350 years of marine corrosion in Western Australia

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1. INTRODUCTION

From the dawn of history man has been using the sea as a source of food and later as a convenient way to transport goods and people. To cater for fishing and trading, villages were established along the seashores and these villages slowly grew into the large trading cities we know today. With the growth of these villages man found anew use for the sea, the dumping of waste and refuse into its limitless capacity. Until very recently fishing, trade and waste disposal were the total of man's interest in the world's oceans. These activities all involve the use of metals in a corrosive marine environment. It was found to be economically, if not technically impossible to build structures to last forever, hence the concept of economic lifetime soon arose. That is, a structure or boat was built to last, with maintenance, for a certain period and after that was either replaced or abandoned.

In the last few years two developments have occurred which are forcing a rep-

apraisal of the economic lifetime concept. The first of these is in the waste disposal area where with some wastes, particularly radioactive material, simple disposal at sea is no longer acceptable and long life containers must be constructed to hold the waste until it decays to a safe level. Secondly the expansion of the mining industries into offshore waters, with it's problems of high construction and maintenance costs and, in case of hydrocarbons, possibility of environmental damage has also produced a demand for metals which have a guaranteed long life in natural marine environments.

The specification of materials, surface coatings and design details to meet these new requirements presents the corrosion scientists with quite a problem. Tradi-

tionally metals in marine environments have been selected with an estimated lifetime of 10 to 30 years. Suddenly the demand is for materials to last centuries if not millenia. Fortunately there is a series of long term marine exposure tests which can be used. I refer to the multitude of known shipwrecks which date from the present right back to the late bronze age (circa 1200 BC). In Western Australia the range is more limited but it does cover a period of 350 years.

The study of metal corrosion on these shipwrecks can provide answers to present industrial corrosion problems. There has been a plethora of publications on the corrosion of metals in a marine environment but there are still many questions which remain unanswered. In particular there is no reliable laboratory test that duplicates the effect of long term exposures (1), or takes into account the effects of marine biological activity.

To answer these types of questions, we must turn to shipwrecks and here the Conservation Department of the Western Australian Museum is in a very favourable position. There are over a thousand wrecks, dating from 1623 to present day, lying off the Western Australian Coast. Under present legislation the WA Museum is the only body which is permitted to excavate materials from historic wrecks and it is actively doing so. The conservation laboratory also has research chemists who are interested in marine metal corrosion and, although time and funds are limited and precarious, we are working on the problems of long term corrosion.

The wrecksites we are studying cover a wide range in factors such as temperature, sediment, salinity and oxygen content. We are limited in that we have no choices of materials type and must be content with whatever metals were on the shipwreck, that is the metals and alloys, which were in common use at that time. These generally are cast iron, mild steel, copper and copper alloys, lead and lead alloys, silver and tin. Quite often. however, a study of the long term corrosion of these metals can assist in pinpointing the problems which

will occur with modern metals such as stainless steel.

2. SOME FACTORS INFLUENCING CORROSION RATES 2.1 Temperature

In general corrosion theory the corrosion rates are considered to increase with increasing temperature. Whilst this effect undoubtedly exists, in the sea an overriding factor is the change in biological activity with temperature. The growth of marine organisms on the surface of the metal produces an encasing concretion. Beneath this concretion a microenvironment forms which may be quite different

from seawater, and often more protective These marine growths generally form more rapidly in warm tropical waters, and hence form a protective coating faster, than in cold waters. Consequently long term metal corrosion can be slower in tropical waters than in colder temperate waters.

2.2 Oxygen content of water

Dissolved oxygen provides the major oxidising force in marine metal corrosion and the corrosion rate is generally determined by the cathodic process, viz reduction of oxygen rather than by the actual oxidation of the metal (2). The depth of the site and the water movement will not only affect the oxygen supply to the corroding metal but will also have a pronounced affect on the growth of marine organisms. Metal objects buried beneath the seabed will have a greatly reduced oxygen supply. Depending on the nature of the sediment anaerobic conditions can readily develop and lead to a complete change in the corrosion mechanism. Variations in site coverage can result from the movement of sediment on a wrecksite, for example during storms and cyclones, thereby changing the microenvironment of the metal from

aerobic to anaerobic and vice versa. In long term planning the possibility of such environmental changes must be con sidered. **2.3 Galvanic coupling**

If two different metals are in contact on a site then the more active metal will cor rode at an accelerated rate and the more noble will be protected. The effect of this reaction depends on a number of factors such as relative surface areas of active and passive metals, how different are the electrochemical potentials and the extent of contact between them.

Table 1 gives a list of electrochemical potentials in seawater for some of the more common metals found in ship wrecks. This table serves as a rough guide to galvanic coupling as the formation of adherent films of oxide, sulphates and marine concretions can result in passivation of the metal.

TABLE 1

Corrosion Potentials in Sea Wa	iter'						
(Volts vs. Saturated Calomel Electrode)							
Magnesium ^a	-1.60 Active						
Zinc ^a	-1.10						
Cadmium ^a	-0.80						
Aluminium ^a	-0.75						
Lead ^a	-0.55						
Tin lead solder ^a	-0.50						
Mild Steel ^b	-0.45						
Muntz Metal ^b (60%Cu,							
40%Sn)	-0.27						
Yellow brass ^b (65%Cu,							
35%Zn	-0.20						
Copper ^b	-0.17						
Red brass ^b (86%Cu,							
15%Zn	-0.15						
Admiralty brass ^b (71%Cu							
28%Zn, 1%Sn	-0.14						

Silver^c +0.02 Noble ^aSea water, ^bFlowing sea water, ^c I.D. MacLeod, unpublished data.

2.4 Marine growths

The growth of marine organisms on exposed metals can exert a marked effect on corrosion patterns. Not only do such sur face coating protect the underlying metal from mechanical abrasion by sea-born grit and sand but they can form an almost im pervious barrier between the bulk of the sea water and the corroding metal. This may result in a microenvironment beneath the concretion layer which is substantially different to that of the sea. An example is found with iron where the pH falls from 8.1 to 4.8 and the chloride ion increases from 0.5M to 1.5M (4), beneath the concretion.

Provided metallic iron is present, con cretions can also be formed on completely buried metals as a result of the iron corro sion process. Although inorganic in origin these concretions are chemically and physically similar to the biological concre tions on exposed metals and act in a Fig 1 The distribution of artifact finds at the Point Cloates wrecksite----- copper and copper alloys---- iron concretions percentage of iron concretions which retained some solid iron.

similar manner as regards formation of an enclosed microenvironment.

3. COPPER BASED ALLOYS

The copper containing materials recovered from historic shipwrecks are either pure copper or alloys such as bronze (copper and tin) and brass (copper and zinc) in assorted variations. In most cases the corrosion of the metal is dominated by the behaviour of the copper. The copper based alloys readily form an adherent film of cuprite (Cu₂O) and tenorite (CuO) during manufacture. When submerged in seawater the initial mechanisms of corrosion is that of copper ions diffusing through the oxide film to the seawater interface where they either precipitate or disperse. Because of this gradual copper ion release, the growth of marine organisms on the metal surface is significantly retarded and concretion formation is absent or limited. This effect has been used by mariners since the early 19th century to prevent attack on ships timbers by Teredo worms and to generally reduce fouling by barnacles and weeds.

However for long term corrosion resistance, the lack of a protective encapsulating concretion is detrimental to the copper alloys, In areas where there is appreciable water movement, the surface of the copper alloys is subjected to a continuous form of sandblasting as small pieces of sediment(sand, shell grit, coral fragments etc.) picked up by the water

movement are impinged on the metal surface. This can lead to very rapid erosion of the metal. In one case we observed in the Abrolhos Islands an erosion rate of approximately 1cm per month was found on a large bronze object accidentally placed (not by the WA Museum) in a tidal wash area having a course sandy bottom.

If erosion does not occur, the chloride ions in seawater penetrate the oxide film and react with the metal to form cuprous chloride. The film of cuprous chloride can subsequently be oxidised to form atacamite or paratacamite (α or γ 3Cu

(OH)₂ CuCl₂), which is the major marine copper corrosion product (See Fig 1). This does not retard corrosion of the underlying metal. Because of the high chloride content and relatively high pH of seawater the formation of basic copper carbonates so typical of land based sites, such as azurite (2CuCO₃ Cu(OH)₂ and malachite (CuCO₃ Cu(OH)₂), does not occur to any significant extent. Similarly no examples of the basic copper sulphates, antlerite and brochantite, have been found in the thirty odd samples examined to date by x-ray techniques.

In the case of copper alloys the corrosion products may also contain compounds of the other alloying elements. This is particularly noticeable with the bronze alloys where the Sn forms Sn02. This mixture of atacamite and SnO2 forms a semiadherent corrosion product which retains



Distance from bow (m)

the shape of the original metal surface, including inscriptions, in the corroded layer. The brasses corroded through a typical dezincification process and although the original shape of the object may be retained for many years or even centuries there is a drastic loss of mechanical strength and the metal becomes very fragile. Although detailed studies have not been carried out to date it appears that, in the absence of a protective marine concretion, the long term corrosion rates of copper

alloy is as high and possibly higher than that given by short term measurements under similar conditions.

However, if local microenvironmental conditions are favourable extreme corrosion resistance can be imparted to certain copper alloys. From wrecksites examined to date, such corrosion resistance is favoured by galvanic coupling to more active metals (usually iron), the formation of a thick coherent marine concretion and the presence of small amounts of certain elements in the original metal. These factors are also interrelated.

If a copper alloy is in direct electrical contact with a mass of iron then galvanic protection of the copper would be expected. However, recent work on the "Point Cloates" wreck, approximately "1812", has suggested that something akin to galvanic protection can also occur even when the objects are only in close proximity and not physically touching. An examination of the material recovered from the first season of excava tion (1978/79) at the "Point Cloates" wreck site shows that a remarkable number of copper/copper alloy objects were found, some 4700 copper nails, 500 copper tacks, 200 spikes plus 300 bolts, bars and miscellaneous fittings. The distribution of these finds is shown in fig 2 as are the number of iron artifacts. Of the 450 iron ob jects registered only 135 of them, mainly canister shot, had any solid metal within

the concretion. The increase in the tage of iron artifacts containing residual metal is seen to rise as the number of cop per items falls which may be due to sacrificial protection of the "copper" materials by the iron - see Table 1 for the relevant corrosion potentials in seawater.

However, site conditions may be more important for galvanic protection than sometimes estimated for in one case reported, that of the "HMS Association" (Scilly Isles, 1707)⁵ little evidence of galvanic action was found despite the objects being piled on top of each other.

A second way in which copper alloys can be protected is by formation of a thick marine concretion which effectively isolates the metal from the sea. However, as pointed out earlier, this will not occur naturally unless the release of copper ions from the underlying metal can be reduced to a non-toxic level. This will occur if an adherent inorganic layer is formed initial



Fig 2. Pourbaix diagram for the following equilibrium conditions for Cu-Cl-H₂O at 25° C at 1 molar chloride.

presence of HS⁻ the formation of chalcocite from cuprite is thermodynamically very favourable, with a ΔG^0 of -110 kJ mole-1. We suspect that the pintle was initially buried in sediment shortly after the shipwreck since this gives the correct conditions for formation of sulphide ions6 and hence copper sulphides. As a result of a later disturbance, possibly from storm action, the sulphide covered pintle was exposed to an aerobic environment.

The layer of chalcocite apparently slowed down the release of copper sufficiently to allow the Bryozoa to colonise the exposed pintle. Once this layer had thickened the supply of oxygen to the surface was greatly diminished and so corrosion essentially ceased. The anaerobic conditions under the concretion would permit sulphate reducing bacterial to grow and the S²⁻ produced by these would convert any free Cu+ ion to more Cu₂S.

We have also found samples of chalcocite on some copper sheet buried under sand from the Point Cloates wreck site while Campbell and $Mills^5$ found some djurelite (Cu_{1.97}S) on copper materials at the "HMS Association" site in the Scilly Isles.

Beneath all the concretion and corrosion products, the metal of the "Pandora" pintle showed no sign whatsoever of corrosion apart from a slightly roughened surface. This surface roughening may have been due to the sand mould used for the original fabrication.

ly on the metal surface. In shipwreck materials there are two ways which this can form. Firstly if the metal is rendered cathodic, the formation of OH- ions may produce a high pH surface layer of seawater adjacent to the metal surface. Under these conditions precipitation of inorganic CaC03 could occur which in time, could provide a substrate for marine growth. Although we suspect this has occurred in certain cases it is very hard to provide definatively as, after many decades, there is often very little difference between inorganic CaC03 and converted organic material. CaCO₃ is not a particularly impervious material and better protection is obtained by the formation

of Cu₂S films. This is much rarer in shipwrecks but a most interesting example has recently arrived in the form of a bronze pintle from the "Pandora" (wrecked in Torres Strait in 1792). The pintle was completely covered with an extensive growth of marine organisms which included corals, molluscs and oysters. Removal of the concretion showed a grey-black adherent layer, about 1 mm thick, of chalcocite (Cu2S) cuprous sulphide) which overlaid a thin film of brick red cuprite (Cu2O) The primary colonizers on the copper sulphide layer were Bryozoa which secrete a calcareous exoskeleton. Other marine organisms then grew over the Bryozoa surface. In the

The third way to prolong the life of cop per alloys in the marine environment is a careful choice of metal composition. In general brass alloys do not survive as well as bronze due to dezincification. In both cases their behaviour can be modified con siderably by the presence of minor com ponents. Compositions of some typical cop per alloys are given in Table II. Although our studies in this area are far from complete some interesting trends are starting to emerge. Corrosion resistance appears to be enhanced by the presence of arsenic and, to a lesser extent lead and an timony. In contrast, iron in copper alloys tends to accelerate the corrosion.

TABLE II

Composition of metal fittings from shipwrecks

Item	Ship	Date	Location	Copper	Zinc	Tin	Lead	Iron	Antimony	Arsenic
Door pintle	Batavia	1629	28°30'S, 113°45'E	92.7	0.5	1.4	1.1	2.1	0.3	0.14
Bronze cascable	Batavia	1629	28°30'S, 113°45'E	66.9	0.28	2.8	22.6	0.13	3.2	4.0
Rudder gudgeon	Rapid	1811	22°44'S, 113°41'E	91.8	0.30	4.8	1.91	n.d.	0.12	-
Pall trace	Rapid	1811	22°44'S, 113°41'E	90.8	1.03	4.8	2.9	0.09	n.d.	n.d.
Copper nails	Rapid	1811	22°44'S, 113°41'E	98.7	n.d.	0.11	0.18	n.d.	0.03	0.13
Copper bars	Rapid	1811	22°44'S 113°41'E	97.7	n.d.	0.05	0.54	n.d.	0.04	n.d.
Rudder gudgeon	HMS Success	1829	32°07'S 115°39'E	87.8	1.42	5.06	1.45	n.d.	0.01	0.60
Copper bolt	HMS Success	1829	32°07'S. 115°39'E	99.4	0.02	0.22	0.09	n.d.	n.d.	0.03
Rudder gudgeon	Chalmers	1874	32°22'S, 115°42'E	63.0	20.5	2.4	13.6	0.8	0.1 '	n.d.
Rudder gudgeon	Lady Elizabeth	1878	32°01'S, 115°32'E	44.0	28.7	0.73	25.6	0.02	< 0.3	0.36
Brass bar	Amur	c.1890	32°09'S, 115°46'E	65.6	32.4	< 0.1	1.15	0.01	< 0.3	0.02

The presence of greater than 0.1 per cent iron in marine bronzes normally has a drastic effect on the corrosion of the metal. An example of this is found in a bronze from the "Batavia", a shallow and well oxygenated site. The door pintle, see Table badly corroded with deep holes penetrating at least 2cm into the metal. Recent work by Bowers et. a17 has shown that 0.08-0.12 per cent arsenic will prevent mineralization in brasses when there are low levels of iron and manganese in the alloy. The high concentration (2.1 per cent) of iron essentially removes the effect of arsenic, probably through arsenide formation, leaving the metal subject to severe corrosion since the rapid attack on the iron particles will greatly increase the surface area of the fitting. By way of contrast the high leaded bronze cascable from the same site has had negligible (0.2mm) corrosion and retains an attractive patina in its non concreted initial state. The very high level of antimony, (probably adventitious with the lead) and arsenic (from the copper) would tend to make the object hard and brittle8 but this is counteracted by the high lead content which also gives a casting free of shrinkage porosity. The presence of 0. 13 per cent iron in the material is effectively removed through iron arsenide formation.7 The rudder gudgeon from the "Chalmers", see Table II, is badly corroded in spite of it being in the sea 250 years less than the Batavia material. The fitting was cast horizontally and this apparently resulted in an in-, homogeneous case for the remaining metal has a mottled appearance with the top of the casting being very soft and porous with extensive pitting. The relatively high level of iron (0.8 per cent) and very low (not detected) level of arsenic may have contributed to the initial corrosion which was followed by extensive dezincification. There were significant amounts of the lead sulphate (anglesite) under the concreted layer which indicates that the lead was not evenly dispersed through the case object. The metal has been mineralized to a depth of approximately 1cm which has resulted in greatly diminished mechanical strength.

The rudder gudgeon from Sterling's ship "Success" is in excellent condition after approximately 150 years in the waters off Carnac Island. Arsenic corrosion products, but no tin corrosion products, were found on the surface. This contrasts with the "Point Cloates" gudgeon which is of a very similar composition (See Table II) but whose corrosion products include Sn0₂. Tylecote⁹ has observed that arsenic tends to prevent destannificaton of bronzes so that the presence of 0.6 per cent arsenic and the absence of iron may be one of the factors determining the difference in corrosion patterns. The metal from the "Success" rudder was mechanically sound and showed no signs of pitting or mineralisation and no casting flaws. The copper bolt which had remained in the gudgeon after

the rudder had broken off showed signs of stress corrosion along the leading edges of the rolled thread but the depth of cracking was less than 1 mm.

The gudgeon from the wreck of the "Lady Elizabeth" off Rottnest Island had a fairly uniform concretion layer between 0.5 and 1cm thick, which was stained with iron corrosion products over the greater part of the object. Removal of concretion revealed a surface that was very smooth apart from areas dented by hammering which had probably occurred during initial fitting. There was no evidence of any dezincification and the eye of the gudgeon appeared to have been machined or simply worn to a high finish. The ship was built in 1869 in Sunderland (UK) and had an iron frame. The presence of the iron stain in the concretion may be an indication of another case of galvanic coupling but in this instance the metals were apparently in contact. The uniform and fairly adherent concretion appeared to be inorganic in the primary layer which tends to indicate that precipitation of calcium carbonate was occurring at a cathodic site. The high level (0.36 per cent) of arsenic would have also prevented dezincification and the high lead content (25.6 per cent) gives a sound casting.

4. LEAD

Although lead has poor mechanical strength it does provide very good resistance to marine corrosion. In this respect its position in the seawater electrochemical series is somewhat misleading (Table 1). In an oxygenated environment lead rapidly becomes coated with a passivating layer of lead sulphate (anglesite) and its corrosion potential shifts by 200mV towards more positive values in less than 24 hours. Some lead musket-balls from the Batavia had a corrosion layer of only a few mm after 350 years under the sea.

When lead is alloyed with tin, to form pewter, the corrosion resistance decreases and it appears that the higher the tin content the poorer the corrosion resistance.

5. IRON

The most distinctive feature of iron corrosion in seawater is the formation of hard thick concretions on the iron. These form on both exposed and buried iron although the mechanisms are somewhat different. If the iron is exposed above the sea bed, it is colonised fairly rapidly (1-3 years) by marine organisms. These marine organisms build up a layer of concretion over the entire surface which effectively isolates the iron from the open seawater. Beneath the concretion the depletion of oxygen and decay of organic materials results in formation of a microenvironment substantially different from normal seawater. If the iron is buried beneath the sea bed then the sea bed materials plays a very similar role to the organic concretions found on exposed iron, that is a microenvironment low in oxygen and rich in sulphides develops near the metal sur face.

As iron corrosion proceeds the corrosion products are incorporated into the concretions, replacing the CaCO₃ generally, which results in both mechanically strengthening the concretion and increas ing further the chemical isolation of the metal (by reducing porosity).

Beneath the concretion the iron appears to corrode by a mechanism involving physically separated anodic and cathodic process. The anodic process, dissolution of Fe, occurs on the surface of the residual metal. The cathodic process appears to oc cur at the seaward surface of the concre tion. The anodic area around the metallic iron becomes acidic (pH of 4.8 ± 0.1 cf seawater 8.3), rich in iron ionic species and high in chloride (approximately 1 to 1.5M). This solution slowly diffuses out wards through the concretion or sea bed material precipitating iron compounds and dissolving CaCO₃.

At the anode the various phases of the metallic iron are attacked at appreciably different rates. In cast iron the order of dissolution, from fastest to slowest, is fer rite, pearlite, cementite, graphite. This is also order of increasing carbon content which suggests a form of galvanic protecton is operating. As a result of this selec tive attack a vaguely layered structure forms in the corroded cast iron. In the outer layer there is a mixture of graphite, Si0₂ and iron corrosion products (FeO(OH), FeOCI). Further inwards fine needles of cementite appear and further still areas of partially corroded pearlite. This mixture of graphite, finely divided cementite and pearlite, and high chlorides is very susceptible to accelerated corro sion. Consequently if the concretion is removed and the iron exposed to the at mosphere very rapid reaction occurs, even to the extent of generating steam. In wrought iron the only major phase is fer rite and corrosion of this does not leave a coherent residue. Corrosion of wrought iron occurs most rapidly along slag inclu sions due to penetration of chlorides and moisture. The slag itself appears to be inert.

In engineering terms there are three im portant conclusions from these studies on iron. Firstly, cast iron undergoes severe graphitization without appearing to be cor roded at all. That is, the residual graphite retains surface structure and detail very well but the underlying metal, which gives the mechanical strength, may be very bad ly corroded or indeed non-existent. Secondly long term corrosion rates for con creted wrought and cast iron are approx imately the same as those found in short term 1-20 years) studies, hence a rough estimate of long term lifetime of steel structure can be made from current data. Thirdly, if stainless steel is used in a marine environment for long term work, the problem of changing environment due to concretion formation must be considered when selecting material. The initial environment will be normal seawater but, after encrustation, the microenvironment will be slightly acidic, deoxygenated, rich in sulphide and high in chloride. With these alternating conditions the susceptibility of the stainless steel to stress corrosion cracking in particular must be carefully considered.

6. CONCLUSIONS

From the study of historic shipwrecks it is becoming clear that, for expected

lifetimes in marine environment in excess of 1000 years, the choice of materials is either copper and copper base alloys or

pure lead. These metals have a markedly better long term corrosion resistance than do any other materials used in the last few hundred years.

With lead care has to be taken to prevent mechanical damage and erosion. In addition the metallurgical structure should consist of small grains to prevent perforation by corrosion along grain boundaries. If these conditions are met a thickness of approximately 5 to 10 cm should last in excess of 1000 years.

For mechanical strength the copper and copper alloys present a better choice. Because of dezincification problems it would probably be best to avoid Cu-Zn alloys but even these may be acceptable in certain conditions. To maximise the corrosion resistance of the copper alloys we should try and duplicate those conditions on shipwrecks which are known to have resulted in good long term corrosion resistance. This suggests three steps to be followed.

(1) Carefully select the correct copper alloy composition. This should include significant arsenic and possible antimony or lead to enhance corrosion resistance. Iron and similar elements must be absent.

(2) Form an artificial primary concretion layer on the material. This could possibly be done on site by using impressed galvanic protection (copper-negative) to induce CaCO₃ precipitation. However, shipwreck observations suggest that better protection would be achieved by slowly forming a thick (2-5mm) Cu2S layer on the metal before immersion.

(3) Prepare the site correctly. During the first few years of immersion the copper

needs to be galvanically and mechanically protected. The galvanic protection would retard the release of copper ions and thus encourage a healthy growth of marine concretions. The mechanical protection is designed to prevent erosion of the copper surface by seaborn grit. Both these could be achieved by placing bulky scrap iron around the copper structure. old car bodies or the like may be useful here. Once the concretion has grown this will provide both mechanical protection against erosion and a protective microenvironment to retard metal corrosion.

The work on shipwreck corrosion has also emphasised the deficiency of most laboratory tests as an indication for choosing metals with long term corrosion resistance. Almost invariably laboratory tests are done using either bare metals or metals with corrosion products in seawater. Such tests do not take into account the importance of marine concretions and the highly modifying effect these can have on the local microenvironment. Remember that if the metal is expected to last for 1000 years or more, the metal will probably be covered with concretion for virtually its entire lifetime. The reaction of the bare metal to normal seawater becomes almost irrelevant in this context.

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