4

Corrosion of metals

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4.1 Introduction

The extent of metal corrosion in shipwrecks is dependent on many different and often interrelated factors. Trying to predict what may happen to a specific object after wrecking is virtually impossible, except in the broadest of terms. Indeed, even on excavated shipwrecks where the metals and their corrosion products have been thoroughly studied, it is still often not clear how certain objects have corroded or why apparently similar objects are so differently attacked.

Over the years there have been numerous studies on the rates of corrosion of metals in seawater. Unfortunately the majority of these studies have been done using idealized conditions which are so far removed from wreck site conditions that the results obtained must be applied with caution. Of somewhat more relevance are several studies carried out on actual marine locations, but the materials and conditions are often quite different to those encountered on wreck sites. Recently there has appeared a number of papers dealing directly with the corrosion of metals on shipwrecks.[138-143] The development of marine disposal of toxic wastes and offshore mining has provided an impetus for continuing this work as shipwrecks provide practical examples of the effects of long-term immersion of metals in seawater, such information being useful for designing long-term marine corrosion resistance.

From various studies it is now possible to identify the major factors which affect metal corrosion on shipwrecks. These factors are metal composition, water composition, temperature, marine growth, seabed composition, position of objects in relation to other shipwreck components, depth of burial beneath the seabed, and extent of water movement. These factors are obviously interrelated and can affect the extent of corrosion in different ways. In addition,

many shipwrecks are in relatively shallow offshore waters and over a long period significant changes can occur in the wreck site conditions which serve to complicate the corrosion patterns. Such changes could be either natural, such as shore line shifting, or man-made, such as pollution and deoxygenation of water following growth of nearby cities, the indiscriminate use of explosives, and salvage or excavation attempts.

The combined effect of all these complex and often interrelated factors is that *each object must be considered individually* when attempting to evaluate its corrosion history or when considering its recovered condition. Some general observations can be made concerning metal corrosion but exceptions are very common, and quite often apparently identical objects, only a few metres apart on the same site, have corroded in totally different ways.

In this chapter we will first look at the general factors which influence metal corrosion before discussing each of the major shipwreck metals in more detail. These discussions will be limited to iron, copper, silver, gold, lead, tin, aluminium and their alloys. Modern metals and alloys (apart from aluminium) will not be discussed as this would make the subject much too diverse.

4.2 General factors in marine metal corrosion

4.2.1 Basic corrosion theory

It is difficult to understand, and hazardous to interpret, metal corrosion in shipwrecks without a thorough knowledge of corrosion theory. In this section the basic concepts of corrosion theory will be reviewed but readers are urged to consult more comprehensive texts for a fuller understanding.[144,145] The

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points covered in this section are only intended as a guide to those aspects of metal corrosion which are relevant to shipwreck materials.

When a metal, such as iron, is placed in water in the presence of atmospheric oxygen, corrosion occurs. The overall reaction, in the case of iron is

$$4Fe + 2H_2O + 3O_2 \rightarrow 4FeO(OH) \qquad (4.1)$$

with FeO(OH) forming the rust-red deposits typical of iron corrosion. However, if this reaction is examined closely it is found to consist of a number of separate reactions occurring at different places on the metal surface.

In some areas Fe^{2+} ions are being produced by oxidation of the iron metal and the surplus electrons are entering the metal. This reaction, written as

$$Fe \rightarrow Fe^{2+} + 2e^- \qquad (4.2)$$

is known as an *anodic reaction* and the areas where it occurs are the *anodic areas*. In other areas, oxygen will be reduced by accepting electrons from the metal according to the reaction

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \qquad (4.3)$$
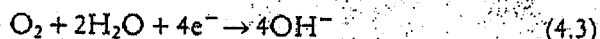
which is known as a *cathodic reaction*, and the areas where it occurs as the *cathodic areas*.

To maintain charge neutrality in the metal both the *anodic and cathodic reactions must occur at the same rate*, i.e. the number of electrons produced and consumed per unit time must be equal. The electrons must also move from the anodic to the cathodic areas and they usually do this through the bulk of the metal. If there is a region of high electrical resistance between the anodic and cathodic areas this will retard the movement of electrons. In this case an accumulation of electrons will occur at the anodic areas, the electro-potential (voltage) of these areas will become more negative, and the anodic reaction will slow down as it is more difficult to push electrons into an area which already has a surplus of electrons. At the same time the cathodic area will become more positive (electron deficient) and the cathodic reaction will also be retarded. This form of corrosion inhibition may occur when the surface of the metal becomes coated with a layer of high electrical resistivity material. The anodic reaction can occur at the metal surface beneath the film, the cathodic reaction at the outer surface of the film and the electrons must pass through the high resistance film when going from the cathodic to anodic areas.

During the corrosion process, positive ions (cations) are generated at the anodic areas and negative ions (anions) are generated at the cathodic areas. To maintain charge neutrality in the solution there must be a net diffusion of cations to the cathodic areas and/or anions to the anodic areas. This diffusion occurs quite readily in solutions of high ionic

conductivity (e.g. seawater). This is one of the reasons why metals corrode faster in seawater than in the lower conductivity fresh water. The anions and/or cations which participate in the general diffusion are the ones most readily moved in the solution. These are not necessarily the same as the ions formed in the cathodic or anodic reactions. For example, in seawater the Cl^- ion, because of its high concentration, is the major anion moving from the cathodic to anodic areas.

In addition to this general movement of ions there must be a specific movement of reactants and products to and from the reactive areas if corrosion is to continue rapidly. For example, in the case of iron corrosion mentioned above, oxygen must be supplied to the cathodic areas to replace that used up in the cathodic reaction. Similarly the Fe^{2+} ions must be

(a)

(b)

Plate 4 (a) Portion of cannonball concretion from *Batavia* (1629) cut to show compositional variation – cannonball's original surface at bottom right, open seawater at top left of photograph.
(b) Micro thin section of the same concretion shows mineral replacement process – conversion of $CaCO_3$ to $FeCO_3$. The dark (red brown) phase is iron oxides while the lighter (bright red) is siderite ($FeCO_3$) – no calcium carbonate is present but note the structure of marine organisms is retained. The white areas are voids, × 300

removed from the anodic areas. The metal ions can be removed by diffusion into the surrounding solution, by formation of insoluble precipitates, or by combination with other species to form complex ions (see *Plate 4*). The course followed will depend on the metal and the solution composition. If a precipitate is formed this may coat over the reactive sites and so reduce the corrosion rate.

Corrosion reactions are essentially oxidation and reduction reactions and like all reactions involving the acceptance or donation of electrons the tendency for these reactions to occur is expressed by their reduction potential. For convenience, these reactions are always tabulated as reduction reactions, that is:

$$\text{Reactants} + \text{Electrons} \rightarrow \text{Products} \qquad (4.4)$$

Reduction potentials (*Table 4.1*) are measured experimentally by placing two separate electrodes in the solution. The oxidation reaction occurs at one electrode and the reduction reaction at the other. The voltage between the electrodes, when no current is flowing, is equal to the difference in reduction potentials of the oxidation and reduction reactions. Abso-

Table 4.1 Standard reduction potentials[190](E^0).

Volts versus hydrogen at 25°C	*Volts*
$Au(OH)_3 + 3H^+ + 3e^- \rightarrow Au + 3H_2O$	1.45
$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$	1.229
$AuCl_4 + 3e^- \rightarrow Au + 4Cl^-$	0.994
$Ag^+ + e^- \rightarrow Ag$	0.800
$Fe^{3+} + e^- \rightarrow Fe^{2+}$	0.770
$Ag_2O_3 + H_2O + 2e^- \rightarrow 2AgO + 2OH$	0.74
$Cu^+ + e^- \rightarrow Cu$	0.522
$H_2SO_3 + 4H^+ + 4e^- \rightarrow S + 3H_2O$	0.45
$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$	0.401
$Ag_2O + H_2O + 2e^- \rightarrow 2Ag + 2OH^-$	0.342
$Cu^{2+} + 2e^- \rightarrow Cu$	0.340
$AgCl + e^- \rightarrow Ag + Cl^-$	0.2223
$SO_4^{2-} + 4H^+ + 2e^- \rightarrow H_2SO_3 + H_2O$	0.20
$Cu^{2+} + e^- \rightarrow Cu^+$	0.158
$S + 2H^+ + 2e^- \rightarrow H_2S\ aq$	0.141
$2H^+ + 2e^- \rightarrow H_2$	0.000
$Ag_2S + 2H^+ + 2e^- \rightarrow 2Ag + H_2S$	-0.037
$Pb^{2+} + 2e^- \rightarrow Pb$	-0.126
$Sn^{2+} + 2e^- \rightarrow Sn$	-0.136
$Cu(OH)_2 + 2e^- \rightarrow Cu + 2OH^-$	-0.224
$PbCl_2 + 2e^- \rightarrow Pb + 2Cl^-$	-0.262
$PbSO_4 + 2e^- \rightarrow Pb + SO_4^{2-}$	-0.356
$Cu_2O + H_2O + 2e^- \rightarrow 2Cu + 2OH$	-0.361
$Fe^{2+} + 2e^- \rightarrow Fe$	-0.409
$3FeO(OH) + e^- \rightarrow Fe_3O_4 + H_2O + OH$	-0.49
$PbO + H_2O + 2e^- \rightarrow Pb + 2OH$	-0.576
$Ag_2S + 2e^- \rightarrow 2Ag + S^{2-}$	-0.705
$Zn^{2+} + 2e^- \rightarrow Zn$	-0.763
$Fe_3O_4 + 4H_2O + 8e^- \rightarrow 3Fe + 8OH$	-0.91
$SnO_2 + 2H_2O + 4e^- \rightarrow Sn + 4OH$	-0.945
$Al_2O_3 \cdot 3H_2O + 6e^- \rightarrow 2Al + 6OH$	-2.33

This data refers to solutions when all ionic species are at unit activity.

lute reduction potentials cannot be measured so for convenience the reaction

$$2H^+ + 2e^- \rightarrow H_2 \qquad (4.5)$$

is arbitrarily given the reduction potential of 0.000 volts at 25 °C when the pressure of H_2 is one atmosphere and the activity of the H^+ is unity. *All other potentials used in this book are expressed relative to this potential.*

The pH of a solution is defined by the following expression:

$$pH = -\log_{10} a_H \qquad (4.6)$$

where a_H is the activity of H^+. (Activities, written as a_x for species x, are related to concentrations written as $[x]$, by the relationship

$$a_x = \gamma_x [x] \qquad (4.7)$$

where γ_x is the activity coefficient of x. The molal activities for major ions in seawater are shown in *Table 4.2*.)

The reduction potentials of all reactions depend on the activities of the species taking part in the reaction. If all of these activities are equal to unity then the potential is called the *standard reduction potential* (E^0). This is the potential which normally appears in tables such as *Table 4.1*. If the species are not at unit activity then the reduction potential (E) can be calculated from E^0 by using the Nernst equation. For example, the reaction

$$Fe^{2+} + 2e^- \rightleftharpoons Fe \qquad (4.8)$$

has E^0 of -0.409 volts. At 25 °C, E is given by

$$E = E^0 + \frac{0.059}{n}\log [a_{Fe^{2+}}/a_{Fe}] \qquad (4.9)$$

where n is the number of electrons involved (in this case $n = 2$), and a_{Fe} is the activity of the iron in the metal. For pure iron ($a_{Fe} = 1$) in a solution containing Fe^{2+} at activity of 10^{-3}M, E is -0.498 volts. The activity of pure solids is unity but the activity in alloys and solid solutions is dependent on elemental composition and distribution, and can vary from one phase to another in the same alloy (see *Plates 5* and *6*). The anodic reactions in corrosion process are oxidation reactions and these are simply the reverse of the reduction reactions. The corresponding oxidation potentials have the same numerical value as the reduction potential but with the opposite sign. For example, the oxidation reaction

$$Fe \rightarrow Fe^{2+} + 2e^- \qquad (4.2)$$

has an oxidation potential of $+0.409$ volts. To avoid confusion all potentials referred to in this book are reduction potentials irrespective of whether the equations are written in the oxidation or reduction form.

Metals are commonly described as 'active' if they have a negative E^0 value for their reduction reaction
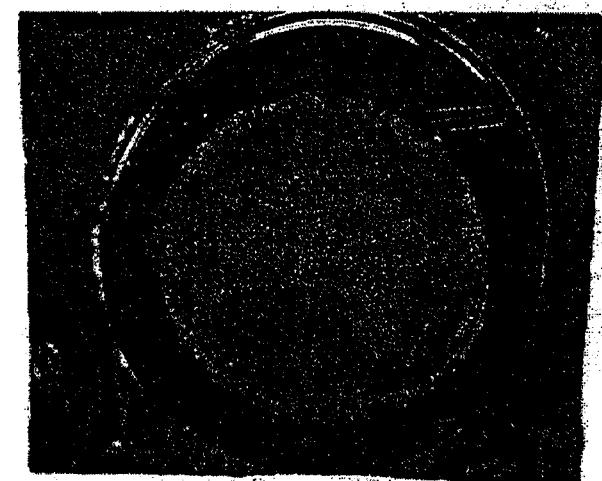
Table 4.2 Major anions in seawater.[198]

Ion	Total molality	g/kg seawater	Free ion %	Molal activity
Cl	0.56	19.85	100	0.319
SO_4^{2-}	2.909×10^{-2}	2.79	69.9	2.20×10^{-3}
HCO_3	1.86×10^{-3}	0.113	74	1.04×10^{-3}
CO_3^{2-}	1.1×10^{-4}	0.007	10.2	2.42×10^{-6}

Mean analytical concentrations, free ion per cent and activities of the main anions found in seawater of salinity 35%o, 25°C, pH 7.87.


(a)

(b)

Plate 5 (a) Sectioned cast iron cannonball, *Batavia* (1629). Note residual metal core does not occur in centre of cannonball due to differences in corrosion rates. Cannonball mounted in polyester for sectioning, × 2.

(b) Micrograph of partially corroded cast iron. Ferrite phase (B) adjacent to graphite nests (A) has corroded completely, and corrosion has commenced on the ferrite component of the pearlite (C), × 600

in a solution of the metal ions at an activity equal to 1.0. Such metals tend to corrode readily. Examples from *Table 4.1* are tin ($E^0 = -0.136$ volts), iron ($E^0 = -0.409$ volts) and zinc ($E^0 = -0.763$ volts). Metals with positive E^0s are regarded as *noble* and they do not corrode readily. Examples are gold ($E^0 = +1.45$ volts) and silver ($E^0 = +0.800$ volts). However, the E value for the corrosion reaction only
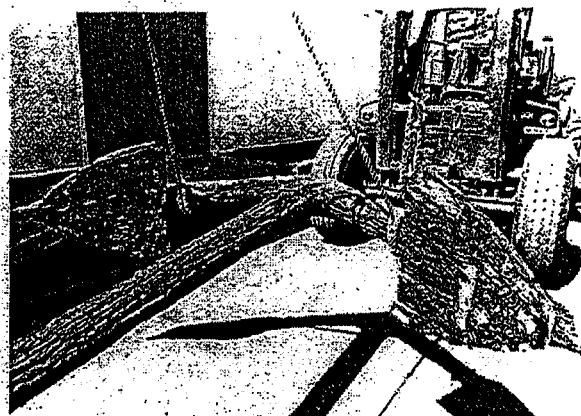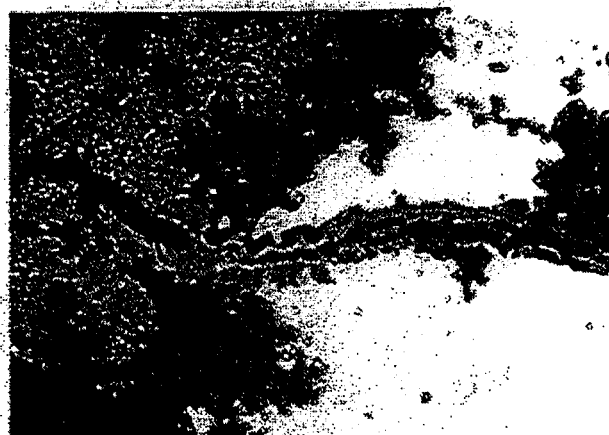
Plate 6 (a) Wrought iron anchor (1802). Note wood grain pattern resulting from attack on metal adjacent to slag inclusions.

(b) Micrograph of corrosion of wrought iron attack occurring deep into metal along slag inclusions, × 200

shows if a particular overall reaction can occur, it gives *no indication of the rate* at which the reaction will occur.

When a piece of metal is placed in seawater, a large number of different oxidation and reduction reactions can occur on the metal surface. Consequently the metal acquires a potential which reflects the combined rate and potential of all these reactions. This potential is thus a mixed electrode potential and in corrosion studies is referred to specifically as the

corrosion potential (*E corr.*) (*Table 4.3*). All reactions occurring at the metal surface which have an *E* more positive than *E corr.* will proceed in the reduction direction (accept electrons from the metal) and so collectively form the cathodic reactions. Conversely all reactions with *E* more negative than *E corr.* will proceed in the oxidation direction (donate electrons to the metal) and collectively form the anodic reactions. For an inert electrode in the solution (e.g. platinum) the measured potential will depend solely on the reactions between species in the solution. The measured potential in this case is referred to as the *Eh* of the solution.

Table 4.3. Corrosion potentials of metals in seawater (volts vs hydrogen at 25°C).

Metal	E corr. (V)	
Silver[a]	0.26	least active
Admiralty brass[b] (71 Cu, 28 Zn, 1 Sn)	0.10	
Red brass[b] (85 Cu, 15 Zn)	0.09	
Copper[b]	0.07	
Yellow brass[b] (65 Cu, 35 Zn)	0.04	
Muntz metal[b] (60 Cu, 40 Zn)	−0.03	
Lead[a] (after 24 hours immersion)	−0.06	
Mild steel[b]	−0.21	
Tin Lead solder[c]	−0.26	
Al + 4% Cu – solid solution[d]	−0.36	
CuAl₂[d]	−0.40	
Al + 2% Cu – solid solution[d]	−0.42	
Al[d]	−0.52	
Al + 7% Mg – solid solution[d]	−0.55	
Cadmium[c]	−0.56	
Zinc[c]	−0.86	
α (Al – Mg)[d]	−0.91	most active

[a] Stationary seawater.[138]
[b] Flowing seawater.[199]
[c] Seawater.[199]
[d] Potentials in 53 gpl NaCl, 3 gpl H₂O₂.[200]

When two metals with different *E corr.* values are brought into electrical contact electrons will flow from the metal with the lower *E corr.* value into that with the higher *E corr.* value. With good electrical contact the metals are at the same potential which is between the values of the individual uncoupled metals. This electron flow will be sustained by a change in the rates of the anodic and cathodic reaction on the metal surfaces. On the metal with the lowest *E corr.* the anodic reaction rates will increase while the cathodic reaction rates decrease. This generates a surplus of electrons which then flow into the metal with higher *E corr.* value. At this metal surface the cathodic rates increase, the anodic rates decrease and the surplus electrons are consumed. As the anodic reactions are usually metal dissolution reactions (such as shown in Equation 4.2), the coupling of two pieces of metal with different *E corr.* values will cause

an increase in the corrosion rate of the piece with lowest *E corr.* and a decrease in that with the highest *E corr.* If the two metals so coupled together have different composition then this is known as *galvanic coupling* with the noble (higher *E corr.*) metal corroding less (*galvanic protection*) and the active (lower *E corr.*) metal corroding more (*galvanic corrosion*). For example, if in seawater iron (*E corr.* −0.21 volts) is in contact with silver (*E corr.* +0.26 volts) the iron will corrode faster than normal but the silver will be protected and corrode less. The actual change in corrosion rates depends not only on the difference in *E corr.* values but also on the relative surface areas of the two metals and the reaction kinetics.

As *E corr.* values depend on both the metal and solution composition a similar effect can also be observed when different parts of the metal object are exposed to different local environments. A copper bar exposed to oxygenated seawater will have a more positive *E corr.* than one which is covered by concretion. When both these areas occur on the same copper bar the major cathodic reaction (oxygen reduction) occurs on the exposed area while the anodic reaction (copper dissolution) occurs mainly in the concreted area. In this case the portion of the covered metal near the concretion edge will suffer accelerated corrosion. Many variations on this phenomena are encountered and these are collectively referred to as *differential concentration* corrosion. When the effect is due to different oxygen concentrations, as in the above use, it is called *differential aeration* or *differential oxygen* corrosion (see *Plate 7*).

Plate 7 Copper hull bolt *Rapid* (1811). Note necking produced as result of differential aeration corrosion. When found, sections of this bolt were covered with wood remnants from the hull
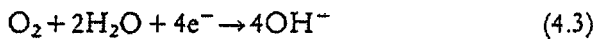
4.2.2 Pourbaix diagrams

Pourbaix diagrams are widely used in the study of corrosion of metals. These are graphs with solution *Eh* on the vertical axis and pH on the horizontal. All other possible factors are constant over the whole of the diagram. The Pourbaix diagrams are basically a

chemical stability map which shows, very quickly, which compound or ionic species is the thermodynamically stable species at particular *E*h and pH values. Typical Pourbaix diagrams are shown in *Figure 4.1*.

A Pourbaix diagram consists of a number of discrete regions bounded by a series of pH and *E*h dependent and/or independent lines. When considering metal corrosion these regions are grouped into the three types: inert, passive and active. The inert region, which is commonly at the lowest *E*h, is that region in which the metal itself is the most stable species, i.e. corrosion cannot occur. The passive regions are those in which an insoluble protective compound (often an oxide) is the most stable product. In these areas some initial corrosion will occur until a surface film is formed to protect the underlying metal. The passive regions for the metal are defined as thermodynamically unstable but kinetically inert as regards metal corrosion. The active regions are those in which the most stable species is either the metal ions in solution or a non-protective insoluble compound. In these areas corrosion will occur and will continue until the metal is consumed.

In Pourbaix diagrams the overall composition of the solution is always specified, for example pure water, seawater, seawater with 10^{-3} molar total sulphide added, and so on. Each metal in each solution produces a different Pourbaix diagram and when studying metal corrosion in a specific solution it is generally necessary to construct a Pourbaix diagram from known thermodynamic data.

A common upper limit in *E*h for Pourbaix diagrams corresponds to reaction

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \tag{4.3}$$

The *E* for this reaction is given by

$$E = 1.228 - 0.059 \, pH \tag{4.10}$$

when the pressure of oxygen is one atmosphere. The line corresponding to Equation 4.10 is designated (a) in Pourbaix diagrams. If the potential of the system rises above this level then oxygen evolution will commence.

A common lower limit for *E*h corresponds to the reaction

$$2H^+ + 2e^- \rightarrow H_2 \tag{4.5}$$

where potential is given by

$$E = -0.059 \, pH \tag{4.11}$$

when hydrogen pressure is one atmosphere. If the solution potential drops below this value hydrogen evolution will occur. This potential is designated by the line (b) on Pourbaix diagrams. In practice, potentials beyond those given by Equations 4.10 and 4.11 do occur as oxygen (and hydrogen) evolution is not rapid until the potential is significantly higher (or lower) than that given by these equations.
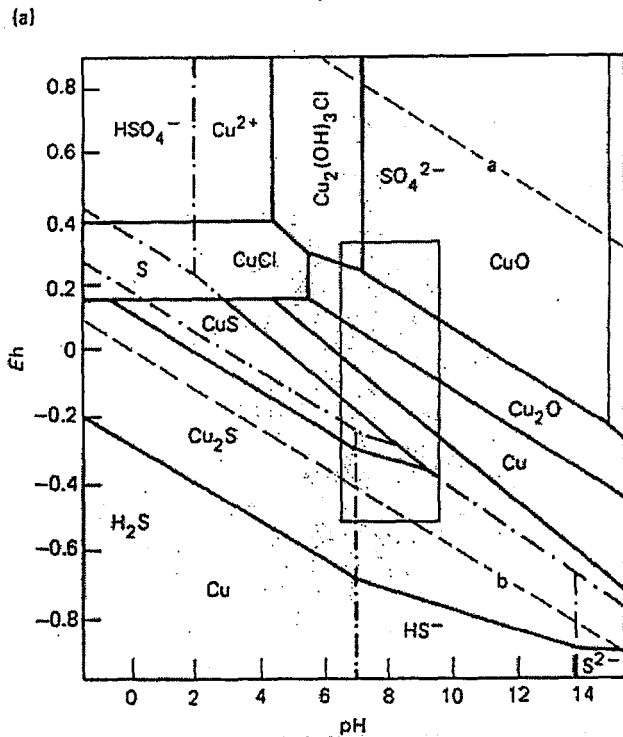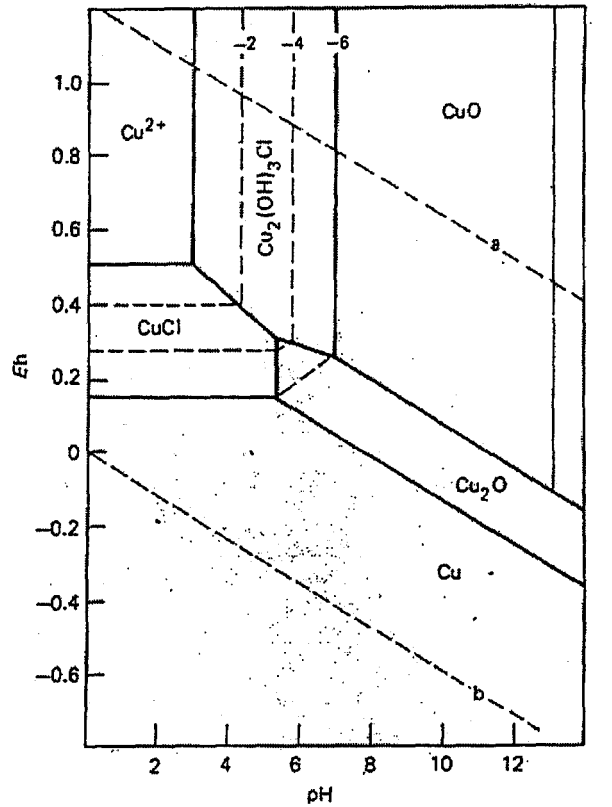
Figure 4.1 (a) Pourbaix diagram for pure copper in aerobic seawater at 25 °C. Dissolved Cu at 1M.

(b) Pourbaix diagram for pure copper in anerobic seawater containing 10^{-3} M additional S^{2-}, at 25 °C. Dissolved Cu at 10^{-2} M. Area within central rectangle represents Eh/pH conditions commonly found in seawater and marine sediments

4.3 Site conditions and corrosion

The main factors influencing the rate and mechanism of corrosion are strongly interrelated, and a change in one usually produces changes in others. As a result the relationships between site, artefact condition and corrosion products are often complex. In this section some of the more important factors influencing on-site corrosion will be examined briefly. For a further description, works on metal corrosion should be consulted.[144,145]

4.3.1 Dissolved oxygen

For metal exposed to seawater the main cathodic reaction is usually oxygen reduction (Equation 4.3). The corrosion rate in such cases is frequently controlled by the availability of dissolved oxygen at the cathodic site.

Surface water is generally saturated with oxygen from the atmosphere. The amount of dissolved oxygen in surface seawater depends on temperature as shown below.[146]

Temperature (°C)	0	5	10	15	20	25
Oxygen (mls/litre)	8.1	7.2	6.4	5.9	5.4	5.4

In the upper layers of the ocean, to a depth of 500 m where most shipwrecks occur, the oxygen content is very dependent on the biological activity and the rate of mixing with surface layers. Estuarine and polluted waters often have very low dissolved oxygen levels due to high oxygen uptake by micro-organisms. Low oxygen levels are also encountered underneath marine concretions and below the seabed even on well-oxygenated sites. In this case the low levels are mainly the result of biological uptake of oxygen combined with slow exchange with external seawater. In such cases the rate of corrosion may well be controlled by sulphate-reducing bacteria (see Section 4.3.6) rather than dissolved oxygen.

During excavation the dissolved oxygen content and Eh of the seawater should be measured to give a better understanding of the corrosion processes.

4.3.2 pH

The pH of normal seawater is well buffered by the action of the HCO_3^-/CO_3^{2-} equilibrium. Any addition of H^+ or OH^- to the system is partially absorbed by conversion of carbonate to hydrogen carbonate, or vice versa, i.e.

$$HCO_3^- \rightleftharpoons CO_3^{2-} + H^+ \tag{4.12}$$

Other minor buffer systems are also present. Normal seawater has a pH range between 7.5 and 8.2[147] but pH can vary from 6.5 to 9.5 in stagnant waters and in the sediments beneath the seabed. Some of the changes may be caused by the action of sulphate reducing bacteria. Values of pH below 6.5 are found in the concretions surrounding actively corroding metals – in the case of iron the pH is usually 4.8. The HCO_3^-/CO_3^{2-} buffer system is weaker or virtually absent in most estuarine and freshwater systems and as a result the pH of these can vary widely depending on local circumstances.

To obtain a better understanding of corrosion rates and mechanisms the on-site pH should be measured not only in the seawater but also in the sediments and beneath the concretions on a range of different metals. A flat surface pH electrode is very useful for these measurements.

If values of both Eh and pH are available then it is possible to make use of Pourbaix diagrams to help understand the corrosion mechanisms and products.

4.3.3 Temperature

The effect of temperature on corrosion rates is complicated by its effects on biological growth. In the absence of biological effects the rate of corrosion would be expected to approximately double for every 10 °C rise in temperature. However, the increased growth rate of biological organisms in warmer water has the opposite effect as it produces a protective concretion on the metal surface. For example, isolated test panels of mild steel at many widely separated geographical locations all showed a corrosion rate of approximately 0.11 mm/year.[144] By contrast copper, which does not support extensive marine growth, was found to corrode approximately twice as fast for every 10 °C temperature rise.[148] Other metals on shipwrecks would be expected to show temperature corrosion effects somewhere between these two extremes depending on the extent of concretion formation. Water temperature should be measured on site and, when possible, the daily and annual ranges should be noted.

4.3.4 Water movement

Movement of water across the wreck site can affect corrosion rates through metal erosion, destruction of protective films or indirectly by changing the rate of oxygen supply to the cathodic reaction.

At one extreme of water movement are those wreck sites in high surge areas where the current and wave actions are so strong the artefacts are physically rolled and bumped back and forth across the seabed. In this case mechanical damage and abrasion are the main causes of 'corrosion' and generally artefacts do not survive long under these conditions unless they

can come to rest in some crevices or depression in the seabed.

Slightly less extreme are those sites where the surge action is normally not strong enough to shift the objects but is fast enough to pick up and carry seabed debris (sand, grit, shells, etc.). Under these conditions the metals are subject to a form of sand-blasting and this can cause very rapid erosion. This effect is most pronounced with copper alloys where formation of protective marine growth is limited.

In contrast, if the seawater is very still or stagnant for long periods then the bottom and near-bottom waters become depleted in oxygen. This condition is most frequently encountered in deep bays which have a narrow shallow entrance. The corrosion behaviour of metals in such an environment is often markedly different from that found in oxygenated sites.

The movement of water across a metal surface can prevent formation of protective corrosion product films. These films are formed when the accumulation of metal ions from the anodic reaction reaches saturation and precipitation follows. If water movement rapidly removes the ions as they are formed, saturation is not achieved and films do not form. Corrosion rates are generally much higher in the absence of corrosion product films.

One extreme of water movement occurs with objects permanently or occasionally exposed to the atmosphere by wave action. This causes periodic wetting and drying of the object, increased oxygen availability, physical destruction of protective concretions and corrosion products, larger variations in temperature and concentration of aggressive salts. Estuarine and river wrecks are also subject to major water level changes as a result of floods and drought. As a result metal corrosion rates are higher near the air-water interface.

4.3.5 Salinity

In general metal corrosion rates increase with increasing salinity. Wrecks in fresh water generally have better preserved metal artefacts than do similar wrecks in seawater.

The major ions in seawater are Na^+, K^+, Ca^{2+}, Mg^{2+}, Cl^-, SO_4^{2-} and HCO_3^-. The salinity of seawater is defined as the total amount of dissolved salt, in grams, contained in one kilogram of water and is expressed as ‰S (see Chapter 1). Salinity in open ocean can vary slightly, but is generally around 35‰S. In coastal regions considerable variations in salinity can occur, major influences being the presence of fresh water run-off from rivers and high evaporation rates. Even though total salinity can change appreciably, the relative concentration of the major ions remains remarkably constant. In rivers

and inland lakes the salinity can vary from virtually zero up to saturated salt solutions. In these cases the ratios of the major ion concentrations are not constant and considerable variation can occur from those found in seawater. The major anions in seawater are generally more important than are the major cations, in metal corrosion. The anion concentrations and activities are given in *Table 4.2*.

Salinity can affect metal corrosion rates in a variety of ways. For example, by providing an ionic conducting solution for the transfer of ions between anodic and cathodic areas, by forming protective surface layers on some metals and destroying those on others, by altering the amount of oxygen dissolved in the water, by supplying ions which can catalyse corrosion reactions, etc. Several of these features will be discussed in detail in other sections, but, in general, an increase in water salinity produces an increase in metal corrosion rates.

4.3.6 Sulphate-reducing bacteria

If the oxygen content of the water immediately in contact with the metal becomes very low then the Eh of this water can fall below the hydrogen evolution potential. Such oxygen depletion occurs when (1) the seawater itself becomes anaerobic due to pollution or high microbiological activity (2) when the metal is buried beneath the seabed and oxygen diffusion from the overlying seawater is restricted or (3) when the artefact becomes covered by a thick layer of marine growth which restricts the oxygen supply.

Once the Eh falls below the hydrogen evolution potential the main cathodic reaction in the metal corrosion process becomes

$$2H^+ + 2e^- \rightarrow H_2 \qquad (4.5)$$

In the absence of catalysis this reaction is generally fairly slow on most metals in the seawater pH range and consequently their corrosion rate is low. The action of sulphate-reducing bacteria speeds up this reaction since their metabolism converts sulphate to sulphide ions which can subsequently react with the metal ions to produce metal sulphides, such as FeS, and elemental sulphur on which the hydrogen evolution reaction occurs more rapidly than on the metal surface. This is also assisted by the enzyme hydrogenase, produced by the bacteria which catalyse the reaction. The sulphate reducing bacteria may also increase the corrosion rate through formation of acids which lower the pH. The resulting corrosion rates are much higher than those in similar environments with low bacteria population.[144]

The growth of anaerobic sulphate reducing bacteria in seawater requires both the absence of dissolved oxygen and the presence of a suitable organic material food source. Under normal conditions this

organic material is derived from the seawater and as a result the maximum bacteria populations are found in the upper levels of the seabed sediment. A typical bacteria-depth relationship[149] is shown in *Table 4.4*.

Table 4.4 Typical distribution of sulphate reducing bacteria in marine sediment.[149]

Depth into seabed (cm)	Bacteria per gram sediment
0 – 2.5	38 000 000
2.5 – 5.0	940 000
10 – 12.5	88 000
23 – 25.5	36 000
35 – 37.5	2 400
48 – 51	400
74 – 76	180
99 – 102	330
150 – 203	250
201 – 203	130
251 – 254	290

In the absence of a supplementary food source bacterial numbers are not significant below more than approximately 50 cm into the sediment. Below about 50 cm metal corrosion rates should decrease substantially with increasing burial depth. This situation should apply to isolated metal objects not associated with other wreck material.

A shipwreck site is not typical of the normal seabed. The organic materials, particularly wooden hulls, provide a supplementary food source for sulphate reducing bacteria and this enables them to exist for a considerable depth below the seabed. As a result the effects of sulphate-reducing bacteria can be seen in the corrosion products on all buried metal artefacts on shipwrecks.

With concentrated artefacts on or above the seabed, sulphate-reducing bacteria occur in the concretion. No detailed studies have been carried out on the distribution of the bacteria in these concretions but features such as nature and distribution of corrosion products, porosity of concretion and available food sources indicate that the majority of the bacteria are not near the metal surface but rather in the inner and middle regions of the concretion layer.

4.3.7 *Galvanic coupling*

If two different metals are in physical contact on the wreck site then the metal with the lower *E corr.* (active) will corrode faster than normal and that with the higher *E corr.* (noble) will be protected. Generally the greater the difference in *E corr.* values the more pronounced is the galvanic corrosion and protection. Values of *E corr.* for various metals in sea-

water are shown in *Table 4.3*. The extent of galvanic corrosion also depends on the relative surface areas of the two metals; the effect being more pronounced in the metal with the smaller surface area (see Section 4.2.1).

In theory, galvanic corrosion should always be present when two dissimilar metals are in physical, i.e. electrical, contact and should immediately cease when the metals are separated. While this generally occurs in shipwrecks some exceptions have been found. For example, Campbell and Mills[139] have reported an absence of galvanic corrosion among the metal artefacts of a Scilly Island wreck, even though the artefacts were piled up on top of each other. On the other hand, on a Western Australian wreck, evidence suggested a form of protection of copper by iron even though there was no physical contact between the metals.[138]

4.3.8 *Marine growths*

The growth of marine organisms on artefact surfaces is a very important factor in marine metal corrosion. First, the marine growth provides a physically protective barrier between the artefact and the seawater. This barrier reduces the mechanical abrasion of the metal by seaborne grit and sand. If the marine growth is prolific it can spread out over different artefacts and the surrounding seabed. This growth cements the artefacts together and 'welds' them into the seabed. When this happens the artefacts are virtually immune to physical damage as even the most severe storms cannot dislodge them.

A second effect of marine concretion growth is that the transfer of chemical species between the metal surface and the open seawater is drastically reduced and this can result in the formation of a microenvironment on the metal surface, beneath the concretion, which is substantially different from open sea conditions. Such microenvironments frequently have low pH, high Cl^- content and low oxidizing abilities.[17] The marine growth also provides high concentrations of certain chemicals at the metal surface. The most obvious example of this is the high S^{2-} levels produced by sulphate-reducing bacteria.[17]

4.4 Iron

4.4.1 *Summary*

The corrosion of iron in nearly all marine environments is dominated by the formation of massive concretions which cover iron artefacts under most conditions. These concretions form a barrier between the iron and the surrounding environment and result in the creation of a significantly different micro-

environment on the surface of the iron. As a result the iron corrodes in an environment which is almost independent of external conditions.

The long-term corrosion rate for isolated mild steel in seawater is approximately 0.11 mm/year.[144] This rate is remarkably constant over a wide range of geographical locations and temperatures. Small additions of alloying elements appear to have little effect on this corrosion rate. The normal long-term corrosion rate of both wrought and cast iron on shipwrecks seems to be around 0.1 mm/year but large variations from this regularly occur.[141] These variations can generally be explained in terms of interreaction with other shipwreck material.

Wrought iron is essentially pure iron. It contains less than 0.2% carbon by weight and the major compositional variation is the presence of slag inclusions. In the forging process these slag inclusions are flattened and squeezed out along the directions of working. On the seabed these slag inclusions allow penetration of seawater deep into the bulk of the metal. Corrosion thus occurs not only on the outer metal surface but also along the walls of the slag inclusions (see *Plate 6b*). This results in the wood grain appearance of the metal which is typical of wrought iron recovered from shipwrecks (see *Plate 6a*). The corrosion products of wrought iron do not retain the shape of the original artefact. However, when all the iron has corroded the original shape can often be recovered from the impression left in the concretion.

Cast iron typically contains 2–6% carbon by weight, some of which is present in the iron as graphite. During corrosion the iron-containing phases of cast iron are corroded but the graphite remains as a three-dimensional network which retains the original shape of the artefact. (See *Plate 5*). The nature of the corrosion products renders this graphitized zone very chemically unstable when exposed to the atmosphere. Consequently the graphitized zone can readily and rapidly disintegrate after excavation if not treated correctly.

The main corrosion products from marine iron corrosion are $FeO(OH)$, Fe_3O_4, FeS, $FeCO_3$ and $FeCl$ containing compounds which still have to be positively identified.

4.4.2 Concretion formation

The most striking feature of iron corrosion is the formation of thick encapsulating concretions (*Plate 4*). Concretions form on iron buried beneath the seabed and on that exposed to seawater. In both cases the concretion is formed by the iron corrosion products interacting with material adjacent to the iron.

Iron is not a biologically toxic material and any iron immersed in seawater is rapidly colonized by marine organisms. This is often referred to as fouling. These organisms build up a layer of skeletal material, predominantly $CaCO_3$. The subsequent diffusion of Fe^{2+} and Fe^{3+} from the underlying corroding iron produces chemical changes in this biological material. This form of concretion growth was found on the *Batavia* wreck.[17]

The *Batavia* site, 28° 30' S and 113° 45' E, is in an area of prolific marine growth. During the first few years after shipwreck the exposed iron was covered with a layer of coralline algae. This then provided a suitable substrate for a secondary growth of seaweeds, hard corals, molluscs, etc. The marine growth formed a rough outer surface which trapped sand particles, coral fragments and other debris swept up off the seabed by surge and wave action. Subsequent marine growth overlayed both the bottom debris and the earlier growths and so incorporated both into the concretion. Such marine growth produces a layer of low porosity on the surface of the iron which greatly retards the interchange of dissolved species between the metal and the external seawater. The oxygen content of the entrapped water, in contact with metallic iron, becomes depleted and the dominant cathodic reactions then occur inside the concretion layer (Section 4.4.4). The anodic reaction still occurs at the metal surface and generates there an acidic solution (pH 4.8) rich in Fe^{2+} and Fe^{3+} ions (Section 4.4.3). The increase in acidity is due to hydrolysis reactions such as $Fe^{2+} + H_2O \rightarrow Fe(OH)^+ + H^+$. This separation of anodic and cathodic reactions produces a corrosion system similar to that encountered in crevice corrosion.[144,150]

Charge neutrality is maintained by the outward diffusion of cations, initially mainly Fe^{2+}, Fe^{3+} and H^+, and the inward diffusion of anions from the seawater. These anions are predominantly Cl^- as these are the most readily available in seawater due to their high concentration (*Table 4.2*). This inward diffusion of Cl^- ions produces a very high chloride content in the iron corrosion products and concretions. Conversely, there is no major force producing an inward diffusion of cations, such as Na^+, from the seawater into the corrosion products and as a result very little sodium is found in marine iron corrosion products.[17]

As the iron-rich acidic solution diffuses out from the metallic iron it first passes through the corrosion product region. This is the volume, originally occupied by metal, that now contains iron corrosion products (called graphitized zone in cast iron). As the ions diffuse through this region they scavenge acid soluble impurities from the corrosion products; principally sulphide, phosphide and alkali and alkaline earth metals. As a result the iron corrosion product region contains lower concentrations of these elements than does the original metal, when expressed in weight/unit volume (see *Table 4.5*). Apart from the

Table 4.5   Element distribution in corroding concreted cast iron.[154]

Element	Residual metal	Graphitized zone	Inner concretion	Outer concretion	Normal reef material
Fe%	~94	~55	49.8	1.2	<0.03
C%[a]	4.6	5.3	2.6	11.1	10.9
P%	0.22	0.18	0.39	ND	ND
S%	0.55	<0.01	2.5	0.03	ND
Si%	0.71	1.6	0.25	0.19	0.23
Ca	115 ppm	20 ppm	0.08%	34.6%	32.9%
Na	120 ppm	75 ppm	0.16%	0.74%	0.56%
Co ppm	150	144	ND	ND	ND
Mn ppm	455	650	ND	ND	ND
Ni ppm	45	40	ND	ND	ND
K ppm	60	5	ND	ND	ND
Density (g/cm³)	~7.2	~2.7	~2.0	~1.8	~1.8

[a] Carbon present in graphite, Fe_3C, CO_3^{2-} minerals and organic compounds.
ND = not determined.

Data in this table was obtained from the concretion, and associated cannonball, shown in *Plate 4*. The data for reef material was taken from an area approximately 200 m from the *Batavia* wreck site.

pick-up of minor impurities, no changes appear to occur in the concentration of diffusing species as they pass through the corrosion product layer. The pH of the solution stays remarkably close to 4.8.

Once the diffusing ions pass out of the corrosion product region they come into contact with the concretion which contains, at least initially, a significant amount of $CaCO_3$. In the concretion, Fe^{2+} ions interchange with Ca^{2+} in the $CaCO_3$ to produce $FeCO_3$. Some of the $CaCO_3$ is also dissolved by the H^+ forming $Ca(HCO_3)_2$ which causes the pH of the solution to increase. The increasing pH then results in the gradual precipitation of Fe^{2+} and Fe^{3+} as oxides, hydrated oxides and hydroxy chlorides. These fill holes and pores in the concretion and so form an iron cementing matrix to replace the original calcite matrix which is slowly dissolving. Reaction between iron ions and the S^{2-} ions produced by sulphate reducing bacteria, result in the formation of FeS and elemental sulphur:

$$2Fe^{3+} + S^{2-} \rightarrow 2Fe^{2+} + S \qquad (4.13)$$

and

$$Fe^{2+} + S^{2-} \rightarrow FeS \qquad (4.14)$$
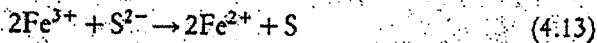
The end result of these processes is that the inner concretion becomes a replica of a purely marine growth but with the $CaCO_3$ of the marine organisms virtually entirely replaced by iron corrosion products (*Plate 4*). In the inner area of the concretion final calcium concentrations are of the order 0.01 to 0.5% by weight compared to approximately 30–35% in original material (*Table 4.5*).

The outer layer of the iron concretions is approximately the same composition as the marine growths on inert materials. The major differences are the presence of up to 2% iron and small, but significant, amounts of inorganic $CaCO_3$. The iron presumably originates from the underlying iron rich layers. The inorganic $CaCO_3$ results from the precipitation of calcium which had dissolved in the inner regions of the concretion and then diffused outwards into the higher alkalinity outer regions. The inorganic $CaCO_3$ can be distinguished from the organic $CaCO_3$ by its different morphology at the microscopic level.

When iron is continuously buried beneath the seabed, negligible marine growth occurs but a hard concretion can still be formed provided the seabed material contains $CaCO_3$ (shell fragments, coral debris, etc.). The mechanism here appears to be basically the same as for exposed iron. As the iron-rich acidic solution diffuses into the surrounding seabed material it dissolves some $CaCO_3$ and precipitates iron compounds which act as a binding cement. Further out from the object the previously dissolved calcium reprecipitates, due to increasing pH, and forms a second cementing layer. As a result any material in the seabed next to the corroding iron is incorporated into the concretion.

The two major differences between exposed and buried iron concretions are the lower oxidation state of the iron compounds and the more random assortment and orientation of biological materials in the buried concretions. Fe_3O_4 is the main iron oxide component of buried concretions compared with FeO(OH) and Fe_2O_3 in exposed concretions.

4.4.3 Metal dissolution (Anodic Reactions)

The anodic reaction in the corrosion of iron is basically,

$$Fe \rightarrow Fe^{2+} + 2e^- \qquad (4.2)$$

which then hydrolyses to produce an acid solution, pH 4.8

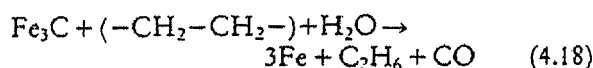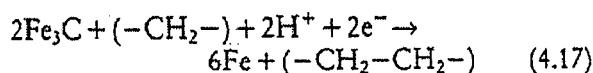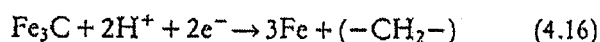$$Fe^{2+} + H_2O \rightarrow Fe(OH)^+ + H^+ \qquad (4.15)$$
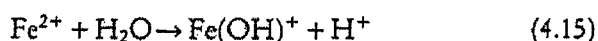
In practise, however, this is a gross simplification of the actual reactions occurring on the metallic iron surface.

In cast iron the situation is complicated as the high carbon contents of cast iron result in the formation of several different solid phases (see *Plate 5b*). The principal phases in cast iron are ferrite (essentially pure iron), pearlite (a combination of ferrite and cementite), cementite (Fe$_3$C) and graphite. There are also generally present, in varying amounts, phosphorus (as iron phosphide), silicon (dissolved) and sulphur (as metal sulphides). All of these phases either participate in or are affected by the corrosion processes.

In partially corroded cast iron, near the original artefact surface, only the graphite remains out of the phases initially present. Closer to the residual metal core, needles of cementite start to appear among the graphite. Deeper into the corrosion layer areas of pearlite appear and right near the residual metal surface there are sections of partially corroded ferrite. From this it is apparent that the susceptibility of the iron phases to corrosion is markedly different and, going from the most readily attacked to most inert, the order is ferrite, pearlite, cementite, graphite. This is also the order of increasing carbon content and increasing (less negative) reduction potentials.

A comparison of the concentrations of carbon in the residual metal to that in the corrosion products, shows that a loss of carbon is occuring during corrosion (*Table 4.5*). Metallographic examination showed that the carbon being lost was mainly that portion originally present as cementite (Fe$_3$C) with the graphite phase being unaffected by corrosion. A vacuum distillation at 100 °C of some cleaned partially corroded marine cast iron revealed the presence of appreciable quantities of a smelly water insoluble oil.[151] The smell was the characteristic odour of freshly excavated marine cast iron. This oil was analysed using a mass spectrometer and was found to consist of a mixture of alkenes and alkanes ranging from C$_4$ to C$_{12}$ with a trace of mercaptans. The number and distribution of molecular weights strongly indicated an inorganic origin for the hydrocarbons. The hydrocarbons could be derived from the cementite by cathodic reactions of the type

$$Fe_3C + 2H^+ + 2e^- \rightarrow 3Fe + (-CH_2-) \qquad (4.16)$$

$$2Fe_3C + (-CH_2-) + 2H^+ + 2e^- \rightarrow \\ 6Fe + (-CH_2-CH_2-) \qquad (4.17)$$

$$Fe_3C + (-CH_2-CH_2-) + H_2O \rightarrow \\ 3Fe + C_2H_6 + CO \qquad (4.18)$$

These reactions have been found to give low molecular weight hydrocarbons in short term studies.[152] A slow reaction over centuries could lead to an accumulation of the higher molecular weight components with the lighter components having diffused out through the concretion.

The behaviour of minor components during corrosion, of both cast and wrought iron, appears to be related to their solubility in dilute acid. Those which normally form acid soluble compounds, such as sulphur, phosphorus, the alkaline and alkaline earth metals, have appreciably lower concentrations in the corrosion products compared to that in the original metals. This suggests that these elements are dissolved by the acidic solution (pH 4.8) formed during corrosion and then subsequently swept out into the surrounding concretion. The acid insoluble elements remain in the corrosion product region with little change in their concentration but sometimes with changes in their form. For example, silicon is generally present in the metal as dissolved silicon but in the corrosion product as silica (quartz).

During the corrosion process most of the iron is converted to soluble iron compounds and these are subsequently deposited in the surrounding concretions. A smaller portion, however, remains in the corrosion product region where it is found as FeO(OH), Fe$_3$O$_4$ and an Fe,Cl unidentified compound. The Fe$_3$O$_4$ is very abundant in iron buried beneath the seabed. In normal seawater, chloride can constitute up to 13% of the iron corrosion products by weight.[151]

The corrosion of wrought iron in seawater appears to follow the same chemical pattern as does cast iron. However, as wrought iron consists almost entirely of ferrite with silicate (slag) inclusions, the resultant appearance of corroded wrought iron is quite different from that of cast iron. Typical corrosion patterns for cast and wrought iron are shown in *Plates 5* and *6*.

In cast iron the residual graphite forms a three-dimensional network which holds the corrosion products together and so retains the original shape and surface details (*Plate 5*). This graphite is not present in wrought iron and consequently the corrosion products of wrought iron are soft and non-adherent, with no retention of original shape and surface. The slag inclusions in wrought iron allow penetration of the salt water deep into the bulk of the iron. Subsequent corrosion along the walls of the slag inclusions widens the inclusions and pushes out the slag. As a result crevices are formed in the residual wrought iron which give it a characteristic wood grain appearance (*Plate 6*). As these crevices follow

the original slag inclusions, much useful information on fabrication techniques can be obtained from a study of the crevice patterns.

4.4.4 Cathodic reactions

The main cathodic reactions in iron corrosion appear to take place in the concretion layer rather than on the metal surface. These areas typically contain large (up to 10% by weight) amounts of FeS and elemental sulphur which indicates the presence of sulphate-reducing bacteria.

In buried iron the corrosion product composition suggests that hydrogen evolution, stimulated by sulphate-reducing bacteria, is the major cathodic reaction. This reaction probably also occurs on concreted iron above the seabed but the presence of Fe^{3+} compounds such as $FeO(OH)$ suggests that oxygen reduction, which gives a higher Eh, is also important in these cases.

4.5 Copper

4.5.1 Summary

Of the non-ferrous metals found on shipwreck sites, copper and its alloys with zinc (brass) and tin (bronze) are by far the most common. Both copper and brass sheet was used as a method of protecting wooden[153] vessels from attack by the Teredo worm and from fouling by marine organisms. Copper-based cannon, rudder fittings, keel straps, nails and bolts are also frequently encountered. Copper alloy artefacts are also often derived from the cargo.

The corrosion of copper in seawater is dominated by two properties of copper compounds. First, many

copper compounds are toxic to marine organisms and this greatly reduces the growth of such organisms on copper alloy artefacts. As a result copper alloys are generally found unconcreted or only lightly concreted (See Plate 20). Secondly, the copper ions can exist in two oxidation states, cuprous (I) and cupric (II), at seawater temperatures. The corrosion mechanisms of copper alloys often involve the interactions of the parent metal and copper corrosion products in both the cupric and cuprous states.

A wide range of corrosion products have been found on copper alloy artefacts recovered from marine environments (*Tables 4.6* and *4.7*). The corrosion products most commonly associated with well-oxygenated marine sites are the copper oxides (cuprite and tenorite), cuprous chloride (nantokite) and the basic copper (II) chlorides (atacamite and paratacamite). Under the influence of sulphide ions found in polluted estuaries and marine sediments a range of copper sulphides from covellite (CuS) to chalcocite (Cu$_2$S) is formed. In order to understand the formation of such a diversity of corrosion products and how they are affected by site conditions the electrochemistry of copper in seawater must be considered.

The biological toxicity of copper compounds affects copper corrosion indirectly by retarding marine growth on the copper surface and preserving any wood attached to the copper. As a result copper objects, in particular hull bolts, are often partially covered by wood fragments and are partially exposed. Beneath the wood the oxygen supply is depleted and differential oxygen corrosion cells are formed (Section 4.2.1). This causes increased corrosion (or necking) of the copper (anodic reaction) on the covered edge of the concretions or wood. In addition the gradual chemical decay of the wood releases acetic acid, ammonia and amine compounds which, by complexing with the copper ions, give a

Table 4.6 Some copper corrosion products from terrestrial and marine environments.[155]

Mineral name	Chemical name	Chemical formula
Malachite	Basic copper carbonate	$Cu_2(OH)_2CO_3$
Azurite	Basic copper carbonate	$Cu_3(OH)_2(CO_3)_2$
Antlerite	Basic copper sulphate	$Cu_3(OH)_4SO_4$
Bronchantite	Basic copper sulphate	$Cu_4(OH)_6SO_4$
Tenorite	Copper (II) oxide, cupric oxide	CuO
Cuprite	Copper (I) oxide, cuprous oxide	Cu_2O
Nantokite	Cuprous chloride	$CuCl$
Paratacamite	γ Basic copper (II) chloride	$Cu_2(OH)_3Cl$ or
Atacamite	δ Basic copper (II) chloride	$CuCl_2 \cdot 3Cu(OH)_2$
Botallakite	α Basic copper (II) chloride	
Covellite	Cupric sulphide	CuS
Anilite		$Cu_7S_4 (Cu_{1.75}S)$
Digenite		$Cu_9S_5 (Cu_{1.8}S)$
Djurelite		$Cu_{1.96}S$
Chalcocite	Cuprous sulphide	Cu_2S

Table 4.7 Corrosion products found on brass/bronze artefacts recovered from the sea.

Formula	Name	Artefact	Site
H_2SnO_3	metastannic oxide	bronze sheaves	*HMS Association* (1707)
$Sn(OH)_2$	stannous hydroxide	bronze sheaves	*HMS Association* (1707)
$ZnSn(OH)_6$	zinc tin hydroxide	bronze mortar	*HMS Association* (1707)
$(Sn, Fe)(O, OH)_2$	varlamoffite	bronze bell	*HMS Association* (1707)
SnO_2	cassiterite	bronze bell	*Rapid* (1811)
$ZnSO_4 \cdot 4H_2O$	goslarite	brass cannon	*Zuytdorp* (1712)
$ZnCO_3 \cdot 3H_2O$	zinc carbonate	brass tubes	Reference 34
$3ZnO \cdot ZnCl_2 \cdot 5H_2O$	zinc oxychloride	brass tubes	Reference 34

Data for wreck material from references [139] and [142].
For elemental composition of some of the above artefacts refer to *Table 4.9*.

general increase in copper corrosion rates beneath the wood-covered areas. Both of these effects are shown in *Plate 7*.

Corrosion rates for isolated copper samples in oxygenated temperate (approx. 15 °C) seawater is approximately 0.02 mm/year and this appears to increase by a factor of two for every 10 °C rise in temperature. This rate appears to decrease in anaerobic waters or sediments, and by galvanic coupling to iron on shipwrecks. Much higher rates of metal loss are generally due to erosion by water-borne debris but can also result from differential aeration (see above).

4.5.2 Copper corrosion in aerobic seawater

In normal seawater (35‰ salinity) the major anions present are chloride, sulphate, bicarbonate and carbonate, in decreasing order of concentrations (*Table 4.2*). Because of the solubility of both copper (I) and copper (II) sulphates and bicarbonates, corrosion products based on these anions are not found. The formation of insoluble copper compounds, with the exception of cuprous chloride, will be pH dependent and the Pourbaix diagrams shown in *Figure 4.1* give the regions of stability of copper compounds in aerobic and anaerobic seawater. The value of Eh in oxygen saturated normal seawater is 0.691 volts which would indicate that the copper (II) oxide, tenorite, would be commonly found while the metal E *corr.* value of 0.09 volts (*Table 4.3*) would indicate that the copper (I) oxide cuprite is stable. The variations in the concentration of copper (I) and copper (II) species in solution, the coverage of the artefact by marine growth and the local pH will effectively promote the formation of one insoluble corrosion product over another. On the well-oxygenated wreck sites off the Western Australian coast only one sample of malachite ($Cu_2(OH)_2CO_3$) has been identified, but this may have resulted from post excavation corrosion.[154] On these sites the researchers have found numerous

occurrences of cuprite, nantokite, atacamite, paratacamite, tenorite and copper (II) hydroxide.[155] There is a competitive precipitation reaction between malachite and atacamite, viz.

$$Cu_2(OH)_3Cl + CO_3^{2-} \rightarrow$$
$$CuCO_3 \cdot Cu(OH)_2 + Cl^- + OH^- \quad (4.19)$$
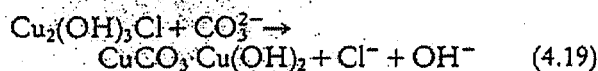
and in normal seawater with a carbonate activity of 2.4×10^{-6} M (pH 8.0) the formation of malachite is favoured. The relative concentrations of bicarbonate and carbonate will depend critically on local conditions and biological activity, and their presence or absence will give an indication of the site conditions since the vessel foundered. The simultaneous presence of both malachite and atacamite corrosion products on copper in seawater has been reported by Mor and Beccaria.[156]

Inspection of the Pourbaix diagrams (*Figure 4.1*) indicates that in the normal range of pH of seawater and sediments (6.5 to 9.2) the formation of cuprous chloride (nantokite) from cuprite is not favoured as the reaction

$$Cu_2O + 2H^+ + 2Cl^- \rightarrow 2CuCl + H_2O \quad (4.20)$$
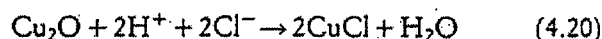
requires a pH below 5.30, at the normal chloride ion activity of 0.319 M, for CuCl formation. The pH of the *bulk* of the seawater tends to remain near 8.0 because of the presence of the seawater buffer systems,[157,158] but large variations can occur in crevices on the metal surface and under concretions or corrosion products, where there is a physical barrier to the free exchange of ions with the surrounding seawater. The presence of nantokite as a corrosion product on copper artefacts recovered from the sea confirms that such variations can occur and demonstrates the importance of measuring the Eh and pH on the metal and within the concretion as well as in the surrounding waters.

Changes in the salinity of a site due to the influx of fresh estuarine waters or to the evaporative concentration of seawater, will alter the stability of the chloride-containing copper corrosion products. For

equilibria involving the formation of cuprous chloride, such as Equation 4.20, a tenfold decrease in salinity would shift the equilibrium from pH 5.3 to 4.3. The reverse argument holds when an increase in salinity would favour the formation of cuprous chloride.

In well-oxygenated sites the slow step in the corrosion of copper appears to be the reduction of molecular oxygen.[159] A relatively high value of Eh from the presence of oxygen will tend to favour the formation of copper (II) ions and once the solution concentration of $Cu(II)$ has reached approximately 10^{-6} M,[160] precipitation of a protective film of some product such as tenorite, malachite or atacamite occurs.

Many wrecks occur in shallow (0–100 m) waters as a direct result of being damaged on reefs, rocks, etc., but material is sometimes recovered from vessels at a much greater depth. Apart from the decreased oxygen supply the pressure may well affect the corrosion mechanism. The only published information relates to laboratory studies[161,162] at pressures from 1–300 atm. (0 to 3000 m depth) at a constant oxygen content 7 ppm (4.9 cm³/litre at atmospheric pressure). The main corrosion products found were tenorite, cuprite and oxychlorides but at high pressures the decrease in pH and increase in solubility resulted in no corrosion product films being formed. In general the corrosion rate increased with pressure up to a maximum at 150 atm. (1500 m depth). At temperatures ≤10 °C the increased rate was due to an increase in the rate of the oxygen reduction process. In the light of the above information it is probable that copper artefacts recovered from deep oxygenated sites may be free of any gross corrosion products but more heavily corroded than material from comparable shallow sites.

For detailed discussion and explanation of the equilibria summarized in Pourbaix diagrams (*Figure 4.1*) the original paper by Bianchi and Longhi should be consulted.[160]

4.5.3　Copper corrosion in anaerobic waters

In water polluted with sewage and waste organic materials and in marine sediments, the corrosion of copper and its alloys is dominated by the sulphide ion. Examples of such include the *Wasa* (1628) in Stockholm Habour and the *Mary Rose* (1545) near Portsmouth. Anaerobic (oxygen free) conditions can be found in the sediment relatively close to the sediment/seawater interface (see Section 4.3.6). The coverage of artefacts with sand can result in an anaerobic micro-environment even in a site which is generally considered aerobic such as that of *HMS Association* (1707) in the Scilly Isles. A protective film of djurelite ($Cu_{1.96}S$) was found on a bronze artefact recovered from this site which indicated that the item

had once been covered by some sediment. A range of copper sulphides from chalcocite (Cu_2S) to covellite (CuS) – see *Table 4.6* – have been found on copper items recovered from the wreck of the *Rapid* (1811) (Western Australia), described by MacLeod and North.[138,155]

At an oxygenated site free of sulphide contamination the burial of metal artefacts under the sand will result in a change in corrosion mechanism. Once the entrapped oxygen has been consumed the main cathodic reaction will be hydrogen evolution stimulated by the action of sulphate-reducing bacteria (Section 4.3.6). The sulphide ions produced by these bacteria form copper sulphide precipitates with copper ions released from the corroding metal. The copper metal thereby forms an adherent protective film of Cu_xS, where the value of x ($1 \leqslant x \leqslant 2$) depends on the Eh and pH of the sediment. The Pourbaix diagram for the copper-sulphur-water system is shown in *Figure 4.1(b)*. Chalcocite (Cu_2S) is seen to be stable over a large range of Eh and pH whereas the region of stability for covellite is much smaller. Since there is a region of mutual stability for covellite and elemental sulphur the presence of a range of non-stoichiometric sulphides between CuS and Cu_2S, such as dijenite, djurelite and anilite, is not surprising. The central rectangle covers the commonly found range of Eh/pH in sediments where CuS, Cu_2S, Cu_2O, Cu and CuO are possible insoluble corrosion products.

If the artefact is subsequently exposed to an oxygenated environment, or if the Eh increases in the sediment, the oxidation of chalcocite to covellite can occur:

$$Cu_2S + S^{2-} \rightarrow 2CuS + 2e^-\qquad(4.21)$$
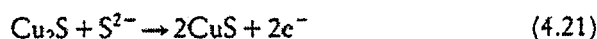
Since the covellite is less dense than chalcocite (density 4.7 g cm^{-3} compared with 5.6 g cm^{-3}) the oxidation process (Equation 4.21) will tend to fill any pores in the film and so minimize ingress of oxygen or other oxidants. The copper sulphide layer may also contain elemental sulphur which is extremely voluminous (density 2 g/cm³) and this may also serve to passivate the underlying metal.[163]

In laboratory studies of the effect of sulphide ions on the corrosion of copper in seawater, Mor and Beccaria[164] found a range of copper sulphides as well as some cuprite and tenorite under conditions that ranged from oxygenated (7.5 ppm) to deoxygenated (0.3 ppm) water containing between 50 ppm and 300 ppm sulphide. The corrosion potentials of copper in these solutions were measured over the pH range 6.5 to 8.6 and ranged from −0.546 to −0.616 volts (vs normal hydrogen electrode, NHE) respectively (see *Table 4.8*). Inspection of the Pourbaix diagram (*Figure 4.1(b)*) shows that the stable copper corrosion product in these regions is chalcocite (Cu_2S) which was experimentally confirmed. On the basis of their data for 48 hours they conclude that the presence of

Table 4.8 Average corrosion potentials [164] of copper in artificial seawater at 25°C after 48 hours immersion in solutions containing between 50–300 ppm sulphide. Potentials are relative to NHE.

pH	E corr.
8.6	−0.616
7.9	−0.606
7.2	−0.576
6.5	−0.546

Original data were relative to the saturated calomel electrode, SCE.[164]

sulphide ions increases the corrosion rate above that normally encountered in the same range of Eh and pH.

By contrast the examination of wreck material, which has been submerged for hundreds of years, generally shows that the layer of copper sulphides has been protective. Insufficient data exists to make valid comparisons as to the long-term corrosion rates of copper in sulphide media and great care must be exercised when comparing the results of short-term laboratory experiments with data based on artefacts recovered from shipwrecks. Sufficient variations exist even on the one wreck site to show that quantitative measurements of corrosion rates should be examined with due consideration of the micro-environment of the artefact.

4.5.4 Formation of concretions

Artefacts made of copper, brass and bronze are often found with little or no concretion on them and this is due primarily to the biological activity of the copper corrosion products, principally cuprite.[165] From the information that is available it appears that there are two distinct types of concretion formation depending on whether the material has been in aerobic or anaerobic environments.[155] The concretions in aerobic environments incorporate inorganic calcite (calcium carbonate), organic calcareous deposits from molluscs, worm casts, and foraminifera, as well as entrained sand grains. Aerobic concretions are typically rather porous and are often associated with iron corrosion products. The concretions formed in anaerobic environments tend to be more closely packed with dense layers of copper sulphides acting as a binding cement with calcite to entrain marine organisms and seabed debris.

Examination of the aerobic concretions on copper alloys often reveals the presence of iron corrosion products (brown) along with copper corrosion products which range from the red-orange cuprite (Cu_2O)

to the blue-greens of paratacamite ($Cu_2(OH)_3Cl$) to the black of tenorite (CuO). Since iron is not very mobile in seawater[17] its presence within the copper concretion indicates adjacent corroding iron artefacts possibly protecting the more noble copper artefact (see Section 4.5.5). The major cathodic reaction for the iron/copper galvanic couple

$$O_2 + 2H_2O + 4e \rightarrow 4OH^- \qquad (4.3)$$
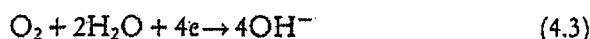
occurs on the copper/copper alloy and so causes a localized increase in pH which can lead to the precipitation of calcite,

$$Ca(HCO_3)_2 + 2OH^- \rightarrow CaCO_3 + H_2O. \qquad (4.22)$$
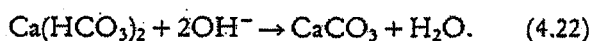
In normal seawater calcium is close to its solubility limit and only a small change in pH can result in calcium carbonate being precipitated. The presence of inorganic calcium carbonate as calcite crystals in these concretions can be detected morphologically by microscopic examination of thin sections.[138] Once an inert layer of calcite has been formed marine organisms such as coralline algae, molluscs, serpulid worms, etc., can colonize the structure. The concretion still allows some oxygen to reach the corrosion front and staining of the calcium carbonate structures of marine growths by copper is often observed up to 1–2 mm into the concretion above the primary copper corrosion product (which is most commonly cuprite). Depending on the composition of the alloy the primary corrosion layers may be richer in the alloying element than was the original metal. This phenomenon is often found with bronze artefacts where large amounts of tin corrosion products – principally cassiterite (SnO_2) – occur in conjunction with the normally encountered copper corrosion products. In concretions freshly raised from the sea large amounts of the gelatinous duck-egg blue cupric hydroxide ($Cu(OH)_2$) can be found under the marine growth but this material is converted into more stable crystalline material on exposure to dry air.[155]

Examination of the concretions under a microscope will often show up patches of elemental copper which have been redeposited at some distance from the residual metal core. Because many of the copper corrosion products are semiconductors of the p and n type, slight changes in site conditions can cause an oxidation site to change over to a reduction site. The interconversion of elemental copper, copper (I) and copper (II) salts is characterized by fairly rapid electrode processes which are faster than the reduction of oxygen to hydroxide (Equation 4.3), so the presence of redeposited copper within the concretion is not entirely unexpected.

The anaerobic concretions are typically banded in structure with a primary corrosion product of cuprite (Cu_2O), less commonly tenorite (CuO), overlaid by bands containing the copper sulphide chalcocite (Cu_2S), or occasionally covellite (CuS). Variations in
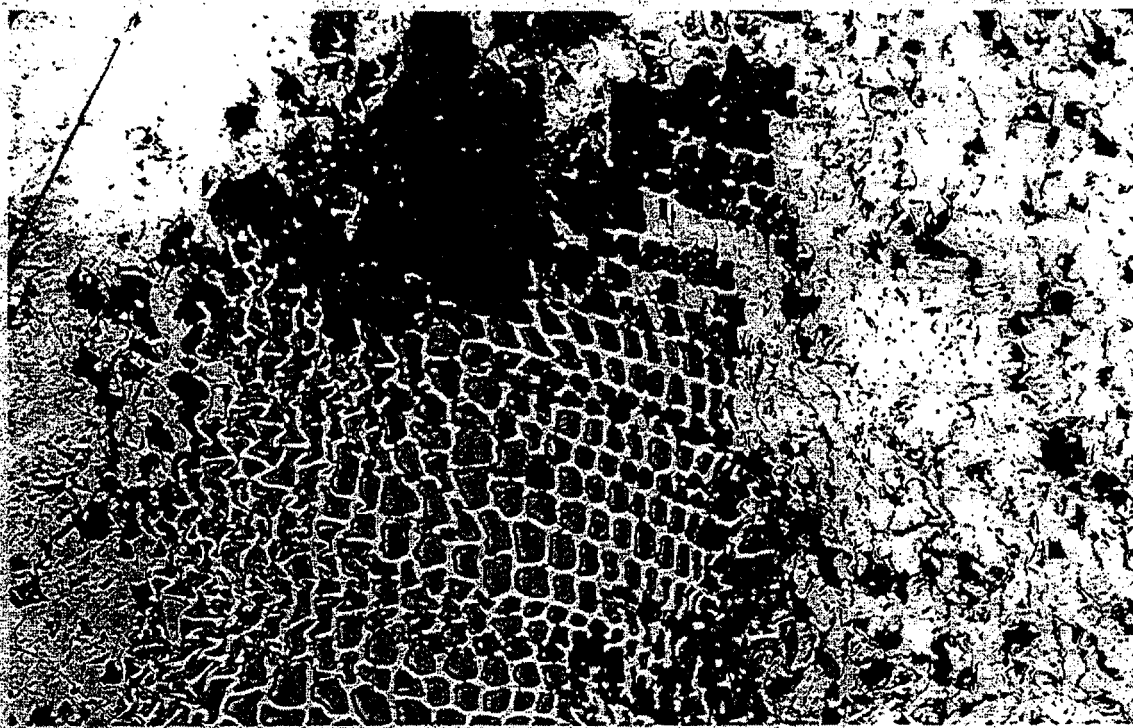
Plate 8 Micrograph showing deposition of copper corrosion products in attached wood. Note deposition on cell walls

the stoichiometry of the sulphides occurs and the formation of the copper-deficient sulphides, such as djurelite, $Cu_{1.96}S$, will depend on small variations in sulphide ion activity in the marine sediment. Beyond the first layer or two of almost pure sulphides there exists a conglomeration of calcium carbonate particles, in the form of skeletal material, as well as calcite crystals with the sulphides, quartz grains, and other sands scattered throughout the concretion. If the copper artefact has been corroding in the presence of wood the sulphides can sometimes be found conforming to the shape of the original cell walls[155] (see *Plate 8*). The presence of copper oxides in the corrosion layer nearest the metal suggests that these materials were formed prior to the development of anaerobic conditions.

It is generally agreed that the presence of sulphide ions increases the corrosion rate of copper and its alloys,[164] but the combination of aerobic and anaerobic concretions on the same marine artefact appears to be remarkably protective. If a copper artefact with an adherent coating of copper sulphides is removed from an anaerobic environment and subsequently exposed in an oxygenated low-sulphide environment, marine organisms can apparently colonize on the sulphide layer and thus form a typical aerobic outer concretion. Examples of this type of protective coating have been reported from the *HMS Association* site in the Scilly Isles,[139] the *Pandora* site in the Torres Strait[138] and more recently from the *Zuytdorp* site off the Western Australian coast.[155]

4.5.5 Copper corrosion mechanisms

Water movement attack

In the marine environment, copper and its alloys are susceptible to increased corrosion attack by water movement. Copper and its alloys are relatively soft and usually do not acquire thick protective marine concretions. As a result they are very susceptible to erosion by water-borne debris, such as grit and sand. Under unfavourable conditions the erosion rate can exceed 1 cm/year and this point should always be considered when copper alloy artefacts are repositioned on the wreck site or when the surrounding seabed is drastically disturbed. The flow of water can also remove the protective oxide film. At high flow rates the concentration of copper in the vicinity of the artefact is not sufficient to allow reformation of the protective film and film-free corrosion rates prevail. At lower flow rates the movement of the sea improves the transport of oxygen to the metal and may increase the general corrosion rate even though the oxide film remains intact. Alloys such as admiralty brass and the bronzes are much more resistant to this form of corrosion. If concretions form on the artefacts these often protect them from water movement effects.

Fretting corrosion

When metal artefacts are rolled around as a result of turbulent site conditions the surface corrosion films

will be deformed and fresh corrosion will occur at areas exposed by a film crack or by dislocation. Because copper oxides have a hardness similar to that of copper metal (3.5 and 3.0 respectively on the Moh scale) impacts will cause the surface film to deform with the underlying metal. Paratacamite has a hardness of 3–3.5 and so it will similarly deform with the metal. As a result pure copper artefacts will not normally be adversely affected by fretting though the harder alloys with tin and zinc may be more susceptible.

Pitting corrosion

The conditions for pit formation[185] include the presence of a deposit of cuprous chloride under a layer of cuprite (Cu_2O) which acts as a bipolar electrode, viz. corrosion (anodic) reactions occur on the metal side of the cuprous oxide membrane while oxygen reduction (cathodic) reactions occur on the seaward side (*Figure 4.2*). The ability of cuprite to act as a bipolar electrode is due to its electronic and structural properties.

The existence of the cuprous chloride layer in the pit will depend on the relative rates of copper corrosion

$$Cu + Cl^- \rightarrow CuCl + e^- \qquad (4.23)$$

and the hydrolysis of cuprous chloride

$$2CuCl + H_2O \rightarrow Cu_2O + 2H^+ + 2Cl^- \qquad (4.24)$$
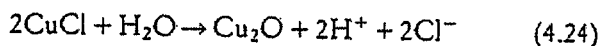
The driving force for the pitting reaction is the concentration gradient of copper (I) species between the bottom of the pit and the corrosion mound above the Cu_2O film. In the presence of chloride ions CuCl can form a series of soluble complexes such as $CuCl_2^-$, $CuCl_3^{2-}$ in the pit. These copper (I) species diffuse through cracks in the Cu_2O membrane and are then oxidized by molecular oxygen to cupric ions

$$Cu^+ \rightarrow Cu^{2+} + e^- \qquad (4.25)$$

while oxygen is reduced to hydroxide ions,

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \qquad (4.3)$$

Reaction 4.3 causes a localized increase in the pH and calcium carbonate may be precipitated. Some of the cupric ions formed by the Reaction 4.25 will be precipitated in the form of the basic cupric chlorides, $CuCl_2 \cdot 3Cu(OH)_2$. Other cupric ions can be reduced to form cuprous ions which are subsequently oxidized by molecular oxygen away from the surface of the pit. The anodic reaction inside the pit is the oxidation of cuprous to cupric ions at the Cu_2O surface:

$$Cu^+ \rightarrow Cu^{2+} + e^- \qquad (4.25)$$

which in turn attack the copper metal to form more cuprous ions:

$$Cu^{2+} + Cu \rightarrow 2Cu^+ \qquad (4.26)$$

causing the pit to deepen. This corrosion process is seen as being cyclic in nature. Since the precipitation of the excess Cu (II) compounds occurs above the corrosion mound the corrosion cell will not be stifled by the formation of basic copper (II) chlorides in the pit.
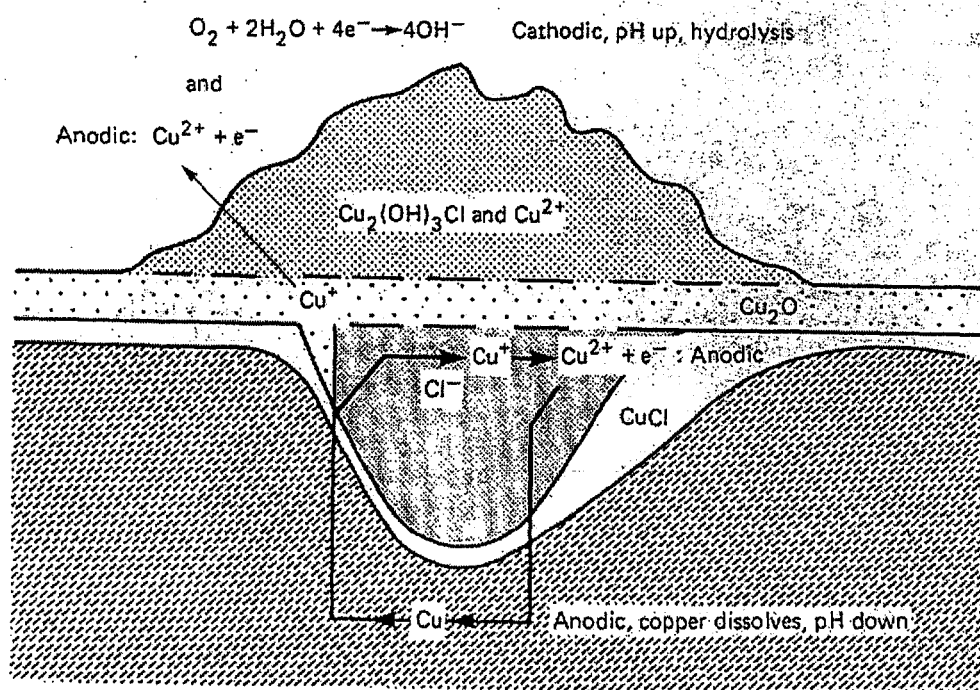
Figure 4.2 Schematic diagram of an active corrosion pit in copper

The reaction above the mound can be formalized as

$$12CuCl + 6H_2O + 3O_2 \rightarrow 4Cu_2(OH)_3Cl + 4CuCl_2 \quad (4.27)$$

though the formation of malachite in preference to the atacamites may occur depending on the carbonate ion concentration (Section 4.5.2). The external concentration of copper has very little effect on the pitting mechanism. Since the anodic reaction of cupric ions on the copper metal (Equation 4.26) provides more cuprous ions the concentration cell is recharged.

Differential aeration corrosion

This most commonly occurs when part of the copper is covered by wood or concretion and the uncovered section is exposed to oxygenated seawater. Beneath the covering the oxygen is depleted and the Eh of the solution drops. This produces a potential difference between the exposed and covered sections of the metal and corrosion occurs (Section 4.2.1). The cathodic reaction, oxygen reduction, occurs on the exposed metal surface and the anodic reaction, copper dissolution, on the covered surface adjacent to the exposed area. This produces deep corroded areas underneath the edges of concretion and wood and is very common on copper hull bolts where it produces a marked necking of the bolt (*Plate 7*).[154]

Galvanic corrosion

This occurs on a wreck site when two metals with different E corr. values are in electrical contact (Section 4.2.1). A list of the E corr. values of metals in seawater is given in *Table 4.3* which shows that copper and brass will normally be cathodically protected by iron alloys.

On a microscopic level a form of galvanic corrosion occurs when one phase of an alloy is more reactive than an adjacent phase. The less reactive phase becomes cathodic while the other phase actively corrodes. This form of corrosion is relatively common in alloys such as zinc-rich brasses and tin-rich bronzes. Solutions in the cracks which develop in the metal do not have a rapid exchange with the bulk of the environment and may become acidic enough to allow the cathodic reduction of hydrogen ions to occur. This type of corrosion can often result in a dramatic loss of mechanical strength (see *Plates 18* and *21*).

4.6 Brass and bronze

4.6.1 Summary

Brass and bronze artefacts on wreck sites typically occur in the form of massive rudder fittings, cannon, bars, spikes and sheathing. Since the methods used for the manufacture of large cast objects were undergoing marked developments between the 18th and early 20th centuries, chemical and metallographic analyses of the artefacts can often give useful information for wreck dating. An alloy is called a brass if the major alloying element is zinc and such materials were often used in the manufacture of wrought objects. If the amount of tin in a metal is greater than the amount of zinc the alloy is generally called a bronze and such materials were often used in casting. There is no clear division between brass and bronze, and alloys often contain both tin and zinc, sometimes in equal proportions. The presence of brass artefacts on a wreck site does not necessarily mean that the vessel is relatively modern since intentional production of brass began in Asia Minor in the first millennium B.C.[166] However, the use of brass sheathing on wooden vessels was not a common practice until the early nineteenth century.[167] Typical compositions of marine brasses and bronzes are given in *Table 4.9*.

The most characteristic form of brass corrosion is dezincification. In this form of corrosion the zinc component of the brass is selectively removed by corrosion and the alloy is transformed to a porous mass of copper which has very little mechanical strength but generally retains the original shape of the artefact. A similar phenomenon is also observed in bronzes where loss of the tin-rich phases occurs, this process being referred to as destannification.

Two mechanisms have been proposed for dezincification, namely, selective dissolution of the zinc which leaves the copper behind or complete dissolution of both copper and zinc followed by selective deposition of the copper. Possibly both processes may occur depending on local conditions. The mechanisms are discussed in references 168 and 169. Both dezincification and destannification are more pronounced under anaerobic conditions.

4.6.2 Corrosion products

The corrosion processes occurring on brass and bronze artefacts are dominated by the corrosion behaviour of copper which is the major constituent of the alloys. A range of copper corrosion products have been found on brass and bronze items which includes most of the oxides, chlorides, hydroxy chlorides and sulphides listed in *Table 4.6*. Relatively few papers report detailed examination of the alloying metal corrosion products but those reported are predominantly compounds of tin and oxygen in the form of oxides and hydroxides, see *Table 4.7*. The chemistry of tin in neutral and alkaline solutions is dominated by the formation of stable and insoluble oxides and hydroxides. At the pH of seawater tin corrosion products will normally remain in place and will often retain the original shape of the artefact. Because of their relatively high solubility zinc compounds are generally

Table 4.9 Analysis of marine copper alloys.

Site	Ship (year wrecked), items	%Cu	%Sn	%Zn	%Pb	%Fe	%Ag	%Sb	%As	%Ni
Scilly Isles 49°57'N, 6°15'W	*HMS Association* (1707)									
	cannon	93.4	4.4	0.9	0.5	0.06	–	0.1	0.5	0.1
	cannon C.	92.9*	4.1	1.4	0.9	–	–	0.1	0.5	0.1
	small cannon	90.3*	6.6	0.4	2.0	0.02	–	0.2	0.4	0.1
	small demountable cannon	74.5*	1.0	22.2	1.3	0.7	–	0.1	0.07	0.1
	bronze sheaves	78.4*	10	0.5	10	0.1	–	0.5	0.3	0.2
	brass dividers	78.42	1.0	20.64	1.0	1.0	–	–	0.1	0.2
	ships bell	75.8*	20	0.2	3	1				
Abrolhos Islands 28°30'S, 113°45'E	*Batavia* (1629)									
	door pintle	92.7	1.4	0.5	1.1	2.1	–	0.3	0.14	–
	cannon cascable	66.9	2.8	0.28	22.6	0.13	–	3.2	4.0	–
	cannon copper sheathing	98.85	0.25	0.01	0.28	0.05	–	–	–	–
Pandora's Entrance Gt. Barrier Reef	*Pandora* (1791)									
	rudder pintle	91.1	7.3	0.04	0.19	0.08	0.01	0.16	–	–
Pt. Cloates NW Australia 22°44'S, 113°41'E	*Rapid* (1811)									
	rudder gudgeon	91.8	4.8	0.30	1.91	ND	–	0.12	–	–
	pall trace	90.8	4.8	1.03	2.9	0.09	–	ND	ND	–
	keel strap	90.7	7.3	0.56	0.87	0.34	0.04	0.23	–	–
	copper bars	97.7	0.05	ND	0.54	ND	–	0.04	ND	–
	copper nails	98.7	0.11	ND	0.18	ND	–	0.03	0.13	–
Carnac Island 32°07'S, 115°39'E	*HMS Success* (1829)									
	rudder gudgeon	87.8	5.06	1.42	1.42	ND	–	0.1	0.60	–
	copper bolt	99.4	0.22	0.02	0.09	ND	–	ND	0.03	–
Star Reef near Murray Reef 32°22'S, 115°42'E	*Chalmers* (1874)									
	rudder gudgeon	63.0	2.4	20.5	13.6	0.8	–	0.1	n.d.	–
Rottnest Island 32°1'S, 115°32'E	*Lady Elizabeth* (1878)									
	rudder gudgeon	44.0	0.73	28.7	25.6	0.02	–	0.3	0.36	–
off Marsala, Sicily 37°40'N, 12°27'E	unknown (32 B.C.)									
	nails from ram	80.9	9.4	0.3	10.7	–	–	–	0.05	–
	nails from ram	73.6	7.3	0.4	17.3	–	–	–	0.05	–
	nails from ram	84.7	7.7	0.2	7.3	–	–	–	–	–
	nails from hull	80.0	7.1	0.6	12.3	–	–	–	–	–
Mounts Bay, Cornwall 51°55'N, 5°30'W	*HMS Anson* (1807)									
	Cutless hilt	86.86	10	1.0	1.0	0.06	–	0.5	0.2	0.3

* By difference.

not found in the corrosion products. When they do occur they are generally found trapped in the concretion matrix. For example, after several years of exposure in seawater the concretions formed on brass tubes incorporated zinc corrosion products such as zinc carbonate, zinc oxychloride and zinc hydroxide gels.[170] There is one report of an arsenic corrosion product found among copper corrosion products on a bronze gudgeon from *HMS Success* (1829).[138]

4.6.3 Corrosion processes

Dezincification

The addition of up to 30 wt% of zinc to copper metal increases its corrosion resistance, thus admiralty brass and red brass have better corrosion resistance than does elemental copper. Materials with a zinc content above 32 wt%, such as yellow brass and Muntz metal, are more reactive than copper. If a brass contains more than 32 wt% zinc it will have both an α (zinc poor) and a β (zinc rich) phase. The β phase is more susceptible to corrosion. If an artefact has suffered from dezincification the surface may appear to be copper-rich and porous with a typically banded structure of cuprite and elemental copper layers until the residual metal surface is reached.

With duplex brasses (those having both α and β phases) the zinc-rich β phase is preferentially attacked at the grain boundaries.[168] In single phase α brasses the loss of zinc is distributed fairly uniformly across the grains.[169] Dezincified Muntz metal and yellow

brass still retain the skeleton of the β phase. The banded nature of dezincified brass is due to changes at the 'corrosion front' as cuprous chloride is hydrolysed to form cuprite (the net result of an anodic dissolution of copper) and the cuprite is reduced back to elemental copper when the conditions change to make the site cathodic.

Brass artefacts recovered from wreck sites which would normally be expected to favour dezincification are often found in a remarkably good state of preservation. Analysis of such metals reveals the presence of small amounts of arsenic, antimony and phosphorus which are effective inhibitors of dezincification.[138,171] If the brass alloy contains traces of iron and manganese these impurities may cancel the beneficial effect of arsenic since they effectively bind the arsenic in the form of stable arsenides.[172] Both arsenic and antimony tend to concentrate at the grain boundaries in brass and this effectively increases their concentration at the main reaction sites.[173] Analyses of some of these materials are given in Table 4.9.

Although variations in site conditions can override the effect of arsenic and antimony on the dezincification process, the Chalmers (1874) gudgeon was dezincified to a depth of 2 cm while the leaded brass gudgeon from the nearby Lady Elizabeth, which had significant concentrations of both arsenic and antimony, was in excellent condition. Part of this preservation may also have been due to cathodic protection from the corroding iron on the site (see Table 4.9 for analyses and site locations).

Destannification

This is the term used to describe the selective removal of tin from a bronze alloy. It is much less common than dezincification and relatively little work has been published on the mechanism of the process. Tylecote[142] has reported that traces of arsenic and antimony are effective inhibitors of destannification of bronzes on shipwrecks.

In a classical study Campbell and Mills[143] showed that under deaerated seawater the tin-rich α plus γ eutectic in a bronze (20% tin 3% lead) bell is preferentially attacked. At higher oxygen concentrations the copper-rich α phase is preferentially corroded. This study predicts that destannification of bronzes should only occur on shipwrecks under partly anaerobic conditions.

Examination of the corrosion patterns on bronze objects recovered from the wreck of the Rapid (1811) at Point Cloates, Western Australia, have confirmed the experimental work of Campbell and Mills.[143] A bronze bell was found lying on its side with part of the lip and the crown covered with sand. The areas under the sand (anaerobic) were more extensively corroded than those parts (aerobic) which had been exposed to the sea. In the sand-covered regions mas-

sive amounts of cassiterite (SnO_2) had formed and the metal was corroded to a depth of 7 mm; the main copper corrosion product was paratacamite which was bound up within the large grains of cassiterite. Where marine growths had created localized oxygen-deficient spots on the exposed surface of the bell the metal had suffered from the same extensive attack on the tin-rich material. By contrast, the corrosion layer on the completely exposed surfaces of the bell was only 1 mm thick as in the absence of destannification the overall bronze corrosion rate is relatively low. The importance of the micro-environment is also seen in a comparison of the corrosion on several bronze keel straps from the same wreck. These straps had identical composition (see Table 4.9) and bore the same foundry stamp, but the straps recovered from under a 15 cm layer of sand were much more extensively corroded than those found lying on the seabed surface.[154]

4.6.4 The effects of minor alloy components on brass and bronze corrosion

Lead

Since lead has a very limited solubility in brass and bronze alloys it will tend to be dispersed as discrete droplets. Apart from tending to fill cracks and voids which occur during fabrication of the material, leaded bronzes and brasses tend to be self-lubricating. High lead content alloys have excellent corrosion resistance[174,175] as is seen in the leaded bronze cascable from the Batavia site. After nearly 350 years in turbulent conditions the depth of corrosion was less than 1 mm. Tylecote reports that the addition of lead to copper apparently makes the metal less susceptible to intergranular corrosion.[142]

The addition of lead to duplex brasses results in the lead concentrating along the interdendritic lines between the two phases.[176] In seawater corrosion this lead may result in the formation of passivating $PbSO_4$ films which could help protect the underlying brass from general corrosion.

Iron

Iron has a limited solubility in brass and bronze (0.5%) and above this limit it will exist as discrete particles dispersed throughout the alloy. Since iron in this form is readily attacked by seawater the corrosion of the iron particles may increase the overall corrosion rate of the artefact by creating small voids on the metal surface and thereby providing sites for pitting corrosion. For example, deep holes filled with iron and copper corrosion products were found on a series of bronze door pintles from the Batavia site which contained 2.1% iron. In spite of the presence of significant amounts of arsenic and antimony (see

Table 4.9) there was extensive pitting (some pits were 3 mm in diameter and 3 cm deep) as well as general corrosion. Generally the presence of greater than 0.5 wt% iron will have a deleterious effect on the corrosion resistance of brasses and bronzes.

4.6.5 Stress corrosion

Brasses are more susceptible to stress corrosion than are bronzes. Stress corrosion arises in situations where there is physical strain in the crystal structure. Under such conditions accelerated corrosion occurs at those strained sites and this often results in the metal cracking. The pins from rudder fittings commonly show stress cracking since the metal under stress during the working life of the vessel is often subjected to extreme loads when the rudder is torn away from the vessel during wrecking. It has been reported that arsenic diminishes the susceptibility of copper alloys to stress corrosion cracking.[177] If the artefact is associated with wood the production of acetic acid and ammonia during wood decomposition will cause increased corrosion of the copper-rich phases which may accelerate the development of stress cracking.

4.7 Lead

Lead has been used as a constructional material for over two thousand years. Lead metal is readily extracted from its ores and is readily melted. Its low melting point, 327 °C, meant that it could be formed into piping, musket balls, sounding weights, etc., without sophisticated foundry techniques. On shipwrecks lead is also often found in the form of lead sheet which was commonly used for minor repair to the wooden hull. Lead ore bodies characteristically contain varying amounts of silver and antimony impurities.

Lead artefacts from land sites are often covered with cerussite, $PbCO_3$, or the related hydrocerussite, $2PbCO_3 \cdot Pb(OH)_2$.[178] Varying amounts of lead (II) oxide (PbO), lead (IV) oxide (PbO_2) and anglesite ($PbSO_4$) may also be present depending on site conditions.[179] By contrast the main lead corrosion products found on marine artefacts are anglesite ($PbSO_4$) and laurionite (Pb(OH)Cl) from aerobic sites, and galena (PbS) from anaerobic or polluted sites.[142] It is interesting to note that $PbCO_3$ has not been found as a major corrosion product of marine lead even though it is 100 times less soluble in seawater than is $PbSO_4$. Marine lead artefacts are often covered with a thin (1–3 mm) layer of concretion. This is generally composed of a mixture of marine seabed debris and anglesite ($PbSO_4$) held together with $CaCO_3$ cement (commonly calcite). Lead items recovered from tropical waters generally do not have any secondary

marine growths and this may be due to a higher toxicity of lead and its corrosion products in warmer waters.

In aerobic seawater the corrosion of lead is dominated by the formation of insoluble $PbSO_4$, which soon forms a passivating surface film and so protects the underlying metal and produces a marked rise in the corrosion potential of the metal. For example, a piece of cleaned 17th century lead sheet from the *Batavia* was immersed by the authors in seawater and its corrosion potential measured. In 24 hours the corrosion potential was found to have increased from an initial active −0.36 volts to a fairly inert −0.06

In anaerobic environments the main lead corrosion product is PbS (galena). The redox potentials for oxidation of lead to lead sulphate (−0.278 volts in normal seawater) and lead sulphide (−0.780 volts in 10^{-6} M sulphide) shows that the formation of PbS is thermodynamically very favourable in anaerobic conditions. From the redox potentials alone, lead corrosion in anaerobic environments would be expected to be higher than in aerobic conditions. The weight loss for several musket balls from the *Wasa* site (anaerobic)[140] and the *HMS Association* site (aerobic)[139] were compared, and the material from the anaerobic site had roughly double the corrosion rate (mg cm^{-2} year^{-1}) of that from the aerobic site.[139] However, the number of musket balls used in this study was small and the comparison should be treated with caution. Although the initial corrosion rate for lead in sulphide containing media is quite high, the formation of an adherent sulphide film rapidly passivates the metal.

4.8 Tin

Elemental tin occurs infrequently on wreck sites and large finds of the metal are normally associated with cargoes of tin ingots. Generally tin artefacts will be extensively corroded since the main corrosion product, cassiterite (SnO_2), does not form an effective passivating film. Some ingots of early iron age or early medieval period were found off the Cornish coast and the major corrosion product was cassiterite (SnO_2).[180] There were smaller amounts of the divalent corrosion products $SnO \cdot H_2O$ and $SnCl_2 \cdot 2H_2O$. The general shape of the artefacts is maintained by the tin (IV) oxide cassiterite but the matrix is often crumbly. Although chloride ions form strong complexes with both tin (II) and tin (IV) the overall effect of seawater on the corrosion of tin is dominated by the natural pH (6.5–8.6) of seawater which favours the formation of oxo and hydroxy species. These are often polynuclear and are characterized by slow electrode kinetics.[181,182] Only under highly acidic conditions are tin (IV) species mobile but tin (II) species are apparently mobile in some

concretions since tin corrosion products were found near the sea edge of a concretion from a bronze cannon.[155]

Both tin (II) and tin (IV) form stable sulphides, SnS and SnS₂, but the sulphides have not been characterized as corrosion products on wreck material. The reason for the lack of reports most probably lies in the fact that few, if any, tin artefacts have been found on wrecks characterized by anaerobic site conditions.

The temperatures on marine sites are too high for the occurrence of tin pest (the change in crystal structure from β tin to α tin).

4.9 Pewter

Pewter artefacts are commonly found in the form of plates, mugs, candlesticks and other paraphernalia associated with shipboard life. Less common are pewter fittings used in the ships pumps and associated channelling. The typical elemental composition of pewter falls into two broad categories namely those containing lead as the major alloying component of tin and those 'lead-free' pewters (such as Britannia metal) which are tin, antimony and copper alloys.

Under aerobic conditions pewter artefacts containing a high proportion of lead are less corroded than those with less lead. Some old pewters contain up to 50% lead. Material of this composition was recovered off the Shetland Islands and showed only superficial corrosion after 300 years in the sea.[142] A pewter pump fitting containing 28% lead from the wreck of the *Rapid* showed uniform corrosion to a depth of less than 0.5 mm after 180 years in an oxygenated environment. In a similar fashion Campbell and Mills found negligible corrosion on a leaded pewter plate found at the *HMS Association* site.[139] Chemical ana-

lyses of the pewters are given in *Table 4.10*. The main reason why such leaded pewters are so well preserved probably lies in the formation of an adherent and highly protective PbSO₄ layer.

From the few detailed reports on corroded lead-free pewters it is clear that they suffer from extensive corrosion in an aerobic marine environment. The main corrosion product from a pewter spoon from *HMS Romney* (1707) was the black intermetallic compound SbSn.[139] A spoon from the *Lady Littleton* (1867) was extensively corroded[183] but the overall shape of the spoon with decorative details was preserved in the grey corrosion product matrix. Analysis of the corrosion products gave the main components in the ratio of 2Sb:3Sn (*Table 4.10*). Although the corrosion product from the *Lady Littleton* spoon was not examined by X-ray diffraction, the ratio of tin and antimony corresponds to one of the known intermetallic phases which are SnSb (reported by Campbell[139]), Sn₃Sb₂ and Sn₄Sb₂. If the intermetallic phases are evenly distributed throughout the artefact they may be cathodic to the rest of the material which is much richer in tin and so the bulk of the tin-rich material will be anodically oxidized.[184] As previously discussed, tin metal is subject to extensive corrosion in aerobic seawater.

Although no residual metal was found in a number of lead-free pewter artefacts recovered from the wreck of the *Batavia* (1629)[183] a typically thin, grey-black powdery film (probably an intermetallic tin antimony compound) was found in the middle of massive pustular outgrowths of corrosion products. The pustules ranged in colour from a browny black to white, and X-ray diffraction analysis showed them to be cassiterite (SnO₂) with varying amounts of iron and copper impurities. The impure SnO₂ averaged more than 90% of the total weight of the corrosion products with the balance mainly calcareous material.

Table 4.10   Analysis (%) of pewter artefacts.[183]

Location	Vessel	Tin	Lead	Antimony	Copper	Zinc	Silver
Scilly Isles 40°57'N, 6°15'W	unknown (1819) pewter platter[143]	balance	11	<1	0.01	<0.01	0.05–0.5
Scilly Isles 40°57'N, 6°15'W	HMS Romney (1707) pewter spoon handle[143]	balance	1	5	1	<0.01	–
Pt. Cloates, W.A. 22°44'S, 113°41'E	Rapid (1811) ships pump base[183]	70.5	27.6	0.26	0.18	0.03	0.007
Princess Royal Harbour[a] (Albany) 35°02'S, 117°50'E	Lady Littleton (1867) pewter spoon[183]	55.6	0.1	38.9	5.41	<0.01	0.004
Abrolhos Islands 28°30'S, 113°45'E	Batavia (1629) filler metal in composite cannon[183]	25.96	73.0	<0.1	0.25	0.006	–

[a] The analysis refers to the alloy phase which remained after selective corrosion attack.

The effect of anaerobic conditions on the corrosion of pewters is not clearly defined because of the scarcity of reports in conservation and maritime archaeological literature. Leaded pewter candlesticks recovered from the *Wasa* (1628) were in excellent condition and the formation of an adherent lead sulphide (galena) and tin sulphide film may have been one of the reasons for the good corrosion resistance. Some Britannia metal plates from the wreck of the *James Matthews*[183] were recovered in excellent condition from what is essentially an anaerobic site, the vessel being covered with a metre of sand. There was insufficient corrosion products on these plates to enable definite characterization but they were probably stannous and stannic sulphides.

At one extreme of the range of leaded pewters are the tin-lead alloys with 30–50% tin which are commonly referred to as solder. Because solders have low melting points they will tend to be found as a filler metal in the manufacture of artefacts or in association with the plumbing on board the vessel. Because of their high lead content the corrosion behaviour is dominated by the formation of passivating films of lead sulphate (aerobic conditions) or lead sulphide (anaerobic conditions). Measurements of the electrode potentials of lead and tin when coupled to the complete range of tin-lead alloys shows that the maximum potential difference is 10 mV.[186] With such small potential differences it is not surprising that no evidence has been found for selective attack on either a tin-rich or lead-rich phase. The soft solder used in the construction of a composite cannon on the *Batavia* (*Table 4.10*) was well preserved as was some 70:30 (lead-tin) solder used in joining lengths of lead piping found on the *HMS Association* site.[139] Although the exposed filler metal in the composite cannon had a thin corrosion layer of lead sulphate the metal was in direct contact with wrought iron bands which may have provided some cathodic protection.[187]

4.10 Silver and its alloys

4.10.1 Summary

Silver and its alloys have been used for thousands of years in the manufacture of jewellery, precious vesselsl and as a coinage metal. Silver artefacts recovered from wrecks normally fit into these major categories. Copper is frequently found in silver as the addition of copper has long been known to improve the working properties of the metal and to reduce its monetary value on unit volume basis. Since the room temperature solubility of copper in silver is only 0.1%[188] precipitation hardening of silver-copper alloys occurs and this causes the metal to become brittle. Depending on the rate of cooling the copper

can be evenly dispersed throughout the silver-rich matrix or it can accumulate along grain boundaries. If the latter occurs then the more reactive copper particles corrode preferentially in seawater and this leads to loss of mechanical strength, i.e. copper-silver alloys are subject to intergranular corrosion. The majority of marine silver artefacts recovered to date are silver coins and consequently the majority of silver corrosion and concretion information is derived from coins. Although silver is one of the most noble metals, chloride and sulphide ions, found in marine environments, dramatically increase the reactivity of the metal, producing a negative shift of 580 and 1500 mV respectively in its standard reduction potentials when compared with oxidation of silver to give the free metal (*Table 4.1*). In contrast to lead (Section 4.7) the formation of insoluble AgCl and Ag_2S does not provide corrosion resistance for the silver. When silver artefacts are recovered from the sea they are almost invariably covered with layers of corrosion products and concretion (*Plate 9*).

Plate 9 Typical batch of coins as recovered from the *Batavia* (1629).

The mixture of corrosion products and concretion on silver artefacts is frequently separated into two layers. The innermost layer, usually referred to as the corrosion product layer, goes from the surface of the residual metal core out to the original surface of the artefact. This layer does not contain any calcareous matter. The outer layer, referred to as the concretion, forms from the original artefact surface out into the surrounding media. The concretion layer typically contains calcareous and seabed material as well as silver and copper corrosion products. The concretion layer is often only weakly bonded to the corrosion product layer and can often be mechanically removed without damage to the corrosion product layer.[189]

The most commonly found marine silver corrosion products are silver chloride AgCl (cerargyrite), silver

sulphide Ag₂S (argentite and less frequently acanthite) and the mixed silver chloride/bromide AgCl/Br. The silver chloride and bromides range in colour from black to grey and purple, while silver sulphides are generally between black and lead grey. Because of the similarity in some physical properties of copper (I) and silver (I) ions it is possible to obtain a series of mixed copper-silver sulphides of the formula $Ag_{2-x}Cu_xS$. The mixed sulphide jalpaite, $Ag_{1.5}Cu_{0.5}S$, has been found on some silver coins recovered from the *HMS Association* site.[143] Corrosion products from the alloying copper include the hydroxy chlorides, paratacamite and atacamite (α and γ $Cu_2(OH)_3Cl$); cuprite (Cu_2O), nantokite ($CuCl$) and chalcocite (Cu_2S).

Although silver is a heavy metal it does not appear to be as toxic as copper to many marine organisms. Serpulid worm casts (made of calcium carbonate) are often found directly attached to the corrosion product layer of silver which has corroded in an aerobic environment. As was found with copper artefacts there are different types of silver concretion associated with aerobic and anaerobic environments. The aerobic concretions are typically artefacts and debris bound together with a calcareous cement (a mixture of organic and inorganic calcite and aragonite ($CaCO_3$)). Iron corrosion products such as $FeO(OH)$ are often incorporated. The iron is normally derived from nearby corroding iron artefacts. The concretion is often stained green as a result of the movement of copper corrosion products away from the underlying metal surface. The underlying corrosion product layer consists of a matrix of either silver chloride or mixed silver chloride/bromide which may contain crystals of native silver up to 200 μm in size. Depending on variations in local site conditions the artefact may or may not have any residual metal, yet the mass of silver chloride comprising the corrosion product layer will often retain all the original surface details of the artefact.

Anaerobic concretions consist principally of copper and silver sulphides bound together by a calcareous cement which incorporates the normal range of seabed debris. The artefacts often appear to be about double the original thickness and the corrosion product layers incorporate many skeletal marine organisms surrounded by the metal sulphides. Cuprous oxide as well as elemental silver and copper are also found within the bands of concretion. Although most of the work reported herein is concerned with silver coins the basic mechanism of concretion formation pertains to all silver objects on a wreck site.

The local environment has a major influence on silver corrosion. On Western Australian wreck sites corrosion rates have been found to range from less than 5×10^{-4} mm per year to greater than 1.5×10^{-2} mm per year. Concretion formation tends to protect

silver artefacts from abrasion by seaborne grit. The cold working associated with the manufacture of silver artefacts, such as coins produced by a screw press or die stamping, makes the coins susceptible to stress corrosion cracking. The accelerated corrosion rate at the areas of high stress leads to the formation of deep fissures in the surface of the artefact (*Plate 10*).

4.10.2 Aerobic corrosion

In silver corrosion the major oxidizing agent in aerobic conditions is oxygen. The reduction of oxygen on silver is characterized by fairly rapid kinetics so the overall corrosion rate will be determined by the anodic silver oxidation.

The formation of both AgCl and a mixed AgCl/Br in seawater is not unexpected if one considers the relative activities of Cl^- and Br^- and solubility products for AgCl and AgBr (there is no data available on AgClBr but its properties would be expected to be between AgCl and AgBr). At 25°C the solubility product for AgBr is 7.7×10^{-13} and that for AgCl is 1.56×10^{-10}; the respective activities for Cl^- and Br^- in normal seawater are 0.319 and 8.14×10^{-4}.[190] Hence precipation of AgCl from seawater should occur when the activity of Ag^+ reaches 2.92×10^{-10} and AgBr at the slightly higher value of 5.04×10^{-10}. AgCl/Br would be expected to precipitate at some intermediate value of Ag^+ activity and the fact that AgCl and AgCl/Br are found but not AgBr suggests the AgCl/Br value lies quite close to that for AgCl. The theoretical difference between AgCl and AgBr saturation levels is so small that kinetic effects may also be very important.

Although silver forms a series of soluble chloro-complexes up to $AgCl_4^{3-}$ the corrosion of silver in aerobic seawater is dominated by the formation of the insoluble AgCl and AgCl/Br. Since silver corrosion products tend to remain in the vicinity of the original metal the formation of soluble $AgCl_2^-$, although thermodynamically favoured, does not appear to be kinetically significant.

The mineralization of silver-copper alloys will be controlled by the corrosion of both silver and copper. If the work history of the artefact has resulted in a uniform distribution of copper in the silver matrix uniform grain corrosion will occur with both copper and silver being oxidized. More commonly the copper tends to be concentrated at the grain boundaries and in these areas there is preferential attack on the copper. The formation of thermodynamically stable and water-soluble copper (I) chloro-complexes results in the copper diffusing away from the metal surface and into the concretions. Because of the differences in pH and chloride ion activity in the concretion, hydrolysis of the copper (I) chloro-complexes can occur to produce cuprite. The chloro-
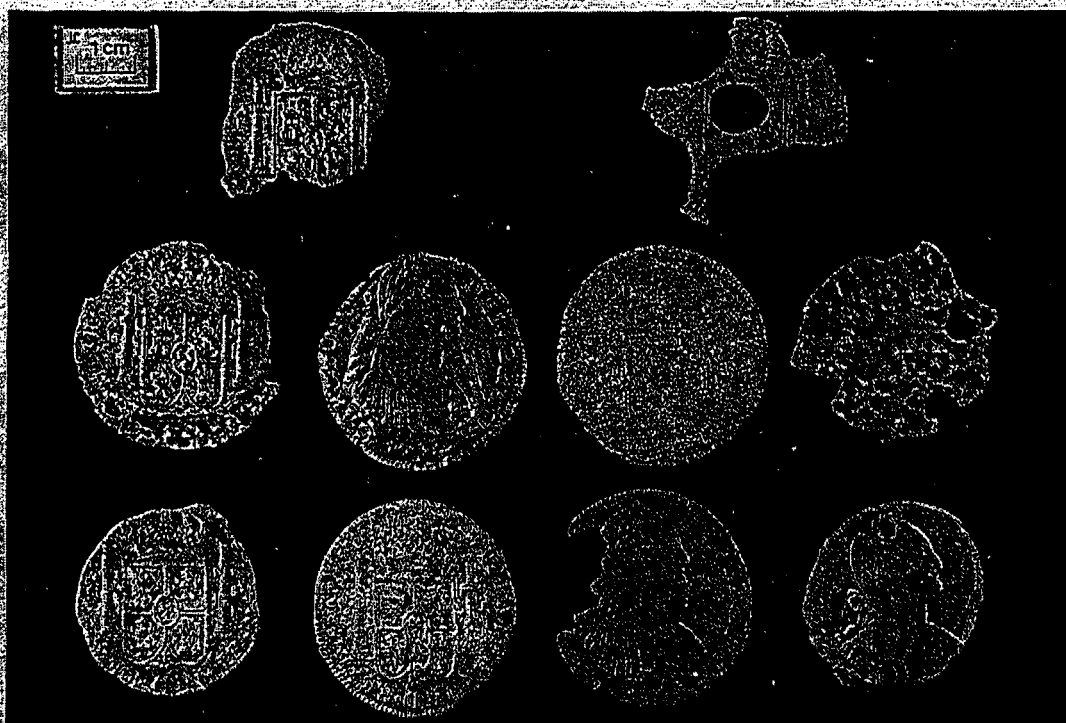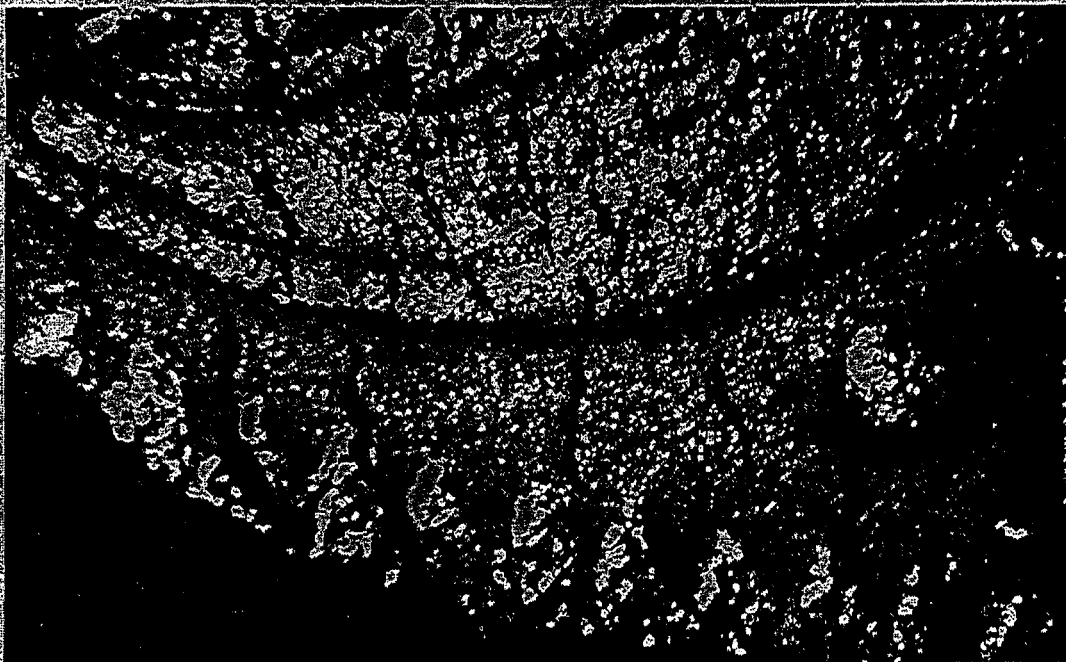
Plate 10 (a) Typical corrosion patterns on silver coins – after cleaning. (*Rapid* 1811)
(b) Residual stress corrosion cracking on milled edge of silver coin – after cleaning. (*Rapid* 1811)

complexes may also be oxidized to form the copper (II) hydroxychlorides. Of the soluble copper (I) species in seawater the $CuCl_2^-$ ion is the major component at 48%.

Inorganic calcite ($CaCO_3$) crystals are found on the surface of silver artefacts corroding in aerobic conditions and these most probably form by reaction of soluble calcium bicarbonate with the hydroxide

ions produced in the cathodic reduction of oxygen (Equations 4.3 and 4.22, Section 4.5.4).

The aerobic silver concretions are typically 70–30% silver, 10–7% copper, 10–30% calcium and 0.6–0.4% magnesium. Generally the copper-to-silver ratio in the concretion is much higher than in the residual metal.

Although silver forms a series of oxides, Ag_2O,
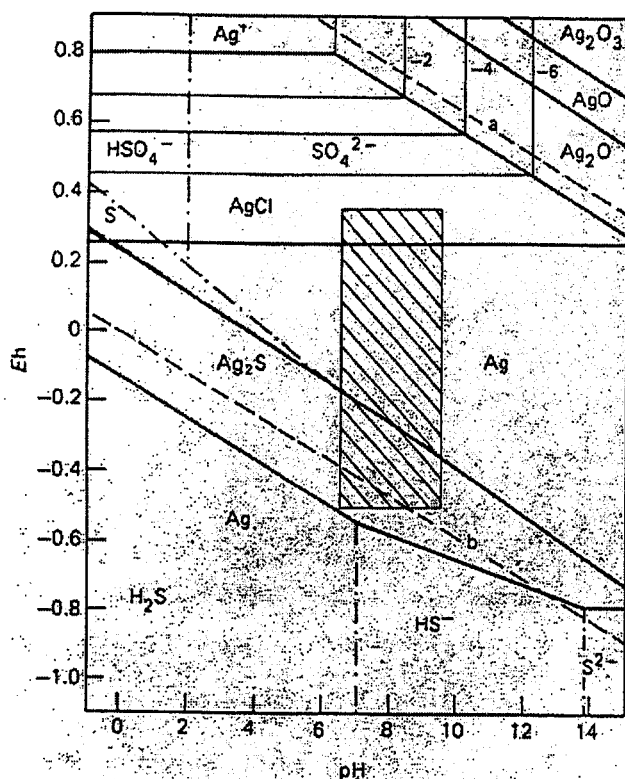
Figure 4.3 Pourbaix diagram for pure silver in seawater at 25 °C. Dissolved Ag 10^{-2} M; additional S^{2-} 10^{-3} M

AgO and Ag_2O_3, none of these have been reported as corrosion products on marine silver. Inspection of the Pourbaix diagram for silver in seawater (*Figure 4.3*) shows that in the range (hatched) of *Eh* and pH encountered in normal seawater these oxides are unstable with respect to the formation of AgCl.

From the Pourbaix diagram it will also be seen that there is a region of silver metal stability between that of AgCl and Ag_2S (in the normal marine range). If the potential of the system is in this silver stability range then the potential is too low for AgCl formation but too high for S^{2-}, and thus Ag_2S, formation. In practice these intermediate values of *Eh* can be found in the upper layers of the seabed where oxygen supply from the overlying seawater is restricted but sufficient still exists to prevent anaerobic conditions developing. A similar region of stability also exists for copper (*Figure 4.1(b)*) although over a small range. It is the existence of these metal stability regions which produces the small crystals of elemental silver and occasionally copper, in silver corrosion products. Consider a silver artefact in aerobic conditions for several years. This will have a corrosion layer of AgCl, AgCl/Br and copper compounds such as CuCl and Cu_2O. If the wreck site is now disturbed, say through storm action, and the coin becomes buried under a few centimetres of seabed the potential will drop into the region of metal stability. Reduction of silver and copper salts can now occur

producing crystals of elemental silver. Such crystals have been observed on coins from the *Batavia* (*Plate 11*) and *Rapid* wrecks in Western Australia.[138] Crystals of silver are far more common than copper crystals. With the *Rapid* coins, elemental silver crystals have also been observed in Ag_2S corrosion products although the crystals are much smaller than in AgCl corrosion products (≤ 12.5 µm compared to ≤ 250 µm). These probably result from coins initially corroding in deep anaerobic sediments (low *Eh*, high S^{2-}) being brought near the seabed as a result of storm or cyclonic activity. The alternating layers of AgCl (or AgCl/Br) and Ag_2S found in the corrosion products of coins from this wreck site are probably a reflection of these changes in site conditions.[191]

The *Eh* conditions favouring the formation of silver crystals can be attained by other means such as coupling with metal-ion concentration cells or by direct galvanic coupling.

4.10.3 Anaerobic corrosion

The major driving force in anaerobic corrosion of silver and its corrosion in aerated polluted waters is the formation of the silver sulphides, argentite and acanthite. Since argentite is the more thermodynamically stable of the two forms of Ag_2S[190] it is not surprising to find it as a major sulphide corrosion product. The oxidation of silver to form silver sulphide

$$2Ag + S^{2-} \rightarrow Ag_2S + 2e^- \tag{4.28}$$
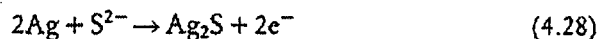
will be pH sensitive since the hydrosulphide ion, HS^-, is a weak acid. The fraction of sulphur ($-$II) existing as the sulphide ion is given by the relationship

$$\log \frac{[S^{2-}]}{[HS^-]} = pH - 12.9 \tag{4.29}$$

For seawater of pH 8.1 only 0.0017% of the analytical concentration of sulphide exists as the sulphide ion. In spite of its apparently very low activity the sulphide ion markedly increases the extent of corrosion of silver.

In aerobic polluted waters the main cathodic reaction in silver corrosion is the reduction of oxygen whereas in anaerobic marine sediments the main cathodic reaction is the reduction of hydrogen ions. The sulphate-reducing bacteria increase the silver corrosion rate in anaerobic water.

Elemental silver, hydrogen, water and silver sulphide can coexist in the range of *Eh* and pH associated with marine sediments as is shown in the Pourbaix diagram (*Figure 4.3*).

Electron microprobe analysis of silver corrosion products from anaerobic environments sometimes shows up a typically banded structure with distinct
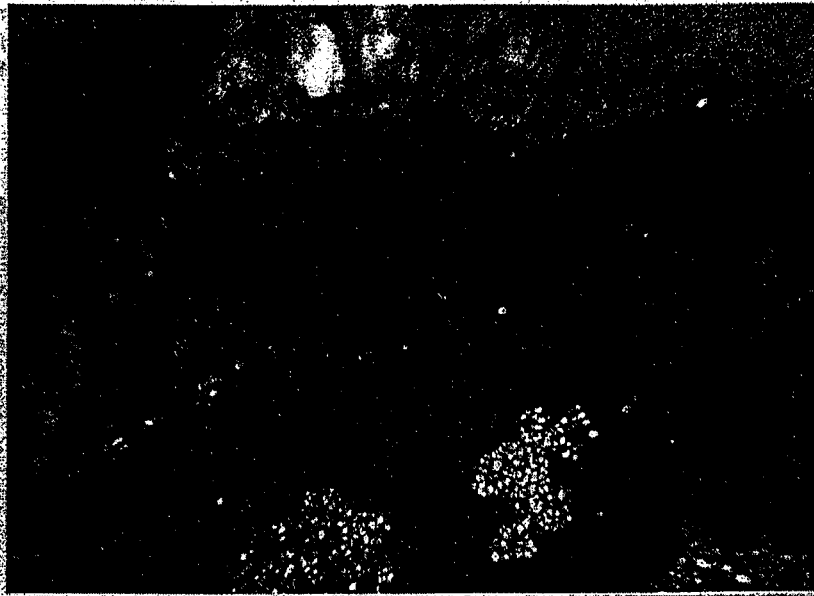
Plate 11 Concreted Rijksdaalder coin from the *Batavia* (1629), showing redeposited silver crystals (sparkling) against a silver chloride matrix. Impression of the lettering is seen in the concretion (1.8 × magnification)

layers of corrosion products. The formation of such bands indicates that variations in the corrosion mechanism (through changes in Eh and pH) can occur over a time-scale of hundreds of years. Data from a typical corroded coin from the *Rapid* (1811) is shown schematically in *Figure 4.4*. The coin shows a copper deficient zone adjacent to the residual metal
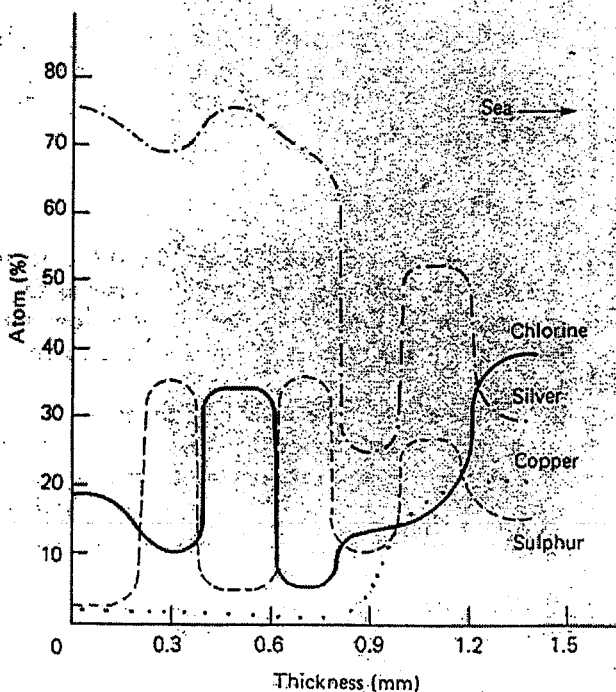
Figure 4.4 Distribution of silver, copper, sulphur and chlorine in the corrosion product layer of a 94.5% Ag 5.5% Cu coin after 170 years in sea (*Rapid* (1811))

where intergranular corrosion had occurred. The chloride ion in the first band is principally associated with a layer of silver chloride formed prior to the development of anaerobic conditions. The outward diffusion of copper chlorides normally results in a gradual increase in the amount of copper corrosion products as the distance from the centre of the coin increases. The formation of a layer of silver chloride in between layers of silver sulphide probably occurred as a result of cyclonic activity which alternately exposed (aerobic) and reburied (anaerobic) the coin.[191]

The potential distribution within a concretion is complicated by the different electrical resistances of the various corrosion product layers and this can result in one part of the concretion being stable for silver metal while another region of the same concretion favours the formation of silver sulphide.

4.11 Aluminium

Aluminium metal is thermodynamically unstable at room temperature and will react with moist air to form an oxide coating which is transparent, adherent and passivating. The metal has been produced on a commercial scale since 1886 but few shipwrecks have aluminium artefacts unless the vessel was lost later than the 1920s. Because of its light weight for volume aluminium and its alloys have been used extensively in the aircraft industry. Material recovered from the sea which was once part of an airplane (airship) is a convenient source of artefacts made from copper-aluminium alloys such as Duralumin. The corrosion mechanism associated with the mineralization of such

alloys in seawater is of direct relevance to conservators of wreck material who are increasingly being presented with historically important airplanes.

The possible corrosion products for marine aluminium covers a range of hydrated aluminium oxides and hydroxides but to date only one, gibbsite ($Al_2O_3 \cdot 3H_2O$), has been positively identified. This was found by MacLeod on the Duralumin alloys from the wrecks of the *Pelikaan* (1944, a DC3) and the *Atlantis* (1932, Junkers seaplane).[192] On the same artefacts the copper corrosion products were cupric oxides of unknown structure and composition.

Aluminium alloys are usually immune to general corrosion attack in the pH range of seawater. The protective oxide film has such a high electrical resistivity that electrons generated in the metal cannot pass through the film to be consumed by the oxygen reduction at the seawater interface. However, when a low resistance defect occurs in the aluminium film, passage of electrons from the internal metal to the seawater interface will occur and, under the right conditions, a spot of localized corrosion will develop in the vicinity of the defect. This type of corrosion is known as pitting corrosion. With aluminium, pitting corrosion occurs in the pH range of 4.5 to 9.0 where the oxide film is stable. In the marine environment the high concentration of chloride ions encourages pitting corrosion of aluminium.[193]

Although the adherent oxide film on aluminium appears to be uniform to the naked eye it actually contains many minute imperfections (up to one million per square centimetre). These defects may be potential cathodic sites where conducting impurities, such as copper or $FeAl_3$ particles, provide a pathway for electrons from the aluminium metal to the oxygen reduction site, i.e.:

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \qquad (4.3)$$

Another type of defect is the potential anodic site where weakness in the oxide film can allow passage of ions between the aluminium and the seawater. These defects may be grain boundaries, slip planes, oxide or sulphide impurities or other similar defects. Under favourable Eh and pH conditions this combination of inherent anodic and cathodic sites will result in pitting corrosion. Once pitting corrosion is initiated the reaction continues as shown in *Figure 4.5*.

The main anodic reaction occurs at the base of the pit where Al^{3+} ions are formed

$$Al \rightarrow Al^{3+} + 3e^- \qquad (4.30)$$

These then hydrolyse to produce aluminium hydroxy species and free hydrogen ions i.e.:

$$Al^{3+} + nH_2O \rightarrow Al(OH)_n^{(3-n)+} + nH^+ \qquad (4.31)$$

where n is 1 or 2. This production of H^+ maintains acidic conditions in the pit with the pH appreciably lower than in the bulk solution. Excessive acidity in

the pit is limited by the reaction of excess H^+ with aluminium metal, namely,

$$Al + 3H^+ \rightarrow Al^{3+} + 3/2\ H_2 \qquad (4.32)$$

The main cathodic reaction is the reduction of atmospheric oxygen (Equation 4.3) which occurs on the outer surface of the conducting impurities (usually copper). Electron balance in this system is achieved by movement of electrons from anodic to cathodic sites through the aluminium metal and conducting impurities.

Ionic charge neutrality in aluminium pit corrosion in seawater is mainly by the inward diffusion of chloride ions and the outward diffusion of positive aluminium species. The inward diffusion of chlorides produces a high chloride concentration in the pit and the formation of aluminium chloride species. When the aluminium and aluminium chloride species diffuse out of the pit the high pH of the bulk solution causes the precipitation of hydrated aluminium oxide which forms a porous corrosion mound over the pit site.

The growth of pits in aluminium is largely controlled by the rate of the cathodic process (reduction of oxygen). However pitting can also cease if the pH increases sufficiently to cause precipitation of aluminium oxide within the pit and thereby clogging it with corrosion products. The influence of chloride ion activity on the pitting of pure aluminium has been extensively investigated by Lowson.[194,195] Chloride ions are selectively absorbed at corroding pit sites and the corrosion potential of aluminium is directly related to the chloride ion concentration, e.g.

$$E\ corr. = -0.475 - 0.060\ \log\ [Cl^-]. \qquad (4.33)$$

For 34.8‰ salinity seawater this gives a corrosion potential of -0.46 volts. The more saline the environment the greater is the tendency for aluminium to develop pit corrosion.

The precise reason for the accelerating effect of chloride on the aluminium corrosion rate is not certain. Chloride ions may assist in the breakdown of the oxide film or they may catalyse the anodic reactions. There is an equilibrium between the formation of $AlCl_3$ in the pit and the formation of hydrated aluminium oxide at the surface, viz.

$$2AlCl_3 + 6H_2O \rightleftharpoons Al_2O_3 \cdot 3H_2O + 6HCl \qquad (4.34)$$
$$(pit) \qquad\qquad (surface)$$

If the pH and chloride concentration favour the formation of $AlCl_3$ instead of $Al_2O_3 \cdot 3H_2O$ the pit will remain active. Sulphate ions tend to inhibit pit corrosion[194] but their concentration in seawater is not sufficient to greatly affect the overall pitting of aluminium.

Copper-aluminium alloys, such as Duralumin, suffer extensively from pitting corrosion in seawater due to their metallurgical structure. The solubility of
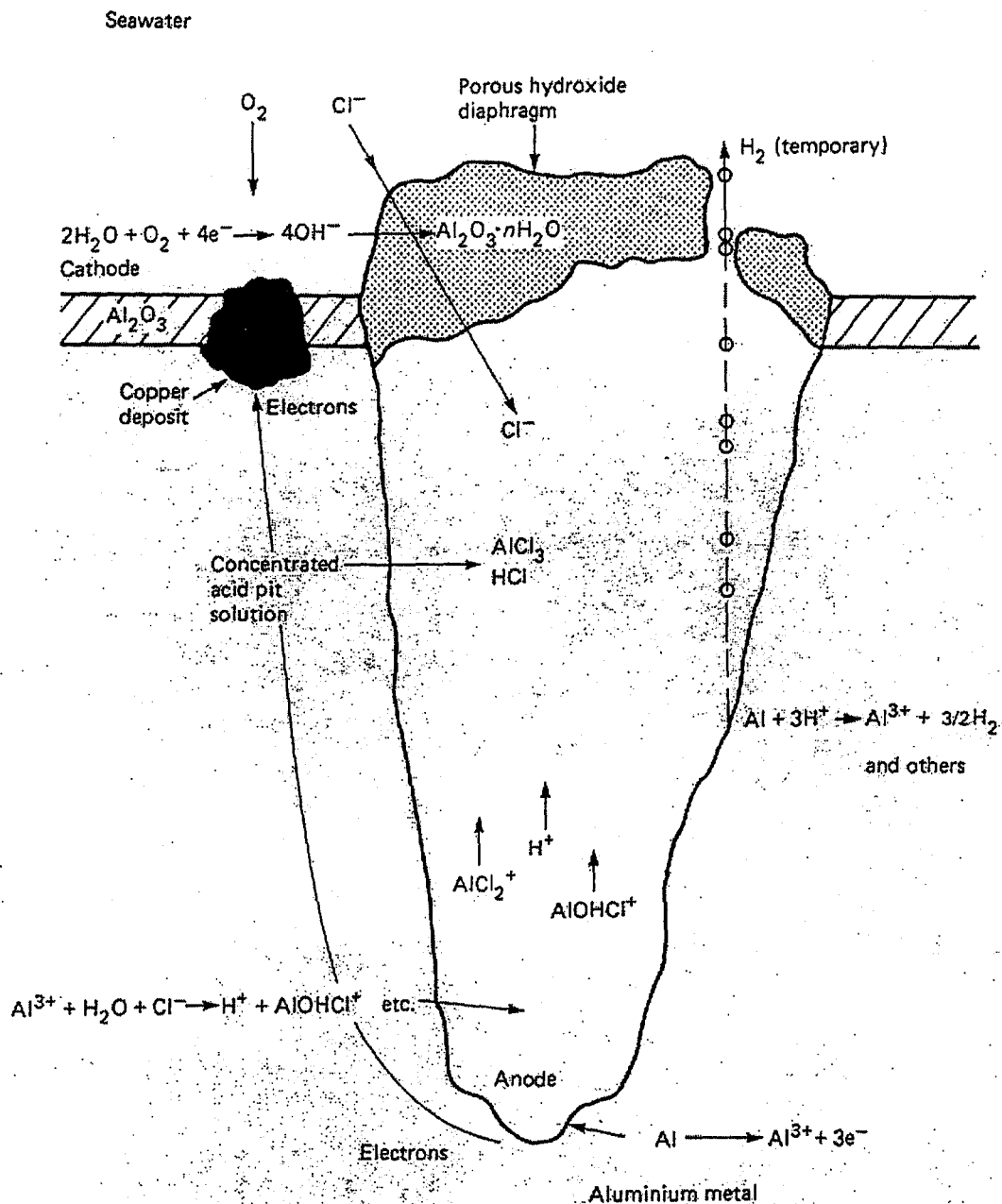
Figure 4.5 Schematic diagram of active corrosion pit in aluminium

copper in aluminium is limited and is exceeded in the Duralumin alloys which contain 3–5% copper. Such metals are subject to precipitation hardening. The precipitation of discrete $CuAl_2$ units from the solid solution will leave aluminium-rich regions at the grain boundaries. Since the grain boundaries are anodic to the $CuAl_2$ units these areas will be preferentially attacked (see *Table 4.3* for the corrosion potentials of various aluminium alloys). The result of this intergranular corrosion is that the effective surface area of the metal is greatly increased and the bulk of the grain is now exposed to general corrosion. When oxidation of the $CuAl_2$ units occurs the copper

compounds as well as aluminium hydroxides will be precipitated by the surrounding seawater.

At defect sites any copper corrosion products in contact with bare aluminium metal will be reduced back to elemental copper by the aluminium[196] and so provide new cathodic sites for the reduction of oxygen. Since the pitting rate is controlled by the cathodic reaction the dramatic increase in the aluminium corrosion rate brought about by a series of copper deposits is not unexpected. Patches of elemental copper were found under the corrosion product mounds on metal recovered from both the *Pelikaan* and the *Atlantis* seaplane float. The adjacent metal was

perforated. It is very hard to inhibit copper-aluminium alloys against intergranular corrosion.[197]

4.12 Gold

Gold has been used for thousands of years in the manufacture of jewellery, ceremonial vessels, utensils and apparel, etc. It has also been used as a precious coinage metal. Gold is often alloyed with other less valuable metals such as silver, copper and platinum. Although pure gold and its platinum alloys are

extremely corrosion resistant in seawater under all conditions its alloys with silver and copper are subject to corrosion. The corrosion in this case takes the form of selective attack on the alloying element which results in similar types of surface conditions as found in dezincification.

The corrosion products formed on the artefact are the same as those found on objects made principally of the alloying metals, for example $AgCl$, $AgCl/Br$, Ag_2S forms on silver-gold alloys. Selective removal of the base metal from the alloy gives a surface richer in gold than is the parent material.