised and attached 30 kg of aluminium-magnesium alloy engine blocks to the anchor using heavy gauge copper cable. Within a few minutes the E_{corr} value had fallen to its predisturbance value as shown in the Pourbaix diagram in Figure 3 (MacLeod, 1987). Measurements on the anchor showed that although it was in an active corrosion zone, the corrosion rate was greatly reduced. Less negative (more positive) values of E_{corr} reflect faster corrosion rates for base metals such as iron.

The anchor was left in shallow water which was well oxygenated by the surge and wave action. The warm sea water ($20.8 \pm 2.0^\circ\text{C}$) and salinity of 35.77 ± 0.04 ppt meant that the aluminium should corrode at a rapid rate and provide the necessary current. Chloride ions break down the normally protective layer on the aluminium alloy and assist in the corrosion process. The anchor was left in this state until the treatment tank was built.

TABLE I
Composition of Sirius Anchor, weight %

	C	S	Si	Ni	Cu	Mn	P	Cl
outer layer	0.25	0.05	0.20	<0.005	0.015	0.090	0.035	1.12
inner zone	0.10	0.04	0.10	<0.005	0.015	0.015	0.15	0.61

Inspection after one year of cathodic protection showed that the "scar" on the shank had healed and that the copper cable was also covered with a white calcareous layer. The anode had lost half of its weight and the corrosion potential of the anchor at -700 mV vs AgCl was 120 mV more negative than its predisturbance value, which shows that it had been effectively protected from any corrosion during the year in the sea by the pier. Although no surface pH measurements were made, the E_{corr} was -0.43 volts vs the Standard Hydrogen Electrode (SHE) and the pH was calculated as 7.43, assuming that hydrogen gas is in equilibrium with the acidity of the solution. This pH represents a reduction in acidity by a factor of more than four hundred during the year of cathodic protection. On breaking the concretion seal copious amounts of gas were released which is not unexpected considering the reduction of acidity, for as the electrons flow into the concreted anchor hydrogen ions will be reduced to hydrogen gas and the chloride ions will diffuse out, viz:



Recent work on a concreted iron cannon from the *Batavia* (1629) has shown that chloride ions diffuse out from the dense concretion under the influence of the electrical current flowing from the sacrificial anode at rates up to $8.7 \text{ g m}^{-2} \text{ hr}^{-1/2}$ (MacLeod, 1988). Based on a net consumption of 7 kg of aluminium, the approximate current density delivered by the engine block anode to the anchor was of the order 150 mA.m^{-2} which will protect iron metal from corrosion in the marine environment (Fischer, 1983: 110).

The anchor was deconcreted and electrolysed in a 2 wt% sodium hydroxide, the details of the procedure are fully described in the report (Carpenter, 1986). A summary of the treatment process and the rate of release of chloride into the wash solutions is shown in Figure 4 where the amount of chloride ions in a solution is plotted against the square root of the treatment time ($\text{hr}^{1/2}$). The initial response of the anchor conforms to the normal behaviour of a diffusion controlled process in that the chloride concentration increases linearly with the square root of treatment time and is described by the equation

$$\text{Cl}^- \text{ ppm} = 26.11 t^{1/2} + 143.$$

The correlation coefficient for the least squares fit is 0.99984. The intercept at zero treatment time had a value of 143 ppm which is the background level of chloride in the solution. The solution volume was 7000 litres, so the release rate of $26.11 \text{ ppm.hr}^{1/2}$ corresponds to 183 grams of chloride ions per $\text{hr}^{1/2}$, or approximately $35 \text{ grams.m}^{-2} \text{ hr}^{-1/2}$ (based on a surface area of 5.2-square metres). In the first wash, 58% of the total chloride ions

released in the 891 days of treatment reported to the solution. A total of four wash solutions comprising of 200 kg sodium hydroxide and 28 tonnes of water were used in the treatment programme. Inspection of the graph in Figure 4 shows non-linear responses of the chloride concentration with square root of treatment time in the second and third wash. The different behaviour is probably due to the variations in electrolysis conditions e.g. sometimes the power was off and the concentration of the electrolyte varied with rainwater contamination.

Results and discussion.

Inspection of the anchor at the end of the treatment programme showed that large areas of original surface had been retained. It was noted during the deconcreting process that the calcareous matrix was extremely hard (Carpenter, 1986) and that the underlying metal was not so prone to spalling as is generally found with wrought iron anchors that have been in the sea for several hundred years. The most likely explanation for these features lies in the pretreatment that the anchor received during its year of cathodic protection. It should be noted that most of the original surface has very little mechanical strength and is very prone to disbondment. The properties of the various zones of wrought iron have been well documented by Chilton and Evans (1955: 113) and they relate to the distribution of impurities in the bands of metal and their effect on the corrosion mechanism. In the extensive hot working of the final surface, the iron was decarburized and sulphur impurities would have been removed by oxidation. Prior to treatment, the anchor was sampled by drilling and the results are shown below in Table 1.

The total amount of chloride released from the anchor was approximately 1.63 wt% which is consistent with the above data since the analyses refer primarily to the metal rather than a mixture of iron and corrosion products, which would have more chloride in them. The low level of sulphur in the anchor indicates that the wrought iron had probably been produced using charcoal rather than coal as the reducing agent in the furnace.

Given that nickel and copper promote the zonal corrosion which results in the typical wood grain finish of corroded wrought iron, the low levels of these noble metal impurities will have helped in reducing the localised corrosion rate, and so help retain vestiges of the original surface. It should be noted that the surface of the anchor could have easily been lost if the electrolysis treatment had been too severe.

A formal representation of one of the many processes occurring during the cathodic protection of the anchor could be summarised by the equation

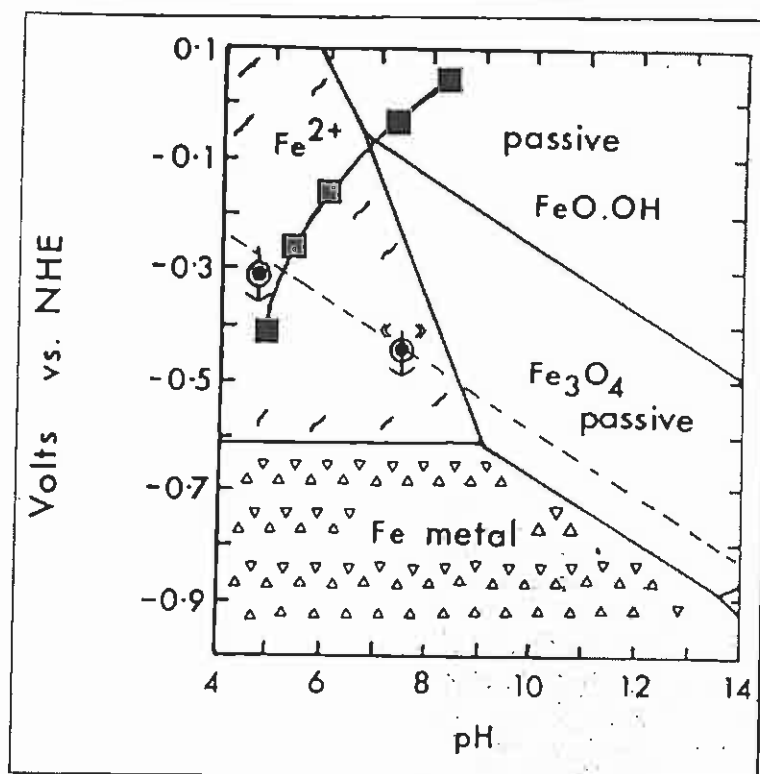


Figure 3. Pourbaix diagram for iron in sea water. The ■ data points relate to measurements on a Rapid cannon, the ⊗ symbol is for the predisturbance corrosion potential of the Sirius anchor and the ⊙ is the E_{corr} value prior to removing the sacrificial anode after one year of treatment

$2 \text{FeO.OH} + \text{FeCl}_2 + 2e^- \rightarrow \text{Fe}_3\text{O}_4 + \text{H}_2 + 2\text{Cl}^-$
 namely, a mixture of iron (II) and iron (III) corrosion products are changed from the reactive and inherently acidic forms to the stable black corrosion product magnetite (Fe_3O_4). In the same process the chloride ions diffuse through the concretion back into the surrounding sea water and the acidity of the solution under the concretion is reduced. The reduction in acidity shifts the iron metal towards a more stable environment. Since the acid from metal ion hydrolysis had dissolved 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). Such a redeposition would harden the concretion and, combined with the production of more magnetite, would act as a "cement" to bind together the original surface material which normally falls away from the corroded metal. The filamentous nature of the slag inclusions ($\text{SiO}_2 \cdot 2\text{FeO}$) may act as a reinforcing matrix for the redeposited minerals.

Corrosion measurements on the HMS Sirius site

During the survey period, when the ballast was being tagged and plotted, samples of weed were collected from the main wreck site. Samples were recovered from the ballast pigs, from the general area around the anchor, from the growth on the anchor ring and from the general reef top and growth on the anchor itself. There appears to be no systematic difference in the species due to the presence of iron or its corrosion products. This is consistent with the fact that the colouration of the concretion on

the wreck site is essentially that of the surrounding coralline environment in that there are no characteristic iron stains and the species are essentially those which are expected from a shallow high energy habitat.

The information provided by the analysis of the soft algae growth on the wreck site is important in gaining the overall understanding of the way in which the material has degraded on the site itself and the high energy nature of the wreck site, which was also confirmed by our measurements of corrosion potentials and pH.

At the start of the 1988 season it was decided to undertake a survey of the corrosion potentials and pH measurements on the corroded iron underneath the protective layer of concretion. Such a survey would be a very valuable asset to conservators and corrosion scientists since, for the first time on a major shipwreck site, there was a statistically large enough number of apparently identical objects, which had corroded in the same environment, to enable proper assessment of the reliability of corrosion potential measurements as an index of corrosivity of the site. One of the biggest problems that has been faced over the last ten years of accumulating data is that there have only been one or two cannon, one or two anchors available for measurement on a given site. Since many of the sites are in locations where there are different water temperatures and different affects of marine growth it had been impossible to see if there were any overall correlations. With this objective in mind a series of corrosion potential and pH measurements were made on the Sirius ballast pigs and on the two remaining anchors once they had all been surveyed. This work was delayed until the pigs had been tagged so that we could

Table 2: Composition of cast iron ordnance, weight%

	C	S	Si	Ni	Cu	Mn	P	Cl
<i>Rapid cannon</i>	4.0	0.18	1.93	0.220	0.023	0.475	0.37	<0.005
<i>Sirius carronade</i>	3.5	0.08	0.10	0.015	0.015	0.480	0.51	0.190

properly relate the measurements to individual objects whose position was precisely located on the site plan. It was rather surprising to find that a large degree of variation existed in the corrosion potential measurements. It had been anticipated that a spread perhaps 20 or 30 millivolts might have been found whereas in fact the difference between the highest and the lowest corrosion potential was greater than 160 millivolts (Fig. 5). These differences in E_{corr} indicated that the objects were showing markedly different corrosion rates. Inspection of the artefacts previously raised on other expeditions showed that there was indeed a wide range of corrosion behaviour of the same cast iron objects in the form of ballast. The least corroded ballast pig had been recovered from the sheltered lagoon area whilst the most corroded pig

sensitive and delicate. Working with such instruments under the given site conditions is not easy. However, we were able to obtain some very useful parameters in that we were able to record the lowest ever observed pH value of 4.18, under the concretion of a ballast pig. The most acidic micro-environment previously recorded on iron artefacts was on the *Batavia* wreck site where the typical value was 4.8, a factor of more than four times less acidic. Inspection of the digital read out of the pH meter showed that equilibrium values were obtained within two minutes. Our measurements have confirmed that the HMS *Sirius* site is the most aggressive of all those measured by the Western Australian Museum team. It should be noted that all the objects have corrosion potentials that are in the active region for corrosion. Analysis of the corrosion

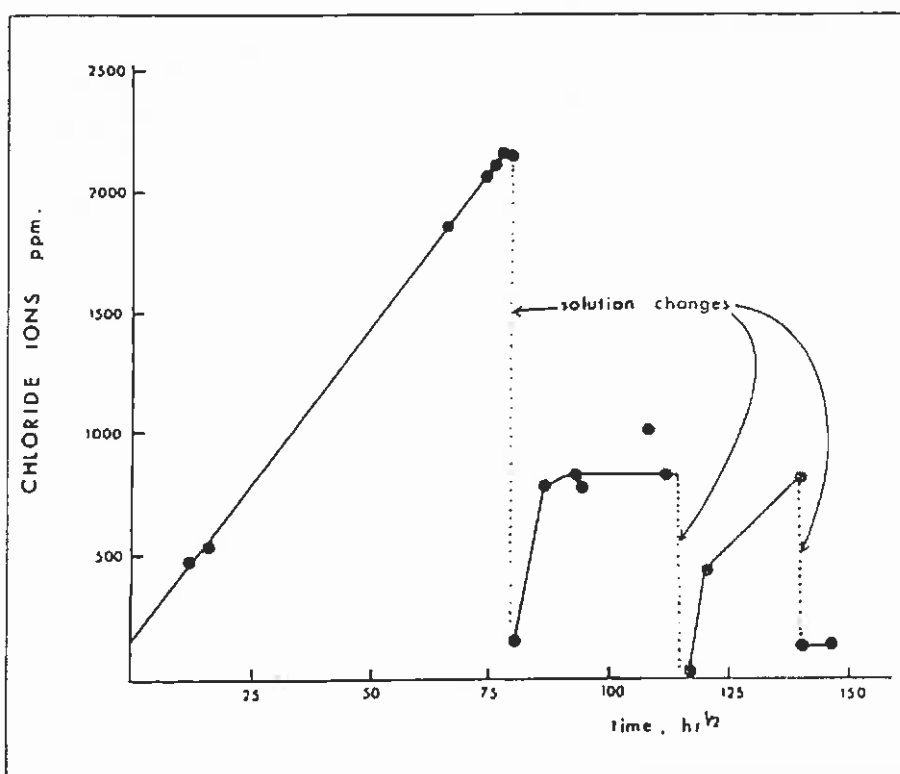
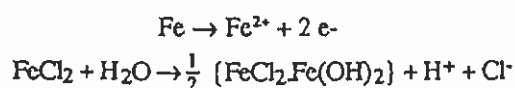


Figure 4. Plot of treatment data for electrolysis of *Sirius* anchor in 2% NaOH solutions. The chloride concentration is in ppm (mg/litre) while the x axis is the square root of the treatment time ($\text{hr}^{1/2}$)

had been recovered from a section of the site that was quite exposed. Under the strong surge conditions experienced on the site the measurement of surface pH is very difficult. Owing to the advantage of having a compressed-air driven drill with a masonry bit we were able to penetrate the protective concretion layer and insert a pH electrode of the same diameter. The electrode has a specially prepared flat glass bulb which is extremely

potentials and pH measurements showed that despite the difficult working conditions a definite relationship between pH and E_{corr} has been established. The corrosion process is apparently related to the surface pH through the partial hydrolysis of the primary corrosion product ferrous chloride viz.



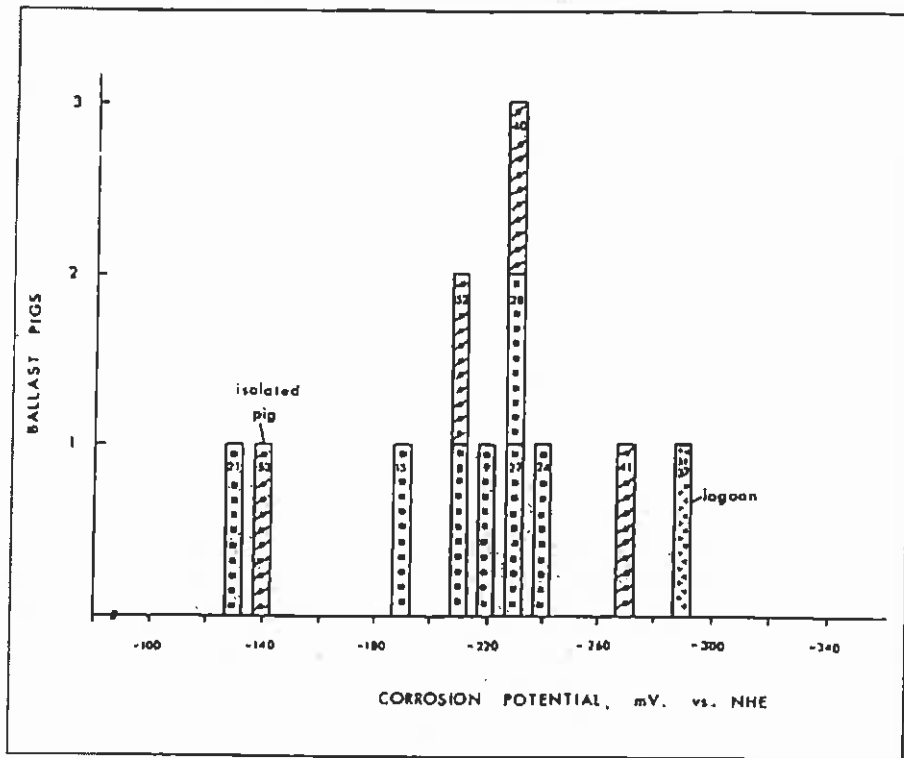


Figure 5. Distribution of the values of corrosion potentials for ballast pigs on the *Sirius* site

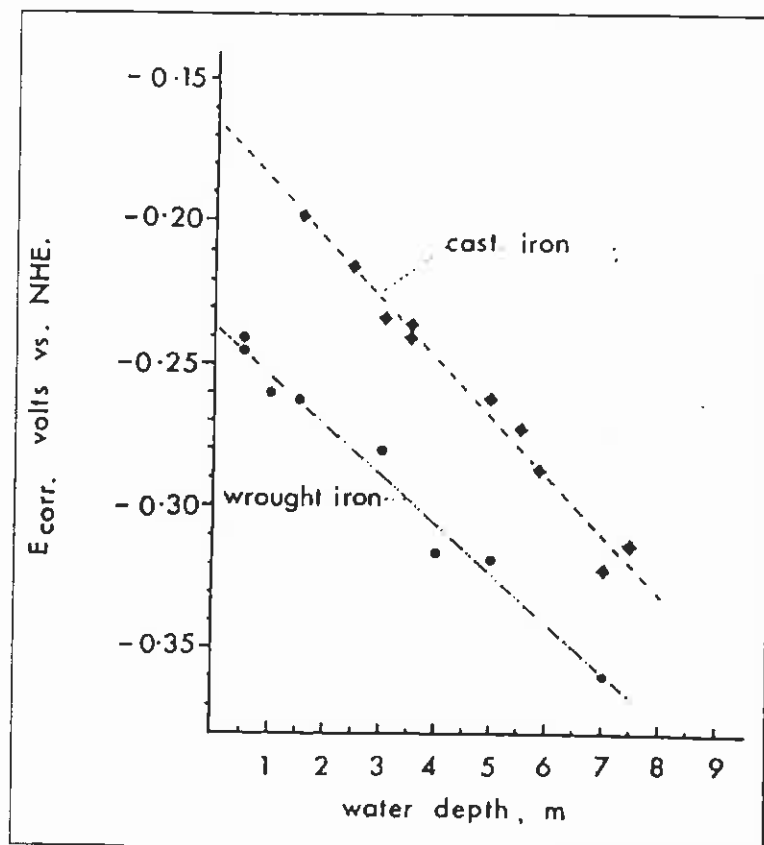


Figure 6. Plot showing dependence of corrosion potential (E_{corr}) on water depth for cast and wrought iron artefacts

The above phenomena are reflected in the on site variables which conform to the relationship for wrought iron,

$$E_{\text{corr}} = -0.029\text{pH} - 0.100 \text{ volts vs.NHE}$$

Cast iron objects showed the same pH dependence as the wrought iron anchors and anchor fluke, but the intercept value (E_{corr} at pH = 0) was different. Corrosion potential measurements on the second *Sirius* carronade showed that it was actively corroding. Given its historic and archaeological significance it was decided to begin conservation treatment as soon as possible whilst it remained *in situ*. A 20 kg lump of aluminium alloy (engine blocks) was attached via a specially fabricated giant G-clamp to the concreted carronade. The electrical connection between the cannon and anode was by way of a twisted double insulated heavy duty battery cable. Within a few minutes the E_{corr} value for the object had fallen 165 mV which showed that a good current flow had been established and that the chloride and acid removal process had begun. Prior to the connection of the anode the E_{corr} of the carronade was measured and the result was within 10 mV of the value previously determined after 198 years of equilibration. The reproducibility of the results proves that the act and mode of measuring E_{corr} causes no real change in the micro-environment of the object. During a violent winter storm in 1989 the bracket became dislodged and so the treatment was temporarily halted.

Corrosion potentials and water depth

The data collected during the 1988 *Sirius* inspection showed the highest (the least negative) corrosion potentials were found in the shallowest water whilst those with more negative values, reflecting less corrosive environments, were found in deeper waters. Objects lying proud of the seabed had higher corrosion potentials than other objects at the same depth which were more buried in the surrounding reef platform. Direct comparison of the E_{corr} values of cast and wrought iron is not possible owing to their different composition so the *Sirius* data was compared with other sites. The cast iron pigs were compared with a cast iron propeller from the steam ship *Xantho*, trypots from the *Lively* and cannon from a number of other sites. The *Sirius* anchors were compared with other wrought iron anchors and objects such as whaling hooks and chain plate. The rate at which the corrosion potentials changed with water depth was essentially the same for both wrought iron and cast iron and the E_{corr} values fell by 18.92 ± 1.5 mV per metre of water depth (Fig. 6). This behaviour was not expected on the basis of the previously understood model (MacLeod and North, 1987) where the concentration of dissolved oxygen had been considered to be of paramount importance. Standard oceanographic data shows that the level of dissolved oxygen generally increases slightly with water depth up to approximately 30 metres owing to the greater hydrostatic pressure. If the rate of corrosion was dependent primarily on the dissolved oxygen concentration, the observed decrease in corrosion rate with increased water

depth could not be explained. However, one parameter that does decrease most markedly with increasing water depth is the total amount of water movement. Such movement depends on the combined action of the channelling effects of reefs and the topography of the seabed (MacLeod, 1989). The combined data from all the cast and wrought iron objects measured on ten different sites show that the corrosion potential is determined by the oxygen flux available to the corroding metal.

The rate of corrosion depends not only on the absolute value of oxygen dissolved in the sea water at the time of measurement but it also depends on the rate of supply of the oxygen. If we are in a region of the corrosion diagram (Fig.2) where the rate of the reaction has been determined by the rate at which oxygen can diffuse to the corroding interface, then any factor that reduces the diffusion layer thickness (the boundary layer thickness) will increase the corrosion rate. The diffusion layer thickness is the distance across which the oxygen concentration falls from its saturated sea water level to zero. In shallow depths there is much greater total water movement and the higher the profile of an artefact on the seabed the greater localised turbulence causes increased corrosion. This new understanding, that was catalysed by the analysis of the corrosion potentials on the *Sirius* site, is essentially of revolutionary significance to the understanding of corrosion phenomena on shipwrecks.

If we refer to Figure 1 we see that the concretion serves two purposes. It not only functions as a semi-permeable membrane but also as a mechanism for separating the two halves of the corrosion cell. Oxidation of metal occurs at a site which is physically separated from the point of reduction of oxygen to hydroxide ions. Recent work in these laboratories has shown that there is a direct relationship between the thickness of the marine concretion and the weight per cent of phosphorous in the metal (MacLeod, 1988). If the rate of corrosion was partly dependent on the thickness of the concretion, i.e. on the electrical resistivity of that pathway, then the artefacts with a greater percentage of phosphorous in them might be expected to be corroding at a slower rate owing to the increase of resistance due to a greater thickness of concretion.

On Norfolk Island one of the causes for the differences in corrosion potential appears to lie in the presence of the black long-spined sea urchin *Heliocidaris tuberculata* (Lamarck, 1816) which has the habit of burrowing into the marine growth on the artefacts thereby short-circuiting one of the rate determining parameters in the corrosion cell, namely the electrical resistance of the concretion layer. However, when we look at the extent of corrosion on pigs recovered from different parts of the site we see that there is a factor of approximately four between the extent of weight loss of one cast-iron ballast pig recovered from the inner part of the site compared with the outer. The small differences in the amount of phosphorus in the metal giving rise to differing concretion thickness cannot explain the corrosion data by itself. So what does all this mean in terms of the corrosion problems of artefacts on the wreck sites?

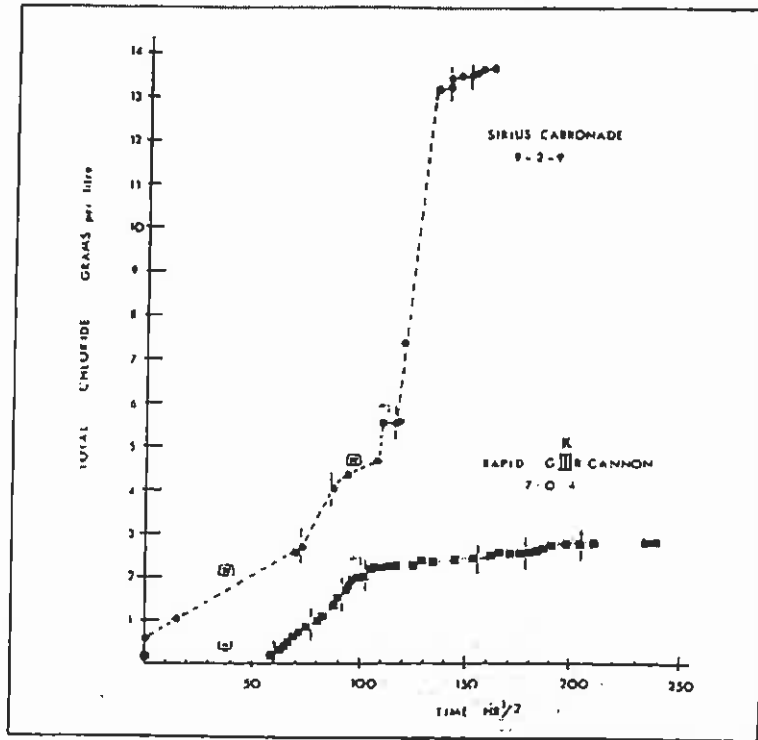


Figure 7. Comparative plot of chloride extraction rates for cannon recovered from the *Rapid* and the *Sirius*

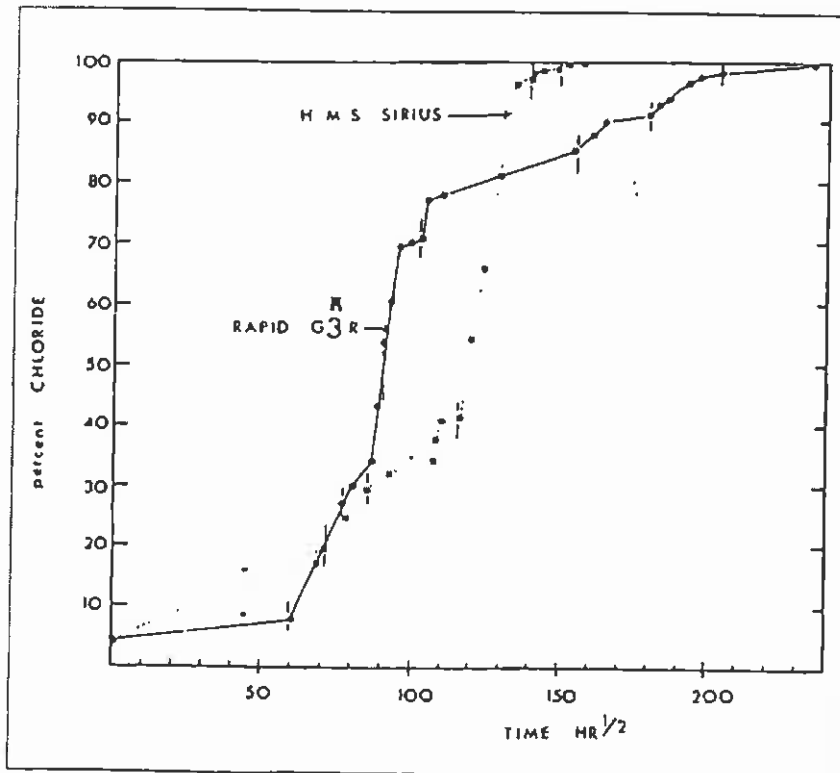


Figure 8. Comparative plot of the weight percentage of the total chloride ions extracted from the *Rapid* and *Sirius* cannon as a function of the square root of the treatment time

Consequences of different corrosion rates

One of the archaeological implications of the measurement of corrosion potentials on wreck sites is that, knowing the way in which corrosion potential and water movement varies with water depth, we can now state fairly unequivocally that for all other parameters being equal, the cannon or anchor with the lowest corrosion potential will be the least corroded and therefore should be the one to be raised. That object should not only be the easiest to treat but also the one involving less bags of caustic, less time and so on. The chosen artefact is also the most likely to have the best preserved surface features. An unexpected consequence of the more extensive corrosion on the *Sirius* was found when we compared the desalination of the carronade with a cannon of approx the same weight recovered from the *Rapid* (1811). The latter cannon had been buried at a depth of 7 metres compared with approximately 2 metres of water for the *Sirius* carronade. A plot of the total amount of chloride (wt%) released from the *Rapid* cannon and the *Sirius* carronade is seen in Figure 7. Not unexpectedly the *Rapid* cannon has much less extractable chloride but when we view the data expressed as a percentage of the total amount extracted it tells a different story (Fig. 8). Although the *Sirius* cannon is much more extensively corroded and has much greater amount of chloride removed from it, 25 kg compared with 4 kg from the *Rapid* cannon, it was able to be treated in a shorter length of time. This is apparently due to the greater porosity of the more extensively corroded *Sirius* carronade compared with the *Rapid*. Although the composition of cast iron has a marked effect on its microstructure and hence the corrosion performance the composition of the *Rapid* cannon was very similar to the *Sirius* carronade (see Table 2) apart from a higher silicon content. Without access to solid samples for comparative metallographic analysis it is not possible to state what effect the microstructure had on the mode of corrosion.

Application of sacrificial anodes to treatment of shipwreck artefacts

Currently the Western Australian Museum is treating the stern section of the steamship *Xantho* (1872) at Port Gregory. Measurement of surface pH underneath the concretion after a period of 8 months of electrolysis showed that the pH had increased from 4.8 down to 6.5. This significant drop of acidity will enhance the mechanical strength of the concretion layer and therefore give protection to the delicate artefact when it is raised from the sea bed. The treatment should also stabilize vestiges of original wrought iron surface details as was observed with the *Sirius* wrought iron anchor. The chloride concentration underneath the concretion will be greatly reduced in the process which means that any post-excavational damage that occurs during the transit to proper treatment facilities in Fremantle, will be minimal. Another most significant use of sacrificial anodes

was found with a heavily concreted and extensively corroded iron cannon from the *Batavia* which was recovered a couple of years ago. The use of a zinc anode in the fibreglass-lined concrete tank containing only tap water proved to be totally ineffective. In fresh water you need the much greater voltage difference between aluminium alloys and the concreted artefact to get effective current flow. The current can be readily measured by the voltage drop across a resistor which is placed in the circuit between the sacrificial anode and the object itself. Currents of the order of 200 mA typically flow into the object and this is normally sufficient to prevent any further corrosion problems. By monitoring the chloride release rate in the treatment solution we find a threefold increase in rate on deconcreting. This has great relevance to both the *Sirius* anchor treatment and the *Xantho* stern section in that we know that the chlorides will migrate outwards under the influence of the applied d.c. current flowing into the object. The application of cheap sacrificial anodes to the treatment of artefacts in cheap containers and without recourse to the hazards of sodium hydroxide solutions has major implications for allowing archaeologists to safely raise material in the situation where there may not be the optimum conservation treatment facilities available.

Conclusion

Recent work has shown that it is possible to obtain a clear understanding of the nature of corrosion and deterioration forces working on a shipwreck site through the application of both surface pH and corrosion potential measurements. More recently this approach has been used in the Philippines on archaeological timber. The most important thing to note is that the data obtained by the underwater conservator measuring these parameters gives the archaeologist a very valuable tool in helping them to decide what artefacts are to be raised. The data also helps to establish if the site is in danger and subject to strong forces of deterioration with major resource management implications. The results to date indicate that the best archaeological values from wrought-iron anchors are obtained with cathodic pre-treatment. This might lead to the pre-treatment of artefacts on the seabed prior to them being excavated in subsequent seasons so that the treatment time above the ground is minimised and that not only is corrosion halted during the remaining time on the sea bed but that active conservation can be carried out at the same time.

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