

1 A FRAMEWORK FOR CONSERVATION OF METALS

1.1 INTRODUCTION

The conservation procedure developed for any artefact is essentially a decision making tool based on gathering, using and recording information on the following:

- The object
- The conservation process
- The risk to the object.

However, the conservation of artefacts of cultural and historical significance is a subject that could benefit greatly from the wealth of experience and knowledge gained from the corrosion control activities that have been employed over many years to maintain the function of engineering systems. The aim of this document is to provide a framework and the technical logic that facilitates the application of best practices to corrosion control in conservation. The advantage of this approach is that it is well established, well understood and the existing infrastructure of corrosion control; the experts, the systems, the process, are readily available.

1.2 RECORDING INFORMATION

The accurate and clear recording of information is essential and should begin at the point where the object is located in its current situation and condition regardless of whether it is found in the field or has already been removed. A simple rule is to record, the who, what, why, where, when, how? of any situation or change.

The first set of information should be based on providing a description of the opening scenario from which other decisions can be made.

1.3 THE OBJECT

Identification of the object

Identification of the object should include; what it is, its significance and its value. Significance includes its location i.e. a common object found in an unusual place may be as significant as a rare object. Value is not only based on a monetary evaluation but includes the object's scientific, historical and cultural worth.

The condition of the object

The condition of the object should be evaluated in-situ to avoid further damage. Any damage caused when it is moved should be recorded.

Control over any conservation process can be best achieved when the materials being conserved are identified in a detailed way. This information may not be available for many artefacts but information from similar examples can be used or small samples taken from the artefact to be conserved analysed. It is worth noting that in the case of metals differences in

the chemical composition within a group of alloys may have a significant effect on the rate that a process occurs. Over a period of time the surface of metals can change and give a false impression of what lies underneath. Removal of a small area of the external layer may provide valuable information.

1.4 THE CONSERVATION PROCESS

The first step in any conservation process is the assessment of the how the object may deteriorate if nothing is done and an estimate of the drop in value that could occur. This should include an estimate of the lifetime of the object based on a projection of its deterioration over time.

When this has been completed the next step is the setting of a series of objectives focussing on the prevention of further deterioration. These need to be described in terms of what needs to be achieved and for how long the object will remain stable.

A strategy should then be proposed to achieve each objective and this should be a step-wise approach including the recording and use of information gained through implementation of the strategy. For example removal of corrosion products can reveal a different situation to that initially observed.

The strategy proposed should then be supported by the investigation of best available methods and technologies to achieve the intended result. The selection of suitable processes and development of an implementation plan should be completed before a final evaluation is made.

1.5 RISK EVALUATION

When the objectives have been set and the conservation methods have been selected an estimate of the risks, costs, safety and environmental implications should be made.

Every conservation method that can be used has the potential to cause damage to the object being conserved. The risk can be evaluated by assessing the likely consequences and the probability that they will occur. The value of the object is a significant factor that also needs to be included in the consequences evaluation.

The risks can be reduced considerably if counter-measures associated with each risk are outlined and implementation plans made before conservation activity begins.

1.6 RECORD KEEPING

When an artefact is selected for conservation it provides a unique opportunity for information valuable to historians, archaeologists and future conservationists to be compiled in a systematic manner. The information is not just a record of the condition of the object but should also be a record of the supporting information used for the decision making process that guided the conservation strategy and the choice of processes used.

The information can take many formats; documents, forms, plans, photographs, sketches, test data sheets, measurements, comments and observations which need to be compiled in a structured way enabling interpretation by someone unfamiliar with the case. This may, of course, be some time in the future when best practices and processes have changed. This necessitates the recording of the basis on which any decisions were made or options chosen as well as explaining the contemporary context of activity.

1.7 CORROSION CONTROL

The control of corrosion of metal artefacts can best be considered by limiting the actions and possible outcomes to a few carefully considered possibilities:

- a) Taking no action and accepting the current rate of degradation (this should be accompanied by monitoring)
- b) Retarding the degradation rate without removal of any material or corrosion products
- c) Removal of the corrosion products to improve the appearance of the object and accepting the current corrosion rate
- d) Removal of the corrosion product accompanied by other actions to retard the corrosion rate

Removal of corrosion Products

Corrosion products can either protect the artefact from further corrosion, accelerate the process of corrosion or cause physical damage.

Removal of the corrosion products can be achieved through mechanical, chemical or electrical means.

Mechanical methods include the use of abrasives, scrapers, and specially designed tools to remove the corrosion product. Care must be taken to prevent the debris from this operation from damaging or becoming trapped in other parts of the artefact. Water jetting is also an example of this type of technique. Ultrasonic cleaning uses high frequency sound waves to break up the corrosion product in a medium such as water.

Chemical cleaning involves the application of a specific solution for a given time at a given temperature to the corrosion product followed by rinsing to remove the solution. The technique relies on the solution's ability to act selectively on the corrosion product without affecting the underlying or surrounding material. Some solutions have a dual role for example inhibited acid cleaners. The acid dissolves the corrosion product and the inhibitor action protects the surface of any exposed metal.

Electrolytic cleaning uses the joint action of an electrical current to remove ionic or polarised materials from the surface of the metal. The action is usually part electrical part chemical and careful control of voltages, currents and application times are necessary.

Corrosion control

Corrosion is an electro-chemical reaction that occurs according to a mechanism specific to the combination of material, environment and component geometry. Once the process is understood it can be controlled by interfering with the chemical or electrical processes, or altering the component geometry.

The first step, therefore, is the identification of the corrosion mechanism you wish to retard.

2 CORROSION PROCESSES AND MECHANISMS

(edited from the original work of Alan Turnbull and Aeronwen Griffiths)

2.1 FORMS OF CORROSION

Corrosion damage can take many forms depending on the nature of the environment, the composition of the metal, and the existence of stresses. The varied phenomena may be classified into the following broad categories:

- general corrosion
- localised corrosion – *pitting corrosion, crevice corrosion, intergranular corrosion*
- environment assisted cracking – *stress corrosion cracking, hydrogen embrittlement, corrosion fatigue*
- galvanic corrosion
- flow enhanced corrosion
- atmospheric corrosion
- microbiologically influenced corrosion.

2.2 GENERAL CORROSION

General corrosion, or uniform corrosion, is characterised by a corrosion reaction that proceeds at a similar rate over the entire exposed surface. It occurs when the naturally existing protective oxide film on a metal either dissolves completely on exposure to a corrosive environment or becomes weakly adherent and non-protective. Without the constraint of protective oxide films, the metal is exposed directly to the solution and corrodes over the whole of the exposed surface, often at a significant rate. The metal surface may become covered with corrosion product, for example rust, but this is not protective. The metal is described as being in the active state.

In general corrosion, the metal dissolution process (the anodic reaction) and the balancing reaction of reduction of dissolved oxygen and/or hydrogen ions (the cathodic reaction) occur at preferential sites on the metal surface; these are usually microscopic in nature and randomly distributed over the surface. The total current flowing between these sites is referred to as the corrosion current and may be converted into metal loss by appropriate application of Faraday's law.

For other metals and alloys, e.g. stainless steels, nickel-base alloys and titanium, the oxide film is stable and protective in neutral solutions. The metal is then described as being in the passive state, the protective oxide film is referred to as a passive film. Nevertheless, the solubility of the passive films on these metals and alloys may increase in acidic or alkaline (as in the case of aluminium) solutions, resulting in a significant rate of general corrosion.

2.3 LOCALISED CORROSION

Localised corrosion generally occurs when an otherwise protective film breaks down. The film may be a passive oxide, or scale. The local breakdown of these films are generally of greatest concern when they support cathodic reactions leading to enhanced local corrosion.

The protectiveness of passive oxide films can be adversely affected in neutral waters if there is an aggressive anion present, for example, chloride (Cl⁻) ions. These aggressive anions become concentrated in regions where there is some constraint to solution mixing, for example in a crevice which may be formed by a mechanical joint or a deposit. The restricted mass exchange between the crevice and the bulk solution means that the main cathodic reaction, reduction of oxygen, occurs outside the crevice. At the same time, the small dissolution current associated with the passive film causes migration of Cl⁻ ions into the crevice to balance the charge associated with the metal cations. This leads to the build up of concentrated metal salt solutions and, via hydrolysis of metal cations, to acidic pHs. Dissolution of the protective oxide film may then proceed and with subsequent localised corrosion.

Localised corrosion can be particularly ruinous since, although the total loss of metal is not significant, the depth of perforation may be such as to lead to significant damage.

2.4 ENVIRONMENT ASSISTED CRACKING

Environment assisted cracking is an all embracing term for stress corrosion cracking and hydrogen embrittlement. Failure by environment assisted cracking can be catastrophic because it undermines the structural integrity of the component or structure.

Stress corrosion cracking refers to brittle cracking caused by the simultaneous presence of an applied stress and a specific environment. The stress can be an internal one caused by manufacture as well as being applied externally.

Hydrogen embrittlement is induced by absorption of hydrogen atoms which tend to localise at microstructural sites such as inclusions, dislocations and grain boundaries. The absorbed hydrogen atoms can be generated through corrosion, galvanic coupling and cathodic protection. Cracking can ensue when there is a critical combination of localised hydrogen atom concentration, stress and a susceptible microstructure.

2.5 GALVANIC CORROSION

When dissimilar metals are immersed and coupled in a conducting solution, they develop different voltages (corrosion potentials) on their surfaces due to the devolution of metal ions and the production of associated electrons. If one of the metals is significantly more noble (i.e. the corrosion potential is more positive), this will result in an increase in the electrode potential of the less noble metal, the extent of which will depend on the area ratio and the solution conductivity. If the less noble metal is in the active state, then enhanced general corrosion will occur; on the other hand if the metal was initially in the passive state, localised corrosion may ensue. Galvanic corrosion can often be avoided by limiting the area ratio of

the more noble material to that of the less noble metal. However, there are many mixed metal systems in which inhibitors are required to combat galvanic corrosion.

2.6 FLOW ENHANCED CORROSION

Flow has an important impact on corrosion rates. For metals in the active state, flow enhanced corrosion is largely associated with the enhanced supply of cathodic reactant to the surface or removal of corrosion products. For systems with corrosion product layers or inhibiting films, localised film breakdown and corrosion-erosion may occur under highly turbulent conditions, particularly where there is particulate matter in the fluid or roughness of the surface. In these conditions the phenomena are described as flow induced localised corrosion.

2.7 ATMOSPHERIC CORROSION

Metals can corrode when exposed to the outdoor atmosphere as a consequence of wet and dry cycles induced by rainfall and condensation. Corrosion is more significant when pollutants such as sulphur dioxide or chloride are present in the atmosphere. It may occur also indoors or in packaging if the humidity is high or significant decreases in temperature create condensation. The corrosion rate is determined by the time of wetting, the frequency and duration of drying out periods, relative humidity, temperature and temperature variation, and by the composition of the atmosphere. The control of atmospheric corrosion by inhibition is usually based on inhibited coatings, greases and water repellent fluids in open systems or by the use of volatile (vapour phase) corrosion inhibitors in closed or semi-closed systems. The latter are often used in packaging or storage of metal parts, for which temporary, i.e. removable, coatings may also be used.

2.8 MICROBIOLOGICALLY INFLUENCED CORROSION

Microbiologically influenced corrosion can occur in natural waters, sea water, and soils. Micro-organisms can affect corrosion in a variety of ways: by the formation of biofilms leading to enhanced oxygen reduction (as in sea water), by producing slimes and deposits under which crevice corrosion can initiate, by creating corrosive (often acidic) conditions through their metabolic products, by destroying chemicals added to the system to provide corrosion inhibition, and by directly influencing the corrosion reactions. Both aerobic and anaerobic bacteria can enhance corrosion, an example of the former being sulfur oxidisers whilst the most important anaerobic bacteria are the sulphate reducing bacteria. In addition to the impact on corrosion, microbial growths also cause fouling. Treatment to reduce biological activity is based primarily on the use of biocides but ozonation and ultraviolet (UV) exposure have been used in specific applications.

Control of microbial activity is mainly by biocides of which chlorine treatment is probably the most common, although there is a drive to reduce the amount of chlorine used, for example, by intermittent rather than continuous chlorination.

Chlorine and other oxidising biocides can lead to decomposition of nitrogen-containing organo-phosphorus compounds present for scale and corrosion control in water cooling systems. This will lead to the production of ortho-phosphates which, in turn, can result in

scale formation. Chlorine can also bring about the decomposition of nitrogen-containing copper corrosion inhibitors, notably the azoles. Chlorine can raise the corrosion potential and increase the risk of localised attack in systems with a passive film.

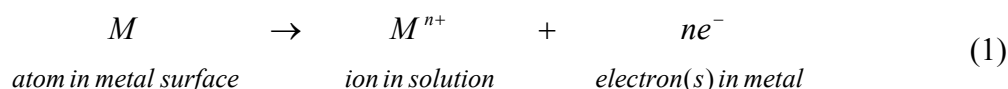
3 CORROSION ELECTROCHEMISTRY

Edited by Gareth Hinds from the original work of J G N Thomas

3.1 INTRODUCTION

The surfaces of all metals (except for gold) in air are covered with oxide films. When such a metal is immersed in an aqueous solution, the oxide film tends to dissolve. If the solution is acidic, the oxide film may dissolve completely leaving a bare metal surface, which is said to be in the active state. In near-neutral solutions, the solubility of the oxide will be much lower than in acid solution and the extent of dissolution will tend to be smaller. The underlying metal may then become exposed initially only at localised points where owing to some discontinuity in the metal, e.g. the presence of an inclusion or a grain boundary, the oxide film may be thinner or more prone to dissolution than elsewhere. If the near-neutral solution contains inhibiting anions, this dissolution of the oxide film may be suppressed and the oxide film stabilised to form a passivating oxide film which can effectively prevent the corrosion of the metal, which is then in the passive state.

When the oxide-free surface of a metal becomes exposed to the solution, positively charged metal ions tend to pass from the metal into the solution, leaving electrons behind on the metal, i.e.



The accumulation of negative charge on the metal due to the residual electrons leads to an increase in the potential difference between the metal and the solution. This potential difference is called the electrode potential or, simply, the potential of the metal, which thus becomes more negative. This change in the potential tends to retard the dissolution of metal ions but to encourage the deposition of dissolved metal ions from the solution onto the metal, i.e. the reverse of reaction (1). Continuation of the dissolution and deposition of metal ions would result in the metal reaching a stable potential such that the rate of dissolution becomes equal to the rate of deposition. This potential is termed the reversible potential E_r and its value depends on the concentration of dissolved metal ions and the standard reversible potential E° for unit activity of dissolved metal ions, $a_{M^{n+}}$, i.e.

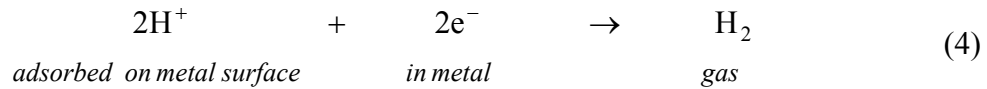


$$E_{r,M^{n+}/M} = E^{\circ}_{M^{n+}/M} + \frac{RT}{nF} \ln a_{M^{n+}} \quad (3)$$

where R is the gas constant, T the absolute temperature, F the Faraday and n the number of electrons transferred per ion. Once the potential reaches the reversible potential, no further net dissolution of metal occurs. The net amount of metal which dissolves during this process is generally very small.

The potential of a metal in a solution does not usually reach the reversible potential but remains more positive because electrons can be removed from the metal by alternative

reactions. In acid solutions, electrons can react with hydrogen ions, adsorbed on the metal surface from the solution, to produce hydrogen gas.

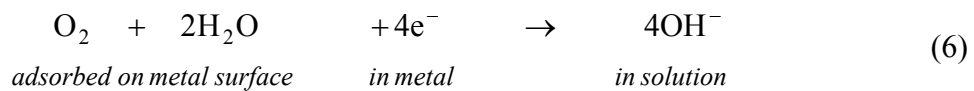


The occurrence of reaction (4) permits the continued passage of an equivalent quantity of metal ions into solution, leading to corrosion of the metal. Reaction (4) is also reversible and has a reversible potential given by

$$E_{\text{r,H}^+/\text{H}_2} = E^{\circ}_{\text{H}^+/\text{H}_2} - \frac{RT}{F} \ln \frac{p_{\text{H}_2}^{\frac{1}{2}}}{a_{\text{H}^+}} \quad (5)$$

where p_{H_2} is the partial pressure (fugacity) of hydrogen gas. If the partial pressure of hydrogen is allowed to build up, then the reversible potential of reaction (4) could be attained. No further net reaction of hydrogen ions would occur and so the net dissolution of metal ions would effectively cease. Normally hydrogen escapes from the system, so that the potential remains more negative than the reversible potential and corrosion continues.

In neutral solutions, the concentration of hydrogen ions is too low to allow reaction (4) to proceed at a significant rate, but electrons in the metal can react with oxygen molecules, adsorbed on the metal surface from air dissolved in the solution, to produce hydroxyl ions



Again, the potential of the metal remains more negative than the reversible potential for reaction (6)

$$E_{\text{r,O}_2/\text{OH}^-} = E^{\circ}_{\text{O}_2/\text{OH}^-} - \frac{RT}{4F} \ln \frac{a_{\text{OH}^-}^4}{p_{\text{O}_2}} \quad (7)$$

Thus corrosion can proceed by the coupling of reactions (1) and (6).

In electrochemical terminology, an electrode at which an oxidation reaction occurs is called an anode. The process of oxidation involves a loss of electrons by the reacting species, as occurs in the metal dissolution reaction (1). Thus an area of a corroding metal where metal dissolution occurs is an anode and metal dissolution is the anodic reaction of corrosion. An electrode at which a reduction reaction occurs is called a cathode. Reduction involves a gain in electrons, as occurs in reactions (4) and (6). The reduction of hydrogen ions and oxygen are thus the cathodic reactions of corrosion and the area of a corroding metal where these reactions occur is a cathode.

3.2 POTENTIALS AND POLARISATION

Since the corrosion reactions involve the transfer of electrons and ions between the metal and the solution the rates are equivalent to electric currents. The rates of these reactions depend on the potential difference between the metal and the solution, i.e. the potential of the metal. As the potential of the metal becomes more positive, the rates of anodic reactions increase and the rates of cathodic reactions decrease. The converse effect on the reaction rates occurs as the potential of the metal becomes more negative. From the relationships between the potential of a metal and the currents flowing (equivalent to rates of the corrosion reactions) the corrosion behaviour can be understood. The relationships between potential and current (termed polarisation curves) can be determined as shown schematically in Fig 1. The potential in the test solution of the metal under study, the working electrode, is measured against that of a reference electrode by means of a voltmeter. The reference electrode is chosen to give a stable and reproducible potential in the solution. The reference electrode most commonly used is the saturated calomel electrode, which consists of mercury covered with a paste of mercurous chloride and mercury in a chloride solution. The potential depends on the concentration of chloride ions and a saturated solution of potassium chloride is used because this minimises the junction potential between the test solution and the solution in the reference electrode in the measuring cell.

Metal/Test solution/KCl (satd), Hg_2Cl_2 (solid)/Hg. Contact between the test solution and the saturated potassium chloride solution of the calomel electrode is usually made through a porous ceramic plug, which minimises the mutual contamination of the two solutions. The potential difference across this cell gives the potential of the metal in the test solution against the saturated calomel electrode (SCE) and is quoted as such. The primary standard of electrode potential is the standard hydrogen electrode (hydrogen gas at 1 atm pressure (unit fugacity) over platinised platinum in a solution containing hydrogen ions at unit activity) which is arbitrarily defined as having a potential of zero volts $E^\circ_{\text{H}^+/\text{H}_2}$ in equation (5) is zero. This is not commonly used as a practical electrode, but potentials are often quoted on this scale, e.g. the potential of the saturated calomel electrode is +0.24 volt against the standard hydrogen electrode (SHE). Another reference electrode used for measuring potentials of corroding metals is the silver/silver chloride electrode, which consists of a silver wire coated with silver chloride in a chloride solution. This electrode is commonly used in seawater. For measuring potentials of metals in soils, the copper/copper sulphate electrode may be used. This consists of a copper rod in a saturated solution of copper sulphate. This electrode can be made very robust, with a wooden plug saturated with the copper sulphate solution to make contact with the test environment.

The potential-current relationship of the working electrode may be determined by either of two main methods. In the galvanostatic method, a fixed current is applied from a constant-current power source connected between the working electrode and a counter electrode, which is usually made of some inert material such as platinum. The change in potential induced in the working electrode by the passage of current is measured against the reference electrode.

In order to minimise the inclusion in the measured potential of any potential drop occurring in the solution due to its resistance, i.e. an IR drop, the reference electrode is brought into contact with the test solution through a tube which ends in a fine capillary known as a Luggin capillary. This is placed close to the surface of the working electrode, though no closer than twice the external diameter of the capillary to avoid screening of the electrode from the flow of current. In the potentiostatic method, as illustrated in Fig 1, the potential of the working

electrode is controlled at a fixed value with a potentiostat. This instrument uses a feed-back circuit to pass appropriate currents to the working electrode so that its potential measured against the reference electrode is maintained at the desired value, regardless of variations in current corresponding to changes in the rates of the corrosion reactions. The potentiostatic method of polarisation has the advantage that it can follow more closely the behaviour of metals during the formation and breakdown of passivating films, where the behaviour primarily depends on the potential of the metal, and very large changes in currents can occur at constant potential.

3.3 POLARISATION BEHAVIOUR OF CORRODING METALS

A corroding metal in a solution takes up a potential, the corrosion potential, such that the rate of the anodic reaction of metal dissolution is equal to the rate of the cathodic reactions of hydrogen and/or oxygen reduction. If the potential of the corroding metal is displaced slightly from the corrosion potential, E_{corr} , either by galvanostatic or potentiostatic polarisation, then the potential E is initially a linear function of the current density i (the current per unit area). This linear relationship holds for a potential displacement of up to about 10 mV. The slope of the linear polarisation curve dE/di is termed the polarisation resistance R_p . The polarisation resistance is inversely proportional to the rate of corrosion expressed as the equivalent corrosion current density i_{corr} , i.e.

$$i_{\text{corr}} = B/R_p \quad (8)$$

where B is a constant. Measurements of the polarisation resistance provide a valuable means of rapidly determining the instantaneous rate of corrosion of a metal, as used in several commercial instruments. The value of the constant B can be determined from weight loss measurements or from electrochemical data.

As the displacement of the potential of the metal from the corrosion potential is increased beyond about 10 mV, the polarisation curve increasingly deviates from the linear relationship between potential and current until a region is reached when the potential exhibits a linear dependence on the logarithm of the current density as shown in Fig 2. This behaviour is characteristic of the occurrence of a single electrochemical reaction on the metal surface, indicating that the displacement of potential is so great that one of the corrosion reactions, either anodic or cathodic depending on the direction of potential change, has been retarded until its rate is negligible compared to the rate of the reaction being accelerated. Then the relationship between the observed potential E and current density i is given by

$$E - E_r = i_0 + b \log i \quad (9)$$

The difference between the observed potential and the reversible potential E_r is the overpotential. The term i_0 is the exchange current density, i.e. the current density of the opposing reactions at the reversible potential. The constant b which is the slope $dE/d \log i$ of the polarisation curve is termed the Tafel slope and is related to the kinetics of the corrosion reaction. For the cathodic reactions of hydrogen ion reduction or oxygen reduction, the value of B is generally about 120 mV. For metal dissolution reactions from active surfaces, values of b are generally smaller and in the range 30 to 70 mV.

Polarisation curves similar to that of Fig 2 are generally observed for both the anodic dissolution of metal and the cathodic reduction of hydrogen ions in acid solutions. Figure 3 shows schematically the juxtaposition of the anodic and polarisation curves (full lines) for a metal corroding in an acid. This diagram also shows the relationship of the polarisation curves to the reversible potentials and exchange current densities of the metal dissolution and hydrogen ion reduction reactions. The observed Tafel regions of the polarisation curves extrapolated to the corrosion potential E_{corr} , intersect there to give the value of the corrosion current density i_{corr} . Further extrapolation leads to the reversible potentials and exchange currents of the reactions, the values of which determine the relative position of the observed polarisation curves. The values of the reversible potentials represent the extreme values which the potentials of the anodic and cathodic areas can reach. If the concentration of hydrogen ions in the acid is increased, then according to equation (5) the reversible potential becomes more positive. The exchange current also increases, but the Tafel slope of the polarisation curve remains unchanged. Thus the polarisation curve of the hydrogen ion reduction reaction is displaced parallel to itself, from AB to CD, to initiate at the more positive reversible potential and large exchange current density, as shown in Fig 4. According to equation (3), the anodic reaction is not affected by the change in pH. Thus the increase in hydrogen ion concentration causes the anodic and cathodic polarisation curves now to intersect at D instead of B, so that the corrosion potential becomes more positive and the current at the intersection, the corrosion current increases. Diagrams such as Fig 4, which represent schematically the polarisation curves of the anodic and cathodic reactions in relation to the corrosion potential and current are known as Evans Diagrams. These are valuable for understanding and predicting qualitatively the influence of changes in the polarisation curves on the corrosion potentials and currents, and conversely the effects of changes in corrosion potential and current on the polarisation curves.

The cathodic and anodic reactions of corrosion will now be considered in more detail.

3.4 CATHODIC REACTIONS

In the cathodic reduction of hydrogen ions or oxygen molecules, these species must be adsorbed on the metal surface in order to react. Thus the hydrogen ions or oxygen molecules must be transported from the bulk solution up to the metal/solution interface. This transport occurs by the processes of diffusion and convection, and in the case of hydrogen ions electromigration. As the potential of the metal is made more negative in the Tafel region, the rate of reduction of hydrogen ions and oxygen molecules may increase to such an extent that it exceeds the rate at which these species can be transported to the metal surface. Then the rate of transport of the reducible species controls the rate of reduction. The cathodic current density attains a limiting value equivalent to the rate of transport and independent of potential, as illustrated in Figs 5 and 6. This is termed the limiting diffusion current density and its magnitude increases with increasing concentration of the reducible species (Fig 5) and increasing movement of the solution (Fig 6). As the potential becomes even more negative, the rate of reduction of water to produce hydrogen



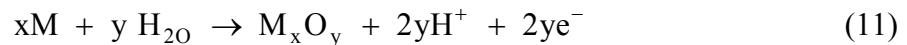
increases until it may exceed the diffusion limited rates of reduction of hydrogen ions or oxygen. The observed current density then increases e.g. along the line JKC in Fig 5, due to

the reduction of water. In this potential region the diffusion limited currents of reduction of hydrogen ions or oxygen continue to contribute to the total observed currents.

In acid solutions the limiting diffusion current density for reduction of hydrogen ions becomes significant in relation to corrosion at hydrogen ion concentrations of 0.01 M (i.e. pH 2) and below. The concentration of dissolved oxygen in air saturated aqueous solutions at ambient temperature is about 0.002 M and so the rate of transport of oxygen often limits the cathodic reduction current and the corrosion rate. The effect on the corrosion currents or rates is illustrated in Figs 5 and 6, which could represent the corrosion of steel in neutral chloride solutions. If the anodic polarisation curve intersects the cathodic polarisation curves in the region of the limiting diffusion currents, the corrosion currents are equal to the limiting diffusion currents and hence increase with increasing flow velocity (Fig 6) and concentration (Fig 5), the corrosion potentials becoming more positive. If there is a change in the position and/or Tafel slope of the anodic polarisation curve, e.g. due to a change in solution composition or for a different metal, the intersections of the anodic curves with the limiting current density regions of the cathodic curves lead to the same corrosion currents, though the corrosion potentials change. Thus under these conditions the corrosion rates depend only on the rate of reduction of the cathodic reactant and the corrosion is said to be under cathodic control.

3.5 ANODIC REACTIONS

On anodic polarisation of a metal, as the potential is made more positive in the Tafel region, as in Fig 3, the current for metal dissolution may reach a maximum value and then decrease abruptly to a small value, as indicated schematically in Fig 7. This behaviour is best observed by potentiostatic polarisation, and is due to the reaction of the metal surface with water to form an oxide, e.g.



$$E_{r,M_xO_y/M} + E^{\circ}_{M_xO_y/M} + \frac{RT}{F} \ln a_{H^+} \quad (12)$$

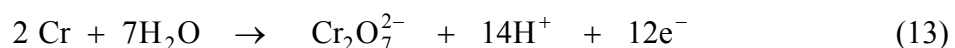
The oxide gradually spreads over the surface to form a thin film. The passage of metal ions through an oxide film takes place very slowly and so the current due to metal ions leaving the metal becomes very small when the surface is completely covered with an oxide film. The metal is thus protected against corrosion by a passivating oxide film. The formation of the passivating oxide film is observed to begin near the peak B of the polarisation curve AB and the potential of the peak is referred to as the critical (primary) passivation potential, E_{pp} . The initial passivation potential depends on the pH value of the solution becoming about 60 mV more negative for a unit increase in pH value. The critical passivation potential also depends slightly on the composition of the solution, particularly with respect to the presence of anions which may favour or hinder passivation. Another important parameter of the passivation process is the critical passivation current density (i_{crit}) which is required to attain the critical passivation potential. The critical passivation current density generally decreases considerably as the pH increases, reflecting the increasing stability of the oxide films with respect to dissolution. The critical passivation current density is also dependent on the nature of the anions in the solution, according to whether these tend to stabilise the oxide film. The

value of the critical passivation current density gives a measure of the ease of passivation; the smaller the current, the easier is passivation.

When the metal surface is completely covered with a passivating oxide film, the oxide film thickness increases to an equilibrium value and the current of metal ions passing through the film becomes independent of potential. The most negative potential at which this state is attained is called the Flade potential, E_F . This represents the most negative limit of stability of the passive state, and is usually determined by allowing the potential to become more negative from the passive state, so that the transition to the active state is observed. The Flade potential is generally close to the critical passivation potential and depends on the composition of the solution in a similar way. The passive current density i_p which passes through the passivating film is a measure of the protectiveness of the film. The passive current density decreases as the pH is made more alkaline and may also depend on the anion content of the solution.

As the potential of a metal in the passive state is made more positive, the passive current density i_p remains reasonably constant until eventually the current begins to increase with potential. Such increase in current may be due to localised breakdown of the passivating oxide film by anions, particularly chloride ions. These anions induce localised dissolution of the passivating oxide film at weak points, usually associated with some discontinuity such as a grain boundary, dislocation or inclusion in the metal, leading to exposure of the underlying metal which can dissolve, giving rise to an increase in the anodic current. Continued dissolution can lead to the formation of pits. The breakdown of the oxide by anions with the initiation of pitting occurs at a critical potential called the critical breakdown or pitting potential E_b , and the current then increases rapidly with potential, as along DE. The value of E_b depends on the concentrations in the solution of inhibitive anions (which stabilise the passivating oxide film) and aggressive anions (which break down the oxide film). If the ratio of inhibitive to aggressive anions is sufficiently high, the breakdown of the film by the anions may be completely suppressed and no critical breakdown potential is observed. As the ratio of inhibitive to aggressive anions decreases, the breakdown potential is observed to become more negative.

If the composition of the solution is such that breakdown of the film by aggressive anions does not occur, then for some metals an increase in anodic current may be observed to occur with positive displacement of potential e.g. along FG, when oxidation of the metal occurs to produce a soluble ion. Thus on chromium containing alloys, such as stainless steels, the chromium may be oxidised at rather positive potentials to form dichromate ions, which are soluble



This process is known as transpassive dissolution and becomes important as a corrosion reaction only in strongly oxidising solutions, e.g. concentrated nitric acid. As the potential is made even more positive, the rate of transpassive dissolution may decrease due to the onset at G of secondary passivity, the nature of which is not fully understood. Further increase in potential leads to the breakdown of water, and the anodic current increases with potential along HI due to the evolution of oxygen



The formation of a passivating oxide film on metal surfaces is an important aspect of corrosion protection. Figure 8 illustrates schematically the anodic and cathodic polarisation curves of a system where passivation is possible e.g. stainless steel in dilute acid solution. If the solution is oxygen-free, the cathodic reaction will be reduction of hydrogen ions with a cathodic polarisation curve UV which intersects with the anodic polarisation curve ABCDE at V, corresponding to corrosion in the active state. The reversible potential U for the hydrogen ion/hydrogen equilibrium is more negative than the critical passivation potential B, and so in this system the potential could not go more positive than U and so passivation could not occur. However, the standard electrode potential for the oxygen/hydroxyl ion equilibrium, equation (7), is 1.24 V more positive than that of the hydrogen ion/hydrogen equilibrium, equation (5). Thus dissolved oxygen is a more powerful oxidising agent than the hydrogen ion, and is more capable of polarising metals into the passive region. However, the reduction of oxygen must occur with such a high current that the equivalent anodic current exceeds the critical current density for passivation, i_{crit} in order to induce transition from the active to the passive state. Thus if a high concentration of oxygen is present, and the solution is flowing, the cathodic polarisation curve will be HIJK. The limiting diffusion current density of the oxygen reduction reaction is greater than the critical passivation density and so the active-passive transition can take place. The anodic and cathodic polarisation curves then intersect at I. This provides a stable corrosion potential in the passive region and the metal will be protected. If only a small quantity of oxygen is present, the polarisation curve will be according to LMNP. If the steel is initially in the active state, the polarisation curves intersect at P and so corrosion proceeds with the corresponding corrosion current. The reduction of oxygen cannot in this case provide sufficient current to bring the potential of the metal to the critical passivation potential. However if the metal is already in the passive state, then the polarisation curves intersect at M. Thus this quantity of oxygen can maintain the passive state. If however the potential of the system falls below N, the anodic current density of dissolution exceeds the limiting current density of oxygen reduction and the potential falls to P and corrosion proceeds in the active state. If a small concentration of chloride ions is present in the solution, then a breakdown potential will be induced at D and the dissolution current will increase along DE. Since the corrosion potential represented by the intersection point I is more negative than the breakdown potential D, then the oxide film remains stable. If the chloride ion concentration is increased so that the breakdown potential is displaced to a more negative potential R, then since the corrosion potential I more positive than R, breakdown will occur and the dissolution current will increase along RS. Thus the protection of a metal by a passivating film depends on the maintenance of the potential at a value between the Flade potential and the breakdown (or transpassive) potential and requires appropriate combinations of concentrations of oxygen, hydrogen ions, and inhibitive and aggressive anions in the solution.

3.6 THE ELECTROCHEMICAL NATURE OF THE METAL

For different metals, the cathodic polarisation curves for reduction of hydrogen ions or oxygen molecules do not change greatly. The reversible potentials for these reactions will not change, but the exchange currents and the Tafel slopes of the polarisation curves may differ somewhat. However, the anodic polarisation curves are very dependent on the nature of the metal. The tendency of a metal to form metal ions in the solution is related to its standard electrode potential for the metal/metal ion reaction, equations (2) and (3), which represents the thermodynamic driving force for the dissolution reaction to occur. Values of standard

electrode potentials for a number of common metals are given in Table 1. The more negative the standard electrode potential, the greater the tendency to form metal ions and hence to corrode. The reversible potential at the appropriate concentration of metal ions in the solution represents the most negative potential that the metal can attain. However due to the polarisation of the anodic reaction the corrosion potential is more positive than the reversible potential. The corrosion of the metal may be affected by the formation of an oxide film, and the tendency to form such a film is related to the standard electrode potential for the reaction, equations (11) and (12). The values for these standard electrode potentials given in Table 1 generally run parallel with the standard electrode potentials for the metal/metal ion reactions. These standard potentials give the potentials at which an oxide can be formed, but a protective oxide film is not necessarily produced at these potentials, either because (a) the oxide may be soluble in the solution, (b) because for kinetic reasons the oxide needs an additional potential to form at a significant rate, or (c) the oxide film is not stable due to breakdown by aggressive ions e.g. chloride. Thus if the corrosion potentials of the metals in 0.5 M NaCl solution, given in Table 1, are compared with the standard electrode potentials for the formation of metal ions and oxides, the order of the metals is somewhat different. Titanium has the most positive corrosion potential despite its very negative thermodynamic potential for metal ion formation. This is because it forms a very protective oxide film at very negative potentials, and the film is resistant to breakdown by chloride ions.

For chromium and aluminium, there are considerable ennoblements of potential due to the formation of oxide films, but these are partially broken down by chloride ions giving rise to localised corrosion. On the other metals, protective oxide films are not formed due to the effects of chloride ions, or film solubility. The corrosion rate in chloride solution is then controlled mainly by the value of the reversible potential for the metal/metal ion reaction in relation to the cathodic polarisation curve for oxygen and water reduction. This is illustrated in Fig 9, which indicates that the anodic polarisation curves of copper, iron and zinc intersect the cathodic reduction curve of oxygen, so that the corrosion potentials become more negative and the corrosion currents increase in the order, copper < iron < zinc.

For each metal, the thermodynamic data for the reactions involving the metal, its ions, and its oxides can be usefully presented as a potential pH diagram, known as a Pourbaix diagram after its originator. Figure 10 shows a simplified Pourbaix diagram for iron in aqueous solutions in which no complex ions are formed and the oxides or iron are the only stable solid phases. The diagram is calculated for concentrations of dissolved iron of 10^{-6} M and for a temperature of 25 °C. In the diagram the horizontal lines represent the reversible (or equilibrium) potentials for reactions which are independent of pH i.e. Fe^{2+}/Fe , $\text{Fe}^{3+}/\text{Fe}^{2+}$. The vertical line represents an equilibrium with no change in valency i.e. $\text{Fe}^{3+}/\text{Fe}_2\text{O}_3$. The sloping lines represent equilibria which involve a change in valency and are pH dependent e.g. $\text{Fe}_3\text{O}_4/\text{Fe}$. The diagram thus shows the zones of thermodynamic stability of the various ions (in solution) and the solid oxides of iron in relation to the standard reversible potentials of the H^+/H_2 or O_2/OH^- reactions, indicated as dashed lines. If the potential–pH condition is such that the thermodynamically stable form of iron is an ion in solution i.e. Fe^{2+} , Fe^{3+} or HFeO_2^- , then iron will corrode to produce this ion. If the thermodynamically stable form of iron is the metal, then the state of immunity exists, and the metal cannot corrode. A corroding metal can be brought into the state of immunity by polarising it cathodically to make its potential more negative such that it falls within the immunity zone. This is the process of cathodic protection. If the thermodynamically most stable state of iron is an oxide then it is possible for a protective oxide film to form on the metal surface so that the iron is in the passive state.

However, as discussed above, the passivating film may not be protective, and so corrosion may occur in the passive state. Conversely a passivating oxide film may be more protective than appears from the potential –pH diagram. Thus iron can be passivated in sulphuric acid at pH 0 by making its potential more positive than +0.6 V, because a metastable oxide film is produced which possesses a low rate of dissolution.

Pourbaix diagrams are available for all the metals and are useful in understanding and predicting the tendency to corrode. However, the only condition which can be predicted with some certainty is the zone of immunity. In the zones of corrosion and passivity, the kinetic factors controlling the rate of formation and dissolution of surface films are generally more important than the thermodynamic stability of the ions or oxides of the metal in determining whether significant corrosion occurs.

Comparison of standard electrode potentials and corrosion potentials in 0.5 M NaCl solution of some common metals

Metal	Standard Electrode Potential for M^{n+}/M	Standard Potential for M_xO_y/M at pH 6	Corrosion Potential in Aerated 0.5 M NaCl Solution pH ~6
	V (SHE)	V (SHE)	V (SHE)
Magnesium	-2.37	-1.27	-1.40
Aluminium	-1.63	-1.84	-0.57
Titanium	-1.66	-1.62	+0.18
Zinc	-0.76	-0.77	-0.78
Chromium	-0.74	-0.93	-0.11
Iron	-0.44	-0.45	-0.44
Copper	+0.34	+0.12	+0.06

4 ATMOSPHERIC CORROSION

Edited from the original work of G O Lloyd

4.1 CAUSES AND CORROSION RATES

4.1.1 Corrosion rates

Atmospheric corrosion is not a very clearly defined subject. It occupies the territory between immersed corrosion and dry oxidation, since metals may be exposed to damp atmospheres or may be subjected to the full force of the weather. It is usually taken to include packaging and storage, painting and preparation for painting, and the effects of climate and air purity. This contribution will concentrate mainly on corrosion of iron and steel, with sideglances at other metals where necessary.

Metals exposed to uncontrolled “normal” atmospheres may corrode more rapidly and by different mechanisms than those kept in pure, dry air – even if they are not exposed to rain. In dry atmospheres, the growing oxide film usually protects the underlying metal, giving rise to a logarithmic or square-root time law. In uncontrolled atmospheres, the rate usually remains constant for a period, but may fall off when the film has grown to an appreciable thickness. If the metal is exposed to rain, it may corrode while it is wet at the rate appropriate to immersion in impure, well-aerated water, but the rate will fall when it dries. Equations for predicting rates of atmospheric corrosion must therefore contain a term for “time of wetness” as well as for average temperature, average relative humidity, atmospheric purity and so on. These equations are of limited value because it is almost impossible to specify the local conditions sufficiently precisely. For example, at ten sites within a few hundred metres of the promenade at Biarritz, rates of corrosion of steel varied by an order of magnitude. The following rates for ingot iron were found by Ambler and Bain at Lagos, where there is a tropical surf beach.

Approx distance from surf (M)	Salt content of air (mg NaCl/dm ²)	Rate of rusting (mm/year)
50	11.1	0.95
200	3.1	0.38
400	0.8	0.055
1300	0.2	0.04
25 miles	-	0.048

Average rates in the UK vary between 0.048 mm/year at rural sites, 0.079 mm/year at marine sites and up to 0.170 mm/year in some industrial atmospheres. In the driest atmospheres, e.g. at Khartoum, the rate can be as low as 0.003 mm/year. Detailed results are often difficult to rationalise but in general it is clear that persistent wetness, high temperatures and contamination by strong electrolytes are responsible for the highest rates of corrosion.

4.1.2 Critical relative humidities

Rates of rusting in impure controlled atmospheres without the complication of rain are low if the relative humidity is kept low, and remain fairly low even at 100% RH in the absence of strong electrolytes. The rate increases sharply at some RH in the region of 60-80% if the surface is contaminated with particles of sodium chloride, or ammonium sulphate, or if the atmosphere contains sulphur dioxide.

Vernon showed that there was an increase in rate at about 60% relative humidity even in pure air, and a further sharp increase at 80% in the presence of 0.01% of sulphur dioxide. The increase was larger and the corrosion product less protective if the surface was contaminated with particles of charcoal. More recent evidence suggests that the SO₂ content in this work was unrealistically high, and that higher RH is needed to initiate rapid corrosion with 1 ppm SO₂ or less. In general, it seems that the “critical” relative humidity is set by the vapour pressure of some salt hydrate in the corrosion product, and that chlorides and sulphates are the most effective corrosive agents.

The effect of moist atmospheres is to set up droplets of some strong electrolyte with the classical pattern of corrosion with a small anode in the centre of the drop acting as a source of ferrous ion and oxygen-reduction cathodes at the edges producing hydroxyl ion. Such droplets become covered by a transparent skin, presumably of ferrous hydroxide, which darkens and thickens and eventually runs through the range of hydrated ferric oxides up to Goethite and lepidocrocite. According to atmospheric conditions, these droplets may remain as discrete scabs, or may spread, or produce tracks that wander over the surface. When the rust layer is completed, the metal surface may become starved of oxygen, and it is quite common for a layer of Fe₃O₄ to form under the hydrated rust. The presence of corrosive salts will, however, prevent this layer from becoming very protective.

Vernon showed that a carefully cleaned steel specimen would not rust even in a normal laboratory atmosphere if it was enclosed by muslin stretched over a wire frame. The protective oxide film continued to develop, and if the specimen was removed from the enclosure after, say, a year, it would remain unaffected by dust particles, perhaps for several weeks, before spots of rust appeared.

4.1.3 Metals other than steel

Other metals than iron and steel show rather similar phenomena on exposure to uncontrolled atmospheres. Copper produces a green film of corrosion product containing hydrated sulphate, or carbonate, or chloride. It shows a rather similar variation of rates of corrosion with relative humidity: rates are, however, much lower than for iron and steel, and copper sheeting on roofs has survived for well over 100 years. Aluminium shows low rates of corrosion in most circumstances, but may corrode rapidly when exposed to alkaline solutions of copper salts derived from copper roofing or from wood preservatives is also deleterious. Rates of corrosion of completely exposed zinc are considerably lower than for iron and steel: the metal becomes covered with a protective layer of basic carbonate or basic sulphate. It may corrode comparatively rapidly if it is subjected to heavy condensation, or to high concentrations of sulphur dioxide. Nickel exposed to moist air containing sulphur dioxide becomes coated with a wet layer of nickel sulphate: nickel catalyses the oxidation of sulphur

dioxide to sulphur trioxide. Silver is rapidly converted to the sulphide by hydrogen sulphide; this reaction is unusual in not being impeded by drying the air.

4.1.4 Stainless steels

Stainless steels (i.e. steels containing at least 12% chromium) show greatly improved resistance to atmospheric corrosion. The austenitic alloys containing 8% nickel and 18% chromium are still more resistant, and alloys containing in addition 2-3% molybdenum are almost completely unaffected by weathering in industrial atmospheres.

“Weathering” or “slow-rusting” low-alloy steels containing 0.2-0.3% copper with minor additions of other elements corrode at about $\frac{1}{3}$ to $\frac{1}{4}$ the rate of plain steels. They have been used unprotected in some structures, but in rainy climates they tend to produce rainwater stains on other materials.

Factors conducive to atmospheric corrosion are therefore:

- Sensible moisture
- High RH (above 70-80%)
- Salt mist
- Surface contaminants (dust, sweat residues, soldering fluxes, etc)
- Atmospheric contaminants (SO₂, HCl, organic acids)
- High temperature.

4.2 PREVENTION OF ATMOSPHERIC CORROSION

Means of prevention include:

- Cleaning, and protection from dust
- Drying the atmosphere, and preventing condensation
- Purifying the atmosphere
- Use of corrosion inhibitors
- Protective coatings (wrappings, temporary protective materials, paint films, surface coatings of metals, polymers or vitreous enamels, conversion coatings)
- Sacrificial coatings.

4.2.1 Coatings

If oxygen, water and strong electrolytes are required to produce rapid corrosion, one or more of these agents may be excluded by a variety of coatings, ranging from noble metals and vitreous enamels through thick polymeric coatings (e.g. polyethylene, nylon and PVC) and paint films to paper wrappings and thin coatings of polymer or greases.

4.2.2 Metal films

In principle, electrodeposits of metals might provide completely impervious barriers: gold, silver, nickel and chromium deposits are used both for decorative and for protective purposes.

In practice, however, electrodeposits are invariably porous, and are also liable to mechanical damage. Exposure of the base metal leads to the damaging combination of small anode and large cathode, so that intense corrosion forms a bulky corrosion product in the pore, which may further damage or detach the coating

4.2.3 Polymer coatings

A number of commercial processes are available for applying polymeric materials from either sheet or powder, and comparatively thick, robust coatings can be obtained which give protection against corrosion and mechanical damage. Like metallic barrier layers, they may, however, allow rapid corrosion if portions of the metal are exposed.

4.2.4 Conversion coatings

Chemical reaction to produce layers of corrosion-resisting scales (particularly phosphate and chromate) can produce a wide range of coatings, suitable both for enhancing the corrosion resistance of the metal or as a preparation for painting. Anodising treatments for aluminium may incorporate phosphate or chromate ion, and so-called “chemical anodising” may be used to enhance the resistance of aluminium to atmospheric attack.

4.2.5 Painting

Paints provide easily applied and versatile organic coatings, which can be adapted to a wide range of requirements. They do not act by excluding water and oxygen; their action depends partly on excluding strong electrolytes and partly on the fact that paint materials usually contain corrosion inhibitors, often in the form of heavy-metal organic salts. Paint films are porous, and they are liable to mechanical damage. Even if corrosive salts penetrate breaches in the paint, however, the inhibitive species will often suffice to prevent serious attack on the underlying metal. If the damaged area is too large, or the contamination too heavy, and corrosion proceeds, the cathodic alkali may soften and detach the paint film, leading to the formation of a blister which remains wet long after the rest of the surface has dried.

A successful protective system should therefore include a priming layer containing a corrosion inhibitor and preferably a layer of metal that can protect the underlying surface by sacrificial action. Steel to be painted may therefore be aluminium – or zinc-sprayed, or primers containing metallic zinc particles may be employed.

Thorough cleaning of the metal surface is extremely important, especially if it has previously been corroded. Abrasive treatment should be sufficiently severe to remove the whole of any previously formed corrosion product. It has been shown that on rusted steel, crystals of ferrous sulphate are present at the base of quite deep pits. Since paint films are permeable to both water and oxygen, corrosion cells can be set up under the paint unless the preparation is sufficiently thorough.

4.2.6 Sacrificial coatings

Zinc, cadmium and aluminium can protect steel by sacrificial action: being anodic with respect to iron, they hold the potential of the latter at a value at which it will not corrode. Since the corrosion product is usually highly protective, these metals build up a surface layer which limits corrosion and prolongs the life of the coating. These coatings can be used alone, or as a foundation for a paint system, and their effect can be enhanced by chemical conversion coatings.

4.2.7 Temporary protectives

Apart from wrapping papers, which may be greased or waxed, temporary protective materials can be applied to metal surfaces to exclude moisture and dust. They may take the form of greases or slushes, pastes, thin films applied with solvents, or thick films of soft thermoplastic materials which give mechanical protection. Vapour Phase Inhibitors offer protection without the need to make direct contact with the metals surface. All these types of protective may contain corrosion inhibitors.

4.2.8 Control of RH

Most atmospheric corrosion can be prevented by maintaining RH below 60%. Desiccators and dehumidified stores can therefore be used for storage. In store-rooms and storage cases it is important to maintain the air temperature at a reasonable level and to avoid large variations in temperature; a fall in temperature overnight or at the weekend may lead to heavy condensation of moisture. Condensation may also occur if massive metal parts are placed while cold into a warm room if the air is not saturated at the prevailing temperature. Stoves and gas heaters must be provided with adequate flues. The air in store cupboards may be dried by the use of desiccants or by refrigerating plant. For special purposes, including display cabinets, where it is essential to ensure immediate access to complex equipment refrigerated surfaces may be the most practical means of protection.

4.2.9 Packaging

Packages may employ desiccants: the two most common agents are silica gel and activated alumina, both of which are non-corrosive and can be regenerated by heating. Desiccated packages need careful design to take account of the permeability of the wrapping material to water vapour, the water content of the interior of the package, and the absorptive capacity of the desiccant.

The metal parts should be carefully cleaned before packaging, to minimise damage if the package is breached or the desiccant becomes exhausted after prolonged storage. It should be remembered that some packaging materials may contain appreciable quantities of soluble chloride or sulphate, or may liberate corrosive vapours. The choice and specification of materials should take these factors into account. Maximum permissible levels are: chloride (as NaCl) 0.05%, sulphate (as sodium sulphate) 0.25%, pH of water extract 5.5 to 8.0.

Desiccated packages are often the best choice for delicate scientific equipment since this can be packed in assembled form without greasing or dismantling, and therefore without the need for cleaning and reassembly.

4.2.10 Atmosphere control

Unforeseen problems sometimes arise because variations in temperature lead to heavy condensation of moisture on steel parts, or because of some source of pollution. Troubles of this kind can often be overcome only by identifying and removing the causative agent.

Fingerprints and traces of soldering or welding fluxes occasionally cause rusting in moist air, and precautions may be needed to prevent or remove contamination, e.g. by the use of non-corrosive fluxes.

PVC insulating materials and other polymers may produce corrosive vapours which lead to heavy attack on metal parts. Acid vapours are produced by some types of wood used in packaging.

Ozone, produced by sparks from electrical contacts, may attack polymers to produce organic acids.

Sulphur compounds liberated by some synthetic rubbers may cause heavy corrosion of silver relay contacts.

Organic acids used in dyeing plastics components may be liberated during the life of the equipment and cause severe corrosion.

Traces of ammonia in the air may cause stress-corrosion cracking of brass or copper.

5 CORROSION OF METALS BY WOOD

5.1 INTRODUCTION

Wood is a corrosive substance by nature, and can be made more corrosive by treatment given to it. Unlike most other corrosive substances, one of the corrosive chemicals in it, acetic acid, is volatile, and in an ill-ventilated space, wood can cause corrosion of metal nearby but not actually in contact. Where there is contact in atmospheric conditions, corrosion can occur by the usual micro-electrolytic mechanisms, and in immersed conditions, large-sized electrolytic cells can form. Corrosion problems caused by wood can therefore arise in three areas:

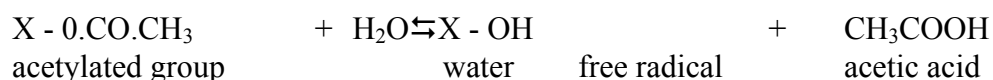
- (a) inside wooden containers, by vapour corrosion without contact;
- (b) at contacts in land-based structures, through attack by wood acids and wood treatment chemicals;
- (c) at contacts in immerse structures, where macro-galvanic mechanisms predominate.

5.2 SOURCE OF CORRODENT

5.2.1 Natural Corrodents

The principle constituent of wood is cellulose, which is a polysaccharide, i.e. a polymer made of sugar molecules joined in long chains. Each sugar unit contains mildly basic hydroxyl radicals, a proportion of which is combined with acetic acid radicals (acetylated) in the form of ester (organic salt) groupings. These groupings can combine with water (hydrolyse) to give free hydroxyl radicals and acetic acid.

The chemical equation is:



where X is the sugar unit in the chain.

This is an equilibrium reaction, which causes the moisture in wood to be always acid, but because the acetic acid is volatile and can escape, the reaction move slowly to the right hand side all the time. The acetyl radical constitutes about 1 to 6% by weight of dry wood, more in hardwoods than in softwoods, and this figure determines the total quantity of acetic acid than can be formed. The rate of emission of acetic acid depends on the species, and a wood of lower acetyl content can liberate acetic acid faster under given conditions than another wood of higher content. In a given wood, the rate of formation of acetic acid depends on the temperature and the moisture content of the wood, and the rate of its escape to the atmosphere depends on the geometry of the piece of wood in question. Besides acetic acid, small quantities of formic, propionic and butyric acids are present in wood, but their effects can be neglected in comparison with those of acetic acid.

Wood contains from 0.2 to 4% of mineral ash, which consists largely of calcium, potassium and magnesium as carbonate, phosphate, silicate, and chloride; aluminium, iron and sodium

are also present. Sulphate contributes 1 to 10% of the ash by weight, and chloride 0.1 to 5%, and these two radicals augment the corrosive action of the acetic acid.

5.2.2 Effect of fungi

In experiments on the development of acidity in wood during storage, and its liberation to the atmosphere, it has been found that wood preservatives which inhibit the growth of fungi and other biological actions do not affect the formation of acetic acid, showing that the mechanism is purely chemical and not biological. On the other hand, free acid does not appear when the wood is infected by certain fungi. These fungi are of the thermophilic type which are able to grow well at relatively high temperatures, but are still active at warm atmospheric temperatures. The mechanism by which the fungi prevent the accumulation of acid is not certain, but it appears likely that they act by neutralising or decomposing the acid as fast as it is produced and not by preventing its formation. The idea of using fungi to inhibit the development of corrosive acid may appear attractive, but these fungi will only grow when the wood is damp and therefore open to attack by wood-rotting fungi.

In extreme cases of fungal attack within enclosed spaces, volatile products from the fungi themselves, mainly carbon dioxide but probably with traces of other volatile acids, can attack metals within the enclosure.

5.2.3 Effect of kiln drying

Kiln drying accelerates the production of free acetic acid in wood, but most of the acid does not have time to escape. Kiln dried wood is more acid and more immediately corrosive than air dried wood, though it contains less combined acid that can be set free in later years.

5.2.4 Effect of chlorides

The natural chloride content of wood is low (0.1 to 5% of the ash, which is 0.2 to 4% of the dry weight of the wood), but cases have occurred of severe corrosion of metals in contact with woods that were not particularly acid, but which were found to contain appreciable quantities of salt, up to 0.8% by weight. Wood can absorb salt; the likely sources of adventitious salt are twofold:

- (a) salt spray and mist near the coast;
- (b) the floating of logs in seawater.

5.2.5 Treatments for wood that introduce corrosion substances

5.2.5.1 Salt seasoning

In Section 5.2.4 above, the accidental contamination of wood by salt was mentioned. Even larger quantities of salt, up to 4% by weight, can be introduced by a salt seasoning process used in some parts of the world for drying certain hardwoods, including maple. In this process the green timber is close piled with layers of salt between the boards. Salt absorbed by the wood lowers the vapour pressure of water in it, so that when the boards are

subsequently dried, the rate of evaporation at the surface, and the extent of surface checking, is reduced.

Salt seasoning was thought to be the cause of corrosion of the screws, brackets and other metallic components in contact with maple in certain pianos, especially some stored in humid conditions, for example, in tropical climates. The maple was found to contain up to 4% salt. Other metals parts in the same pianos in contact with other woods not containing salt did not corrode.

5.2.5.2 Flame retardants

The salts most commonly used in the UK are mono- and di-ammonium phosphate, ammonium sulphate, boric acid and borax. Most proprietary materials are mixtures of such substances. Formulations may include copper-chrome-arsenic fungicide to give a dual purpose material, and corrosion inhibitors may be added. The concentration of flame retardant in the surface of the wood can be quite high. Of these salts, ammonium sulphate is considerably corrosive. The ammonium phosphates are less corrosive, but not negligibly so. Boric acid is not appreciably corrosive, and borax is a mild inhibitor. All the salts increase the moisture content of the wood in contact with air of given relative humidity. The ammonium compounds can reduce the mechanical properties of the wood, especially if the wood is kiln dried after impregnation. Corrosive flame retardants can contribute markedly to the corrosion of metal in contact with wood, but not, except in the unusual circumstances described in Section 4.5 below, to vapour corrosion.

5.2.5.3 Preservatives

Treatments to prevent attack by fungi and wood-boring insects fall into four main types:

(a) *Creosote or tar oil* These substances have little corrosive action, except towards lead; in so far as they waterproof the wood, the effect may be protective.

(b) *Copper-chrome-arsenic (CCA)* This is widely used. The chromium salt constituent may have a small protective effect, and the arsenate radical a small corrosive one, but other salts formed during the process, notably sodium sulphate, remain soluble and are corrosive. In addition, the copper itself is potentially corrosive, for copper-based preservatives can leach soluble copper compounds to the extent of parts, or tenths of parts per million, and this copper can then plate out as metal on to iron, zinc and aluminium, forming galvanic cells that accelerate the corrosion of the substrate metal. The leaching is much greater from freshly treated wood, and it is recommended that preserved wood be allowed to age for seven days before fasteners are inserted in it, thereby giving time for the preservative to become fixed in the wood.

(c) *Naphthenates* Copper naphthenate has the same potential hazard by formation of soluble copper as copper-chrome-arsenic. Zinc naphthenate does not.

(d) *Boron compounds* These have a negligible corrosive effect on fasteners but prolonged exposure to damp causes the formation of alkali which might degrade the wood.

(e) *Organic solvent types* Examples are pentachlorophenol and lauryl pentachlorophenate, sometimes containing water repellents. They have a negligible effect on corrosion unless alkali produced by other corrosive action decomposes them to form soluble chloride. Any water repulsion they confer will be beneficial.

5.3. RELATIVE ACIDITIES OF WOODS

Table 5.1 lists the acidities of a number of woods (the pH values of a standard quantity of 5 parts of distilled water in contact with 1 part of wood raspings or sawdust).

Table 5.1 Acidities of woods

Wood	Typical pH values	Vapour corrosion hazard
Oak	3.35, 3.45, 3.85, 3.9	High
Sweet chestnut	3.4, 3.45, 3.65	High
Steamed European beech	3.85, 4.2	Fairly high
Birch	4.85, 5.05, 5.35	Fairly high
Douglas fir	3.45, 3.55, 4.15, 4.2	Fairly high
Gaboon	4.2, 4.55, 5.05, 5.2	Fairly high
Teak	4.65, 5.45	Fairly high
Western red cedar	3.45	Fairly high
Parana pine	5.2 to 8.8	Moderate
Spruce	4.0, 4.45	Moderate
Elm	6.45, 7.15	Moderate
African mahogany	5.1, 5.4, 5.55, 6.65	Moderate
Walnut	4.4, 4.55, 4.85, 5.2	Moderate
Iroko	5.4, 6.2, 7.25	Moderate
Ramin	5.25, 5.35	Moderate
Obeche	4.75, 6.75	Moderate

These pH values are probably reasonably representative of the acidities of the wood stored at temperate temperatures and humidities. Under extreme storage conditions, much greater acidity can develop, as shown in Table 5.2.

Table 5.2 Acidity of birch stored under damp conditions at 48 °C

Storage time (days)	pH of moist wood
0	4.60
7	4.40
14	4.12
19	4.11
36	3.85
55	3.80
103	3.48
126	3.32

It is probable that other woods will develop much greater acidity in this way if stored under extreme conditions.

Values of pH give a measure of the content of free acetic acid in the wood at the time of measurement. An idea of the total reservoir of potential acid, i.e. the content of combined acetyl groups, and the rate at which the acetyl groups can hydrolyse to form free acetic acid, is given for five woods in Table 5.3:

Table 5.3 Acetyl content of wood before and after damp storage for two years at 48 °C

Wood	Acetyl content, %wt of wood		Acetyl hydrolysed %wt of wood	Acetyl hydrolysed % of that present
	Before storage	After storage		
Oak	2.59	0.13	2.46	95
Beech	3.21	1.40	1.81	56
Birch	3.64	1.67	1.97	54
Douglas fir	1.10	0.38	0.72	65
Obeche (18 months)	1.41	0.96	0.45	32

The figures in Table 5.3 illustrate:

- (a) there is a wide range of initial acid contents in different species of wood;
- (b) that woods vary in the ease with which the acetyl is hydrolysed to free acetic acid;
- (c) that a wood with a lower acetyl content (oak) can give more free acid in a given time than woods with higher content (beech and birch);
- (d) that even after two years' damp storage at 48 °C, five of the six woods still retained an appreciable amount of acetyl yet to be hydrolysed – only the oak is harmless, so far as potential production of further acetic acid is concerned.

The experiments above were done under extreme conditions of storage. The writer estimates that the equivalents to two years at 48 °C are four years at tropical temperatures and 20 years at temperate temperatures; if the wood were moistened only intermittently, the periods would be much longer. The general conclusion is that all woods produce acetic acid as they age, and that acid continues to be formed for many decades after the wood is felled, even from those woods in which initial production is relatively rapid.

The acid in the wood, as revealed by the pH value, can cause corrosion by contact, and that evaporating from the wood can cause vapour corrosion within enclosed spaces. The third column in Table 4.1 classifies the woods broadly for the vapour corrosion hazard they give. It will be seen that there is a rough, but only a rough, correlation between the pH values quoted and the vapour corrosion hazard. We have seen, however, (Table 5.2), that pH values can change markedly during storage, so not much reliance can be placed on them. As a rough rule, woods with acidities of pH less than 4.0 are likely to be highly corrosive, and those of pH more than 5.0 relatively safe. A better rule is to rely on the practical results given in column 3 of Table 5.1; oak and sweet chestnut, long known for their corrosive properties, should be avoided, and choice made where possible from woods classified as only moderately corrosive. As with attack by other corrosive substances, the influence of moisture on the rate of attack, by contact or by vapour, is paramount, and will be considered in Section 5.4.2 below.

5.4 VAPOUR CORROSION INSIDE WOODEN CONTAINERS

5.4.1 Metals susceptible

The corrosive agent is acetic acid emitted by the wood, and the metals most susceptible are those readily attacked by it. The following list shows the degree of susceptibility to attack:

Group 1 – Severe attack

- Cadmium,
- Carbon steels
- Low alloy steels
- Lead and lead alloys
- Zinc and zinc alloys
- Magnesium and its alloys

Group 2 – Moderate attack

- Copper and its alloys (but see section 4.5 below)

Group 3 – Very slight attack

- Aluminium and its low strength alloys; slightly greater for Al-Cu and Al-Zn alloys
- Nickel

Group 4 – Insignificant attack

- Austenitic stainless steel
- Chromium
- Gold
- Molybdenum
- Silver
- Tin
- Titanium and its alloys

5.4.2 Effect of humidity

Table 5.4 gives typical results of the corrosion in an enclosed vessel of four metals by 1% acetic acid dissolved in various solutions chosen to maintain the relative humidity within the vessel at the levels stated. The vessels were kept at 30 °C.

Table 5.4 Corrosion of metals by an acetic acid atmosphere at various humidities

Metal	Corrosion, g/dm ² , in 40 days			
	72% RH	85% RH	96% RH	100% RH
Cadmium	0.12	1.4	1.6	Very large
Zinc	0.12	0.75	1.05	Large
Steel	Trace	0.9	Very large	Very large
Copper	Trace	Trace	0.65	1.0

These figures show the paramount influence of relative humidity on vapour corrosion by acetic acid. Even steel, which is particularly heavily attacked at high humidities, is attacked only very slowly at 72% RH (and below). It is interesting that this threshold figure is the same as for the corrosion of steel by the sulphur dioxide in an industrial atmosphere. Copper, on the other hand, has a threshold above 85% RH, and a not too high rate of corrosion at 96%

and 100% RH, hence its classification as a Group 2 metal in section 5.4.1. Some other evidence puts the threshold for magnesium alloy at 63% RH.

Although no figures are available, it is a reasonable assumption that water promotes the formation of acetic acid in wood (the forward reaction in the equation in Section 5.1). It then follows that high humidity has a twofold effect, in that it both promotes the formation of acid and the subsequent corrosion by that acid.

5.4.3 Effect of concentration of vapour

Table 5.5 shows the threshold concentration of acetic acid solutions whose vapours cause corrosion in a close space of the five metals listed at 100% RH and 30 °C. The rates of corrosion below the thresholds are low but not nil.

Table 5.5 Threshold concentrations causing corrosion

Metal	Threshold concentration, %vlv, of acetic acid solution in water	
	For appreciable corrosion	For rapid corrosion
Cadmium	0.01	0.05
Zinc	0.001	0.01
Steel	0.001	0.01
Copper	0.1	1.0
Brass	0.1	1.0

Note 1 The concentration of acetic acid in the vapour phase, mg/l (ppm) = 0.13 x the acid content of the solution, %vlv.

Note 2 “Appreciable” corrosion means 0.005 g/dm²/day, “rapid” means 0.05 g/dm²/day.

At humidities lower than saturation, the arbitrary thresholds would be higher.

Unfortunately, no determinations have been made of the actual concentrations of acetic acid vapour inside wooden boxes, but it is clear that corrosion is caused by only very small quantities.

5.4.4 Cycling of acetic acid vapour

Although some metals exposed to high concentrations of acetic acid vapour give a corrosion product of the metal acetate, the normal corrosion product is basic and may contain little acetate. This implies that the initial acetate corrosion product hydrolyses to release acetic acid again, so that a small initial quantity of acid causes a disproportionate amount of corrosion. The same cycling effect is well known in the corrosion of steel by sulphur dioxide.

5.4.5 Conditions inside wooden boxes

If a sealed *metal* box is warmed, the relative humidity of the air inside decreases, the absolute humidity (g water vapour per m³) remaining the same. If a sealed *wooden* box is warmed, however, so much moisture is released from the wood that the relative humidity actually increases, the absolute humidity increasing sharply. This effect is illustrated indirectly by Table 4.6, which shows the approximate moisture content of wood required to give rise at

different temperatures to a relative humidity of 80%, a level at which acid vapour corrosion proceeds rapidly.

Table 5.6

Temperature, °C	Moisture content of wood to give 80% RH
15	20
25	18
40	16
70	12-14

The moisture content of well dried wood is of the order of 16 to 18%. The figures show that even with well dried wood, a corroding humidity can be reached easily in a temperate climate, and all the time in a tropical one. If the wood becomes wetted, corrosive conditions can develop at any temperature, and be very severe at higher temperatures.

5.4.6 Avoidance of vapour corrosion inside wooden boxes

5.4.6.1 General note on avoidance of vapour corrosion

Vast numbers of metal objects are transported in wooden boxes without loss by corrosion. The metals are protected, the wood is of the less corrosive sort, is dry to begin with and does not become wet for any length of time, and the packs are opened promptly. It is when one or more of these conditions does not apply that vapour corrosion can become a hazard.

5.4.6.2 Choice of wood

Use Table 5.1 to avoid the more corrosive woods and to choose from the less corrosive ones. For woods not in the table, use past experience or, as a last resort, go by the pH value and choose a wood with pH greater than 5.0. (Any laboratory can determine the pH value quickly and easily.)

5.4.6.3 Condition of wood

Avoid fresh wood. Avoid kiln dried wood. Avoid damp wood. Keep wood in a dry atmosphere for as long as possible before use.

5.4.6.4 Ventilation

Acid vapours will not corrode if they blow away, but a small amount of ventilation is useless, especially if venting is blocked when boxes are piled. Only open slats are likely to give enough ventilation.

5.4.6.5 Coating the wood

The emission of acetic acid vapour from wood is retarded, but not stopped, by paint or lacquer applied to the wood. *It must not be forgotten, however, that oleoresinous and some other paints and phenolic varnishes themselves emit corrosion vapours* (formic and acetic acids). Choice of coating must be made from those known not to emit corrosive vapours, viz: nitrocellulose (a fire risk), shellac (probably a poor barrier) or preferably acrylics and two-pack epoxides and polyurethanes.

Lime washing, which might be expected to absorb acetic acid vapours, has been found ineffective.

5.4.6.6 Impervious linings

Boxes can be lined with aluminium or zinc foil. If the lining is complete and remains intact, no vapours can pass it. Glues must not spill inside, as many glues emit corrosive vapours.

5.4.6.7 Inner packs

The safest way of protecting valuable goods is first to pack them in a vapour-proof wrapping, heat-sealed or zipped, and preferably desiccated inside, with a transparent window behind which is lodged a cobalt chloride humidity indicator. Polyethylene of thicker gauges is a fairly good barrier, but the best is the sandwich containing a centre layer of aluminium foil. With a first class barrier, even wood shavings could be used as an outer cushioning material, though if the barrier becomes torn, dire trouble would ensue.

5.4.6.8 Protective coatings on steel

Corrosion by acetic acid vapour resembles that by sulphur dioxide in an industrial atmosphere, though in the most severe cases it is more rapid than anything caused by an atmosphere that is still breathable. It follows that protective treatments effective against industrial atmospheric corrosion show an equal order of effectiveness against vapour corrosion. For smaller items, the following protective treatments, additional to those that might be thought adequate for service use, should be considered:

- (i) Full colour chromate passivation of zinc and cadmium gives some useful protection.
- (ii) A tin flash (2.5 μm) over cadmium plate gives useful protection provided the tin is not porous.
- (iii) Etch primer gives very fair protection to zinc and cadmium plate. A full paint scheme, applied over etch primer or over chromate passivation, gives excellent protection.
- (iv) Tin plating, itself highly resistant to vapour corrosion, gives excellent protection, until it breaks down, when corrosion is accelerated. A minimum thickness of 25 μm) is recommended. Tin can be lacquered or painted for extra protection.
- (v) Tin, cadmium and tin zinc alloy plating have no consistent advantage over cadmium and zinc.
- (vi) Nickel plus chromium coatings should give the same order of protection

5.4.6.9 Protective coatings on other metals

Zinc should be treated as for zinc plate in Section 4.4.6.8 above. Magnesium alloy, being highly susceptible, should never be crated in other than the fully protected condition.

Aluminium and its alloys with their normal protective treatments, and stainless steel, will be safe. Copper and its alloys will need protection by lacquering or painting; plating with tin, silver or gold will give good protection.

5.4.6.10 Temporary protectives

These will give the same order of protection as against atmospheric corrosion, see later Section.

5.4.6.11 General note on protection

The relative corrosivities of rural, industrial and marine atmospheres are fairly well known, and good choices of protectives can be made. Conditions inside a wooden box are less predictable and can be worse than any natural atmosphere; a box made of freshly felled oak stored out of doors in the tropics would corrode even a highly resistant metal in time. The statements about protective efficiency given above apply only when precautions have been taken to avoid severe accumulations of corrosive vapour.

5.4.6.12 Precautions during storage

Boxes should be stored under ventilated top covers. If storage in the open is unavoidable, white plastic drapes can be used for protection against rain and sunshine, with the proviso that enclosing a box already damp is worse than useless. The drape should be white, to prevent the box becoming too warm in the sun, for the relative humidity inside a wooden box *rises* with a rise in temperature.

5.5 CORROSION IN CONTACT WITH WOOD, INLAND STRUCTURES

5.5.1 Woods

The pH values of woods (Table 5.1) are of direct relevance to corrosion by contact, but the information they give is only relative. The values are those of the aqueous extracts, not of the actual moisture within the wood. Values vary within a species, from heartwood to sapwood (heartwood being usually somewhat more acid) and with storage. For deeply embedded fasteners, the permeability of wood towards water, oxygen and carbon dioxide also plays a part. Iron fasteners in impermeable woods, such as the white oaks, can last a long time even in immersed conditions, probably because of lack of oxygen and of carbon dioxide to decompose the initial acetate corrosion product. Some authors have suggested that the tannins in wood act as corrosion inhibitors, but it may be that their effect, in any, is as oxygen scavengers. Notwithstanding the reservations above, experience has shown that the four most acid woods in Table 5.1 are oak, sweet chestnut, Western red cedar and Douglas fir, and are indeed those most liable to corrode metals embedded in them, or in contact with them under damp conditions.

5.5.2 Metals

The order of susceptibility to corrosion by contact is broadly the same as that to vapour attack, as given in Section 5.1. That the susceptibility of zinc is as high as steel does not mean that it is not worth while using zinc coated steel; the steel will not rust until the zinc has corroded away, which under less than severe exposure conditions, can take a long time.

5.5.3 Moisture content

The moisture content of dry wood is some 16 to 18% by weight and at this figure the corrosive effect is mild. Under damp conditions, however, moisture is absorbed and the wood becomes corrosive. The passage of moisture across the grain is a slow process, and occasional wetting will affect only the surface layer. Conversely, saturated wood takes a long time to dry out. Diffusion along the grain can be a hundred times more rapid, and exposure of end-grain to the weather should be avoided.

5.5.4 Wood treatments

The additional corrosion hazard from sea salt, salt seasoning, some flame retardants and some preservatives have already been discussed. A simple test paper can be prepared for detecting the presence of chloride in wood.

5.5.5 Degradation of wood by corroding metal

Wood corrodes metals, and corroding steel also degrades wood, as anyone who has tried to mend an old fence will know. Alkali produced at local cathodic areas and iron salts at local anodic areas both cause degradation of wood and loss of strength. Iron stains on wood around steel fasteners are produced by interaction between iron salts and tannins and related substances in the wood; they indicate that corrosion and degradation are starting. Iron stains are not always associated with present corrosion, however, as they can be caused by traces of iron salts left behind from wood working and smoothing operations.

5.6 CORROSION IN CONTACT WITH WOOD, IMMERSED STRUCTURES

5.6.1 Electrochemical mechanisms

By definition the wood is always wet, and the acid in it, aided by salt if immersion is in seawater, acts as a bulk electrolyte in which various electrochemical cells can be formed, which can be more vigorous than the micro-cells set up in atmospheric corrosion; in particular, the wood can be degraded by alkali formed at a cathode as well as by iron salts formed at a rusting iron anode.

- i) *Oxygen concentration cells.* The shaft of a fastener inserted into wood becomes starved of oxygen and anodic, and the exposed head becomes cathodic. The cathodic alkali gives negligible protection to the head as it is soon washed away, but may cause alkaline degradation of the wood at the area of emergence.
- ii) *Other concentration cells.* A cell may be set up when a single piece of metal passes through two different woods, caused by differences between the contents of

acid, salt and oxygen in the two woods. A case has been reported of severe corrosion and degradation of parts of a fishing vessel made of beech planking fastened by galvanised nails to oak frames (see front cover). The metal in the beech planks became severely corroded, and corrosion product softened the oak frames at contact with the beech. As other parts of the ship, made of oak planks on oak frames, were in good condition after 20 years, the failure in the composite part of the structure was attributed to a complicated concentration cell effect.

- iii) *Bimetallic corrosion cells.* Wet wood, especially salty wood, is an electrolyte, and bimetallic cells are readily set up between two different metals in contact with one another and embedded in wood. A common case is where copper-base fasteners are used to attach wooden planking to a steel framework, where the corrosion of the steel is accelerated and the alkali formed on the cathodic copper degrades the wood and loosens the fastener.

Stray currents from electrical apparatus can accelerate corrosion by forming an imposed galvanic cell. Corrosion takes place where the positive current enters the metal (where the electrons leave); reversal of normal galvanic polarity can sometimes occur, leading to unexpected effects.) This effect can also occur on the positive side of an unconnected piece of metal embedded in wood carrying a stray current, for the current will pass through the metal in preference to the surrounding wood.

5.7 CHECK LISTS

5.7.1 Wooden boxes

<i>1A Risk of corrosion</i>				
Conditions		Risk of Corrosion		
		Low	Medium	High
Length of storage	less than 1 month 1-5 months 6 months and longer	X	X	X
Conditions of storage	indoor temperate outdoor temperate indoor tropical outdoor tropical	X	X X	X
Metals (Section 4.1)	Group 1 Groups 2 and 3 Group 4	X	X	X
Corrosivity of wood (Table 4.1)	high or fairly high moderate, seasoned moderate, kiln dried	X	X	X

Balance the high, medium and low entries; if the risk is low to medium, protective measures are advised, if it is medium or higher, protective measures are essential.

<i>1B Effectiveness of protective measures</i>			
Protective measure	Effectiveness		
	Low	Medium	High

Temporary protection on metal, thin	X		
Temporary protection of metal, thick		X	
Full paint scheme on metal			X
Permeable wrap	X		
Dessicated pack			X
Lining of box (or paint, Section 4.6.4)		X	
Ventilation, good		X	
Ventilation, poor	X		

Balance the effectiveness against the risk; if the risk is in excess, consider more effective protective measures.

5.7.2 Structures

Before erecting a timber structure with metal parts, estimate the risk of corrosion from the table below.

<i>2A Risk of corrosion</i>				
Conditions		Risk of Corrosion		
		Low	Medium	High
Life of structure	semi-permanent permanent		X	X
Exposure	indoor, heated covered, unheated open	X	X	X
Corrosivity of wood (Table 5.1)	high or fairly high moderate		X	X
Situation	within 1 km of coast 1-5km from coast inland	X	X	X
Wood treatments	salt seasoning fire retardant inorganic preservative, fresh inorganic preservative, aged organic preservative	X X	X	XX X

Balance high, medium and low entries, and select an appropriate metal from Table 4.2B below.

<i>2B Corrosion behaviour of metals in wood</i>				
Metal		Corrosion behaviour		
		Poor	Medium	Good
Steel	uncoated zinc coated zinc coated plus paint plastic coated	X	X	X X

Aluminium			X	
Copper alloy			X	
Stainless steel				X
Monel				X
Insulation, plastic or bituminised				X

6 BIMETALLIC CORROSION

Edited from the original work of Dr. R. Francis of Weir Materials and Foundries

6.1 INTRODUCTION

Bimetallic corrosion can occur when different metals are placed in contact with each other and this section provides information on how this corrosion mechanism operates and how it can be controlled. More detailed information can be obtained from British Standards Institution Published Document PD6484: 1979 (1).

When a metal is immersed in a conducting liquid it takes up an electrode potential (also known as the corrosion potential). This is determined by the equilibrium between the anodic and cathodic reactions occurring on the surface and it is usually measured with reference to a standard electrode such as the saturated calomel electrode (SCE).

Bimetallic corrosion occurs when two metals, with different potentials, are in electrical contact while immersed in an electrically conducting corrosive liquid. Because the metals have different natural potentials in the liquid, a current will flow from the anode (more electronegative) metal to the cathode (more electropositive), which will increase the corrosion on the anode. This additional corrosion is bimetallic corrosion. It is also referred to as galvanic corrosion, dissimilar metal corrosion or contact corrosion. In general, the reactions which occur are similar to those that would occur on single, uncoupled metal, but the rate of attack is increased, sometimes dramatically. With some metal combinations the change in the electrode potential in the couple potential can induce corrosion which would not have occurred in the uncoupled state (e.g. pitting). In some environments the change in potential of the cathode in the couple can also introduce problems (e.g. hydrogen embrittlement). The effect of coupling the two metals together increases the corrosion rate of the anode and reduces or even suppresses corrosion of the cathode. Hence, coupling a component to a sacrificial anode can prevent corrosion, and this is the principle of cathodic protection.

The basic requirements necessary to cause bimetallic corrosion are:

An electrolyte bridging the two metals - which may not always be aggressive to the individual metals when they are not coupled, and may be in the form of a bulk volume of solution, a condensed film, or a damp solid such as soil, salt deposits, or corrosion products. Electrical connection between the metals. This usually involves direct physical contact but it can also arise where electrical continuity is established between two metals, for example, by an insulation-coated conductor, by structural metal work or electrical earthing. It is not necessary for the metal junction to be immersed in the electrolyte. A sufficient difference in potential between the two metals to provide a significant galvanic current. A sustained cathodic reaction on the more noble of the two metals by one of the mechanisms described in the previous section; in most practical situations this is the consumption of dissolved oxygen.

6.2 FACTORS THAT EFFECT THE RATE OF CORROSION

6.2.1 Electrode potential

The electrode potential is determined by many factors but the only fluid for which these factors are really well documented is sea water. The value of the potential for any alloy, even in sea water, can be changed by a variety of factors such as temperature, velocity, biocide treatment etc. However, the relative ranking of alloys remains largely unchanged by these factors.

Alloys which are coupled to metals which have more electropositive potentials are the ones which may suffer bimetallic corrosion. Stainless steels, such as 316, have a thin, protective film and while this is intact corrosion rates are very low and the alloy is said to be in its passive state. When breakdown of the film occurs, usually localised, such as crevice corrosion, then the stainless steel is said to be active.

However, the magnitude of the potential difference alone is not sufficient to predict the risk of bimetallic corrosion. For instance, metals with a potential difference of only 50 mV have shown bimetallic corrosion problems, while other metals with a potential difference of 800 mV have been successfully coupled together. The potential differences between the metals provides no information on the kinetics of bimetallic corrosion which depend upon the current flowing between them. There is a wide range of factors which affect the severity of bimetallic corrosion such as area ratio, temperature, flow rate, composition of the electrolyte etc. The important ones are discussed below.

Ranking of metals in terms of there electronegativity

Electropositive (more noble)end

Gold
High Alloy Stainless Steels {Super Austenitic}
{Super Duplex}
Titanium
Nickel Chrome {625; C-276}
Molybdenum Alloys
Low alloy stainless (PASSIVE) steels (e.g. 316)
Alloy 400/Alloy K-500
Silver
Nickel Aluminium Bronze
Copper nickel (70/30; 90/10)
Gunmetals/Tin Bronzes
Brasses
Tin
Lead
Austenitic Cast Iron
Low alloy stainless (ACTIVE) steels (e.g. 316)
Cast Iron
Carbon Steel
Aluminium alloys
Zinc
Magnesium
Electro Negative end

Even potentially dangerous combinations may be made to work in service if appropriate steps are taken at the design stage to minimise the risk. More details on the likely behaviour of bimetallic couples are given in the extensive tables in reference 1. Note: Unalloyed aluminium is anodic towards most copper containing aluminium alloys. At the junction between the two, the alloy is often protected at the expense of the aluminium.

6.2.2 Electrode efficiency

Current flow between the two metals in contact is accompanied by a shift in the potential of the anode to a more electropositive value and in the potential of the cathode to a more electronegative value. These changes, called polarisation, result in the two metals approaching the same potential, any potential difference between them being equal to the product of the current and the resistance through the electrolyte. The extent of polarisation depends upon both the metal and the environment. In neutral electrolytes the cathode is almost always polarised much more than the anode, which accounts for the fact that a small area of sacrificial anode will effectively provide protection to a relatively large cathodic area. The extent of polarisation will determine how effective any particular metal may be as a cathode. Some metals, such as titanium, are not very efficient at reducing dissolved oxygen compared with copper alloys. So it is possible for a less noble metal to corrode more if coupled to a copper alloy than to titanium, despite titanium being much more electropositive.

6.2.3 Variable potential

Changes in the corrosion potential of individual metals and, therefore, in the polarity of a couple, from commonly encountered values can result from the presence of complexing ions, from changes in pH and temperature, and from intense aeration which enhances film formation on the (hitherto) anodic metal. Large differences in area ratio, especially with metals of nearly the same corrosion potential, can also influence the relative polarity of metals by causing intense polarisation. Tin is usually cathodic to iron in neutral salt solution, but in the presence of the complexing organic acids found, for instance, in fruit preservation, it is anodic and therefore an effective sacrificial coating for 'tin' cans. Lead, tin, and their solder alloys form soluble corrosion products in alkaline solutions and are anodic to iron, whereas in acid solutions they are usually cathodic to iron. Non-oxidising acid solutions can cause breakdown of the natural oxide film on passive metals; for example, in oxalic acid, titanium can be anodic to stainless steel and in concentrated sulphuric acid it is anodic to aluminium. Reversals of significant practical importance are encountered with zinc and aluminium, which are usually anodic to iron in natural waters. At temperatures above 60 °C iron becomes anodic to zinc, which explains why problems are sometimes encountered in galvanised steel hot-water systems. In fresh waters, polarity reversal is enhanced by the presence of bicarbonate and decreased by sulphate and chloride. The aluminium/iron couple undergoes polarity reversal at elevated temperatures in fresh water and in sea water (about 95 °C) and the aluminium/zinc couple exhibits polarity reversal in seawater at about 90 °C.

6.2.4 Electrolyte

Electrolyte factors that have a major influence on bimetallic corrosion are composition, pH and, in particular, electrical conductivity, which affects both the intensity and distribution of corrosion. The severity of corrosion often increases with increasing electrical conductivity of the electrolyte because, in practice, high conductivity is often caused by the presence of aggressive ions such as chloride, or by acid or alkali.

The electrical conductivity of electrolytes can vary widely: typical values are as follows:

Distilled water 0.5 - 2 μ S/cm

After storage 2 - 4 μ S/cm

Supply water 50 - 1,500 μ S/cm

Saturated sodium chloride solution 250,000 μ S/cm

Sulphuric acid up to 8,000,000 μ S/cm

Molten salts 20,000 - 107 μ S/cm

In a solution of inherently low conductivity (or when the metals are covered with only a thin film of a highly conducting electrolyte), corrosion is confined to an area near the junction between the two metals and, while the total amount of corrosion may be low, it is likely to be relatively localised and therefore may also be intense. Corrosion will still be more intense at the metal junction than elsewhere in a highly conducting solution but it will also be more widespread. Intense corrosion is likely to arise even with nominally pure water under condensing conditions if the atmosphere is polluted with acid gases such as sulphur dioxide, or with salt, for example at industrial or coastal locations.

In common with local-cell corrosion, bimetallic corrosion is sensitive to the presence of constituents in the electrolyte that effect stability of the corroded-metal ions. Thus, with lead the presence of bicarbonate, silicate and sulphate in water enhances formation of insoluble and adherent corrosion products. In some cases insoluble corrosion products from the anodic metal can deposit upon, and induce crevice corrosion of, the cathodic metal of a couple; stainless steels are susceptible to this type of corrosion, especially when in contact with aluminium or mild steel. In some cases the composition of the environment can be modified by adding inhibitors to control both local-cell and bimetallic corrosion. This practice has proved effective in the treatment of waters in engine cooling systems and industrial cooling plants. Bicarbonate, cyanide and tartrate ions form soluble complexes with copper and zinc, and thus their presence increases the rate of corrosion.

6.2.5 Area ratio

The area ratio is very important in the consideration of the likelihood of bimetallic corrosion. The larger the cathode compared to the anode, the more oxygen reduction can occur and, hence, the greater the galvanic current and, therefore, corrosion .

Under static conditions, where the bimetallic corrosion current is often dependent upon the rate of diffusion of dissolved oxygen to the cathode, the amount of bimetallic corrosion is independent of the size of the anode and is proportional to the area of the cathodic metal surface. This is sometimes known as the catchment area principle, and has important

implications in designing to minimise the risk of bimetallic corrosion. Thus, for a constant area of cathode metal the amount of corrosion of the anode metal is constant, but the intensity of corrosion is increased as the area of the anodic metal is decreased.

If the electrical conductance of the electrolyte bridging the bimetallic contact is low, either because the bulk conductivity is low or because the electrolyte is present only as a thin film, the effective areas taking part in bimetallic cell reactions are small and the total corrosion is relatively small, although it may be severe immediately adjacent to the metal junction. Under immersed conditions in many supply waters, which have a relatively low electrical conductivity, adverse effects are uncommon if the contacting metals adjacent to the junction are of similar area. Thus, galvanised steel pipes can be used with brass or gunmetal connectors, but serious corrosion to the pipe end is likely to result if the contact is directly to a large area of copper, such as a tank or cylinder. Similarly, stainless steel and copper tubes can usually be joined without problems resulting, but accelerated corrosion of the copper tube is likely to occur if it is attached to a stainless steel tank.

Adverse area ratios are likely to occur with fasteners and at joints. Weld, braze or rivet metal should be of the same potential or, better still, cathodic to the base or parent metal. For example, the use of mild steel rivets to fasten nickel, copper or stainless steel plates should be avoided. Under immersed conditions in a highly-conducting electrolyte, such as sea-water, effective areas will be greater, and severe corrosion may be encountered on small anodic areas of many metals.

Extremely small anodic areas exist at discontinuities such as cracks or pinholes in cathodic coatings such as magnetite (millscale) on iron and copper plating on steel. Where electrolyte conductivity is high it is necessary to apply protection or, in the case of metal coatings, to specify a thickness of adequate integrity. Similar considerations apply to pores or defects in a paint coating if the metal is in contact with a more electropositive metal, i.e. the cathode to anode area ratio is dramatically increased compared with bare metal. By correct selection of area ratio, dissimilar metals have frequently been used successfully together in sea water. One example is the use of 316 pump impellers in austenitic cast iron pump casings. Another is the use of high alloy trim (seats, stems etc.) such as alloy 625, alloy K-500 etc. with gun metal or aluminium bronze valve bodies. In both cases the large area of the anode compared to the cathode means that the increased corrosion is small and is well within the design limits for the unit.

6.2.6 Aeration and flow rate

The majority of practical situations involving bimetallic corrosion arise in aqueous solutions under conditions where the cathodic reaction is reduction of dissolved oxygen. As with single metal corrosion, bimetallic corrosion is therefore partly dependent upon the rate at which oxygen can diffuse to the surface from the bulk of the electrolyte.

The bimetallic corrosion rate of many copper-based and nickel-based alloys, and of stainless steels in sea-water, depends upon the flow rate of the water as well as on the area ratio. Copper and copper-nickel alloys tend to become less noble with increasing flow rate and to corrode more, while nickel alloys and stainless steels become more noble and corrode less. In well-aerated flowing solutions nickel alloys and stainless steels are also likely to become passive and corrode less.

Noble metals such as platinum, silver and copper, on which the naturally formed oxide films are very thin and are readily reduced to metal, act as efficient cathodes without polarising and therefore tend to promote bimetallic corrosion. However, aluminium, stainless steel and titanium have a stable oxide film and tend to polarise; in flowing, aerated electrolyte the oxide film is likely to thicken, thus diminishing bimetallic corrosion of the coupled metal even further.

In neutral electrolytes complete de-aeration will, in many instances, suppress single-metal and bimetallic corrosion. However, under such anaerobic conditions cathodic depolarisation and corrosion can occur if sulphate-reducing bacteria are present.

6.2.7 Metallurgical condition and composition

In some cases differences in corrosion potential can exist between coupled metals or alloys of nominally the same composition. Subjection to cold working often tends to make a metal/alloy more anodic. In some alloys heat treatment can produce galvanic differences; for example 2014 aluminium copper alloy in the artificially aged condition is anodic to the same alloy in the naturally aged condition. Such conditions account for this risk of bimetallic corrosion on contact between aluminium alloys as indicated in. Local changes in composition can also arise at joints made by welding, both in the weld bead and in the heat affected zone of the parent metal. Problems are usually avoided by selecting the appropriate filler metals and welding techniques, or in some cases, by painting the joints.

Bimetallic corrosion can occur between alloys of similar type but somewhat different composition; thus 90/10 cupro-nickel can be anodic to 70/30 alloy, austenitic stainless steels are cathodic to the martensitic type, and austenitic cast iron is more cathodic than, and can induce corrosion of, other types of cast iron. Cast iron that has become graphitised will induce additional corrosion of non-graphitised alloy i.e. the surface of the cast iron is essentially just graphite which is strongly electropositive to most metals.

6.2.8 Stiffling effects

In general the rate of corrosion of coupled and non-coupled metals decreases with time of exposure. This is partly due to the diminishing rate of diffusion of oxygen through the electrolyte and through films of corrosion product to cathodic regions and, partly owing to the protection afforded to anodic regions by the corrosion product. To some extent, therefore, the bimetallic corrosion rate is affected by the permeability of the corrosion product. In sea-water and, to a lesser extent, in hard supply waters, the alkaline conditions produced at the cathode result in the formation of calcareous deposits of calcium and magnesium carbonates and magnesium hydroxide which may decrease the rate of bimetallic corrosion. With steel, for example, corrosion is decreased by one order of magnitude after less than a year's exposure. Where corrosion products are water-permeable or hygroscopic, however, their presence can sometimes increase the rate of bimetallic corrosion, either because they are more aggressive than the bulk environment or because they maintain wet conditions at the metal surface.

6.3 BIMETALLIC CORROSION WITHOUT PHYSICAL CONTACT

Localised corrosion of a metal may give rise to soluble corrosion products which deposit by a displacement reaction onto a less noble metal exposed in the same solution and form local, intense bimetallic cells. This is particularly evident with the more electropositive metals such as copper, and problems have been encountered in water-heating systems as a result of copper dissolving from pipework and depositing onto steel radiators, aluminium alloy sinks and pump impellers, and galvanised tanks. Insulation of joints between dissimilar metal components is not necessarily a safeguard if cuprosolvent water flows or diffuses from copper to aluminium parts of the system. Similar problems can also be encountered with aluminium in the near vicinity of steel under conditions where the iron corrosion products flow over the aluminium and are deposited as strongly cathodic magnetite or where alkaline solution formed at the steel cathode flows onto the aluminium.

Copper can also cause corrosion of steel and galvanised steel, particularly in warm or hot water. Hence, it is usual to specify that copper and its alloys may be used downstream of galvanised steel but not vice versa.

In plant and equipment that involves recirculated electrolyte such as vehicle cooling systems, central heating systems and industrial heat exchangers, this type of problem can sometimes be avoided by removing oxygen from the system or by adding inhibitors.

6.4 BIMETALLIC CORROSION IN SOME COMMON ENVIRONMENTS

6.4.1 Sea water

Although the comments in this section refer to sea water they can be applied more or less across the board to all near neutral aerated waters with 3 g/L chloride or more. In sea water the corrosion data show that the commonly used alloys can be collected into four groups.

Group 1 are all passive alloys which adopt electropositive potentials in sea water. The nickel alloys include alloy 625 and C-276, while the super austenitic and super duplex stainless steels have PREN values, where PREN (the pitting resistance equivalent number) = % Cr + 3.3% Mo + 16%N, exceeding 40.

Group 2 includes alloys which have low corrosion rates but are susceptible to crevice corrosion in sea water. These alloys are only used when coupled to an alloy from group 3 or 4, where the anodic metal effectively protects the group 2 alloy from crevice corrosion. This assumes a suitably large ratio of anode area to cathode area.

Group 3 covers alloys with moderate corrosion resistance and essentially comprises the copper alloys, although austenitic cast iron can be included in this group. It includes single phase brasses (e.g. aluminium brass) but the inclusion of those containing beta phase, e.g. naval brass and manganese bronze, is debatable. This is because brasses containing beta phase will dezincify in sea water and this can be exacerbated when coupled to a more noble alloy from groups 1 or 2 or even when coupled to 70/30 copper nickel.

Group 4 includes alloys of low corrosion resistance. It has been subdivided to separate the aluminium alloys from the steels and cast irons because of the variable effects which can occur in couples depending upon alloy composition. The Al-Mg alloys (5000 series) generally form protective films in sea water and can be coupled to iron or steel if the area ratio is not too adverse. However, alloys such as the 7000 series can suffer pitting and stress corrosion cracking which can be exacerbated by a bimetallic couple. Hence couples between these two subdivisions of group 4 must be examined on a case by case basis. The rules for selecting alloy compatibility are, subject to the exceptions above;

- 1) Alloys within each group can be coupled together with no significant problems.
- 2) When coupling an alloy to one from a higher group a high anode to cathode area ratio (e.g. valve trim) or a generous corrosion allowance is needed, unless measures are taken to avoid bimetallic corrosion (see next section).

Zinc and magnesium corrode rapidly in seawater and coupling to any more noble alloy will increase the dissolution rate. Zinc is sometimes used as a sacrificial anode to provide cathodic protection. Magnesium is not normally used in this application because its corrosion rate is very high and substantial quantities of hydrogen are evolved on the cathode, increasing the risk of embrittlement.

GROUP TYPE ALLOY

- 1 Noble; Passive Ni/Cr/Mo alloys (Mo>7)
Super Austenitic Stainless Steel
Super Duplex Stainless Steel
Titanium and its alloys
- 2 Corrosion Resistant; 22 Cr Duplex Stainless Steel
Susceptible to Alloy 825
Crevice Corrosion Alloy 400
Alloy K-500
316
- 3 Moderate Corrosion Copper alloys
Resistance Austenitic Cast Iron
- 4 Poor Corrosion Carbon Steel
Resistance Cast Iron
Aluminium Alloys

When using alloys from groups 1 and 2 there is another factor to take into account, and this is the cathodic efficiency. In natural sea water at ambient temperature, a thin biofilm forms on these alloys which results in very electropositive potentials and, more importantly, a very efficient reduction of dissolved oxygen. Both affects promote bimetallic corrosion. In systems where the water has been heated to 25°C - 30°C above ambient the biofilm does not form and cathodic reduction of dissolved oxygen is 2 to 3 orders of magnitude less efficient. If chlorine is injected in small quantities (0.5 to 1.0 mg/L) to prevent bio-fouling, the potentials increase still further, but the cathodic reaction is now the reduction of hypochlorite

to chloride. This is one to two orders of magnitude less efficient than the reduction of oxygen by the biofilm. Hence, in hot sea water or chlorinated sea water, the reduced rate of the cathodic reaction means that the extent of bimetallic corrosion is substantially reduced compared with that in natural seawater.

An example of this is super duplex stainless steel coupled to nickel aluminium bronze.

6.4.2 Atmospheric environments

Because an electrolyte is a necessity for corrosion it tends to occur where rainwater and/or condensation cannot run off or becomes trapped. As with fully immersed conditions, the tendency for bimetallic corrosion to occur in atmospheric environments increases with increasing conductivity of the electrolyte bridging the coupled metals. However, corrosion is usually more localised at the metal junction than under immersed conditions. The severity of the environment depends upon general and local climate conditions; it is low in dry or low-humidity regions, moderate in temperate and semi-arctic regions and in open rural locations; and greatest in tropical and marine locations of high humidity and in polluted industrial atmospheres. With the exception of couples involving magnesium, aluminium, zinc and low-alloy or carbon steels, the additional corrosion in environments of low to moderate severity is often negligible unless contact is with carbon or a precious metal. Due consideration must be given to local conditions, however, as the electrical conductivity of rain water or condensation is increased by pollution with fuel-combustion products, fertilizers and road salt, which produces aggressive conditions in a nominally clean atmosphere.

Bimetallic corrosion at sea-coast locations is usually more severe than at industrial/urban locations, and the effect is similar to that experienced under fully-immersed conditions in a low-conductivity electrolyte with small, equal areas of dissimilar metals in contact.

The general behaviour of metals in bimetallic contact in rural, industrial/urban and marine environments is fully documented in PD 6484 (1). Information which is specific to electrical power equipment, but also summarises the service experience with a wide range of metallic and non-metallic protective coatings on aluminium, copper and steel under different climatic conditions, is contained in CP 1014 (4).

6.4.3 Buried and embedded metals

In general, the behaviour of metals in contact in soils is similar to that under immersed conditions in water. The quantitative effect depends upon a number of factors including moisture content, pH, salt content, permeability to oxygen, and electrical conductivity, of which the last is of major importance. Soils are regarded as aggressive if the electrical conductivity is greater than about 1000 $\mu\text{s}/\text{cm}$. Bacterial activity can be a significant factor in poorly-aerated, waterlogged soils and the presence of sulphate can sustain a cathodic reaction by sulphate reducing bacteria.

Other microbial systems can have corrosive effects by producing sulphuric and organic acids, or organic and inorganic sulphides, or by oxidising and removing nitrogen-containing inhibitors, thus increasing the corrosiveness of the environment and the amount of bimetallic corrosion. Behaviour of coupled and uncoupled metals varies widely in soil because of the wide range of environmental conditions encountered. Satisfactory performance may be

encountered with apparently incompatible metals because of passivation or stifling resulting from the precipitation of insoluble salts by local alkalinity.

However, severe corrosion has been encountered - and, in general, protective measures are necessary to avoid problems - where ground water has a high conductivity, for example with lead/copper and copper/iron pipe junctions. From a consideration of area ratio effects it is evident that failure of bolts is likely to precede that of structures to which they are attached unless they are made of materials which are cathodic to the larger area of metal.

Soil analysis is not a completely reliable guide to the likely behaviour of coupled metals, and specialised advice based upon service experience should be sought.

Corrosion of metals embedded in concrete is often not significantly affected by contact with a second embedded metal; aluminium for example, tends to form a surface film when coupled to steel in the alkaline environment of concrete, plaster and mortar. Behaviour will depend upon the permeability to water and air and the salt content of the concrete, and corrosion is more likely to occur where the concrete is damaged. Special care is necessary when attaching inserts to reinforced concrete to avoid making direct contact with steel reinforcing bars.

6.4.4 Acids and alkalis

Alkalis are used in a range of industrial processes, for example from 4 wt% to 70 wt% caustic soda at temperatures up to 250 °C. There are no published data on galvanic corrosion in alkalis but, because of the risk of caustic cracking under coupled conditions with many metals, it is advisable to carry out testing or seek previous experiences with such couples.

In most acids, particularly the mineral acids, corrosion rates can be high and the tendency is to select high alloy materials which resist corrosion. However, couples between different alloys can produce a variety of effects which are not seen in other electrolytes. A galvanic series has been produced for some acids (5) but it is of limited value for the following reason. The corrosion resistant alloys used in acids are usually in their passive region, but at lower potentials these can move into the active region where general dissolution occurs

Another possibility may arise on coupling two corrosion resistant alloys, the anodic one having its uncoupled potential in the active region. When coupled the corrosion rate of the anodic alloy can be reduced if its potential is being moved into the transition region. The electropositive member of the couple may suffer no corrosion if it remains in its passive zone, but corrosion could occur if its potential is moved into the transition zone or active zone. This would create a situation where the corrosion on the anode decreased and the corrosion on the cathode increased (6).

As the performance of metals in acids can change dramatically with acid concentration, temperature, and the presence of small quantities of other chemicals, it is imperative that alloy performance be evaluated under conditions as close to the expected service conditions as possible.

6.5 PREVENTION OF BIMETALLIC CORROSION

The extent to which bimetallic corrosion is likely to occur and the selection of counter-measures should be considered at the design stage. Ideally, metals should be selected that are close to each other in the galvanic series, but engineering requirements for different material properties in various parts of equipment or an installation often necessitate the use of several different metals. A major consideration, however, is to identify the composition and conductivity of the environment, since these will play a significant role in defining the extent and severity of any corrosion. Other objectives are to maximise the area of the anodic metal and minimise that of the cathodic metal. Experience in similar situations should be sought where possible because it is not uncommon for dissimilar metals to be coupled without adverse effect, especially when the electrical conductivity or oxygen content of the electrolyte is low. Under immersed conditions in static or slowly moving aerated electrolyte, the catchment area principle can be usefully applied to assess whether intense corrosion will arise, but it becomes less influential as the electrical conductivity of the electrolyte diminishes, because the effective area of the cathode is then less than its geometric area. The catchment area principle does not often apply in atmospheric environments, and design considerations are then more important to effect good drainage and thus minimise accumulation of condensation and rain-water at joints and in hollow sections.

Methods of preventing or minimising bimetallic corrosion are based upon breaking the electrical path in the metallic or electrolyte parts of the system, by excluding oxygen from the electrolyte, by adding inhibitors to the electrolyte, and by sacrificial corrosion.

Similar considerations also apply to verifying the conductivity of the electrolyte. For instance, flux residues can promote bimetallic corrosion in otherwise non-aggressive electrolytes, and joints should be thoroughly cleaned after assembly. Jointing compounds applied to the contacting surfaces of fasteners and lap joints do not normally provide electrical insulation. They are very useful, however, in excluding water from the joint and thereby preventing bimetallic (and crevice) corrosion within the joint, and the exuded flexible fillet will prevent cracking of subsequently applied paint along the line of the joint.

In the case of microbial corrosion, materials can be protected by coating with resistant synthetic polymers or inhibited paints, by dosing with biocides or by avoiding conditions that favour microbial growth.

6.6 REFERENCES AND BIBLIOGRAPHY

- 1) PD6484: 1979 Commentary on Corrosion at Bimetallic Contacts and Its Alleviation, British Standards Institution.
- 2) E. Bardal, R. Johnsen and P.O. Gartland, Corrosion 40 (1984) 12.
- 3) R. Johnsen and S. Olsen Paper 397, Corrosion '92; Nashville, USA, April 1992, NACE.
- 4) CP1014: 1963 Protection of Electrical Power Equipment Against Climatic Conditions. British Standards Institutions.
- 5) J.R. Crum, 'Development of a Galvanic Series in Various Acid and Water Environments'. Int. Conf. Corros. of Nickel Base Alloys, ASM, Ohio, 1984.

- 6) G.O. Davis, J. Kolts and S. Sridhar, Corrosion 42, 6 (1986) 329.
- 7) M. Wilhelm, Paper 480; Corrosion '92 Nashville, USA, April 1992, NACE.
- 8) T. Hara, H. Asahi and H. Kaneta, Paper 63; Corrosion '96; Denver, USA, March 1996, NACE.
- 9) T. Hara, H. Asahi and H. Kaneta, Paper 118; Corrosion '98; San Diego, USA, March 1998, NACE.
- 10) R. Francis, Brit. Corr. J. 29, 1 (1994) 53.

7 CATHODIC PROTECTION

7.1 INTRODUCTION

This Section describes the basic principles of cathodic protection, the areas of use, and the general factors to be considered in the choice and design of a system. It gives a basic introduction and simple technical data on cathodic protection.

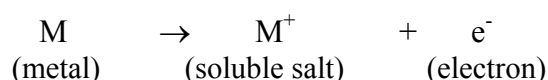
The first reported practical use of cathodic protection is generally credited to Sir Humphrey Davy in the 1820s. Davy's advice was sought by the Royal Navy in investigating the corrosion of copper sheeting used for cladding the hulls of naval vessels. Davy found that he could preserve copper in seawater by the attachment of small quantities of iron, zinc or tin. The copper became, as Davy put it, "cathodically protected". It was quickly abandoned because by protecting the copper its anti-fouling properties became retarded, hence reducing the streamline of the ships, as they began to collect marine growths.

The method is now well established and is used on a wide variety of immersed and buried facilities and infrastructure, as well as reinforced concrete structures, to provide corrosion control.

7.2 THE PRINCIPLES OF CATHODIC PROTECTION

Metal that has been extracted from its primary ore (metal oxides or other free radicals) has a natural tendency to revert to that state under the action of oxygen and water. This action is called corrosion and the most common example is the rusting of steel.

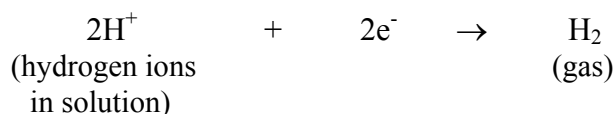
Corrosion is an electro-chemical process that involves the passage of electrical currents on a micro or macro scale. The change from the metallic to the combined form occurs by an "anodic" reaction:



A common example is:



This reaction produces free electrons, which pass within the metal to another site on the metal surface (the cathode), where it is consumed by the cathodic reaction. In acid solutions the cathodic reaction is:



In neutral solutions the cathodic reaction involves the consumption of oxygen dissolved in the solution:



Corrosion thus occurs at the anode but not at the cathode (unless the metal of the cathode is attacked by alkali).

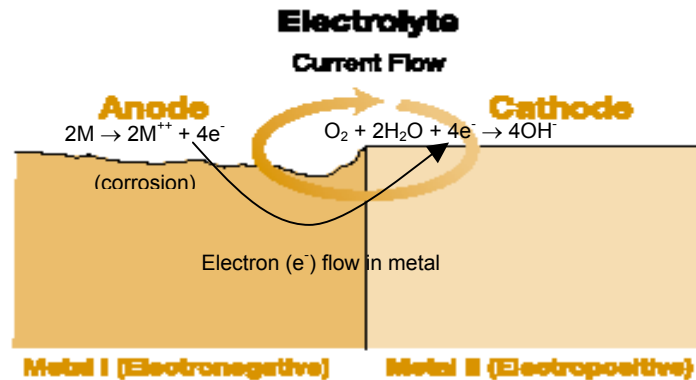


Figure 7.1. Corrosion cell / Bimetallic corrosion

The anode and cathode in a corrosion process may be on two different metals connected together forming a bimetallic couple, or, as with rusting of steel, they may be close together on the same metal surface. This corrosion process is initially caused by:

- Difference in natural potential in galvanic (bimetallic) couples.
- Metallurgical variations in the state of the metal at different points on the surface.
- Local differences in the environment, such as variations in the supply of oxygen at the surface (oxygen rich areas become the cathode and oxygen depleted areas become the anode).

The principle of cathodic protection is in connecting an external anode to the metal to be protected and the passing of an electrical dc current so that all areas of the metal surface become cathodic and therefore do not corrode. The external anode may be a galvanic anode, where the current is a result of the potential difference between the two metals, or it may be an impressed current anode, where the current is impressed from an external dc power source. In electro-chemical terms, the electrical potential between the metal and the electrolyte solution with which it is in contact is made more negative, by the supply of negative charged electrons, to a value at which the corroding (anodic) reactions are stifled and only cathodic reactions can take place. In the discussion that follows it is assumed that the metal to be protected is carbon steel, which is the most common material used in construction. The cathodic protection of reinforcing carbon steel in reinforced concrete structures can be applied in a similar manner.

Cathodic protection can be achieved in two ways:

- by the use of galvanic (sacrificial) anodes, or
- by “impressed” current.

Galvanic anode systems employ reactive metals as auxiliary anodes that are directly electrically connected to the steel to be protected. The difference in natural potentials

between the anode and the steel, as indicated by their relative positions in the electro-chemical series, causes a positive current to flow in the electrolyte, from the anode to the steel. Thus, the whole surface of the steel becomes more negatively charged and becomes the cathode. The metals commonly used, as sacrificial anodes are aluminium, zinc and magnesium. These metals are alloyed to improve the long-term performance and dissolution characteristics.

Impressed-current systems employ inert (zero or low dissolution) anodes and use an external source of dc power (rectified ac) to impress a current from an external anode onto the cathode surface.

The connections are similar for the application of cathodic protection to metallic storage tanks, jetties, offshore structures and reinforced concrete structures.

7.3 ADVANTAGES AND USES OF CATHODIC PROTECTION

The main advantage of cathodic protection over other forms of anti-corrosion treatment is that it is applied simply by maintaining a dc circuit and its effectiveness may be monitored continuously. Cathodic protection is commonly applied to a coated structure to provide corrosion control to areas where the coating may be damaged. It may be applied to existing structures to prolong their life.

7.4 THE APPLICATION OF CATHODIC PROTECTION

The design and installation of a CP system should always be carried by, or in consultation with, a qualified expert in this field. Although the principle is simple there are many factors which can compromise the effectiveness of the system. Anode suppliers can often provide good advice for simple systems.

8 THE USE OF TEMPORARY PROTECTIVES

Edited from the work of C.W. Lea and J. Dunn

8.1 INTRODUCTION

A simple method of controlling corrosion is the use of temporary protectives. This involves the use of a wide range of techniques to produce a protective layer on the surface of the metal which can be readily removed at a later stage and replaced. One of the advantages is that for some techniques interference with the object to be protected is minimal and the risks of producing damage small.

The metal to be protected may be ferrous, aluminium alloy, copper based alloys, or other non-ferrous materials, each of which may require a different specific approach to the formulation of the protective. The metal may be part of an assembly together with other metals, with plastics or rubber seals, and contact compatibility with other parts of the assembly will require consideration.

In many cases, the overall protection is provided by a combination of individual materials, such as a surface coating in combination with outer wrapping, often combined with VCI (vapour phase corrosion inhibitors). For instance, a machined part may be dehydrated, the same dehydrating fluid may leave a protective film, which is then augmented by wrapping in VCI treated paper, or stored in VCI poly-film containers. It is therefore important that both corrosion protection and subsequent packaging be considered together, not in isolation.

The use of some VCI products on their own allow protection without the inhibitor being in direct contact with the protected surface enabling use or assembly without the need for removal.

Sometimes, the temporary protective may perform other additional functions, such as serve as a lubricant or as a cleaning fluid. As a lubricant it may be, for instance, for press forming of steel strip, where the same coating carries out both the corrosion protection and the lubrication of the forming process. As a cleaner, it may be used for rinsing or cleaning machined parts, and the film left by the cleaner may serve also as the temporary protective.

This guide helps to explain the concept of temporary corrosion protection, it describes the various types of protection available, points to ongoing trends, and gives guidance in the selection and application.

8.2 PURPOSE - WHAT ARE THEY FOR?

A Temporary Corrosion Protective is by definition a material that can be easily removed from the metal surface after treatment. It is not designed to be permanent, or difficult to remove in the same way as a paint system or plastic coating. The material may need to provide protection when exposed to a variety of differing corrosive atmospheres, indoors, outdoors either under cover or fully exposed, in a marine environment, under effects of direct sunlight, perhaps in a radiation flux, in the presence of specific chemical corrosives in an industrial environment etc

During its protective period, it needs to give adequate freedom from corrosion of bare metal surfaces for a predetermined length of time in manufacture, assembly, storage or distribution. The term of protection will need to be determined for each application, in line with other requirements, and the type of protective selected to suit. Since temporary protectives are invariably used in inter-stage manufacturing operations, they may need to be compatible or in harmony with later stages in the production operations. Particularly compatibility with any materials such as paints, adhesives, sealants etc., which may be applied to the metal surface at a later stage is important, even though there may be prior removal/ degreasing/ cleaning operations.

8.3 GENERIC TYPES—WHAT VARIETIES OF PROTECTIVE ARE AVAILABLE?

A number of different types of temporary protective are classified in BS1133:1991, Section 6.2, Protection of Metal against Corrosion during Transport and Shipment, Temporary Protectives and their Application; these designations are also used below. There are however a number of other classifications or specifications for achieving temporary protection from corrosion for example the UK Ministry of Defence have their own Corrosion Preventatives specified in Defence Standard 01-05 issue 13 section 4 PX- Corrosion Preventatives; some of these have NATO Reference numbers and all have NATO Stock Numbers. The USA specify similarly under MIL Specification Numbers. The classifications and designations in BS1133 are

A. Solvent based fluids: Coatings deposited on surfaces by the evaporation of solvents.

TP 1 a Deposits a *hard* film, quick drying

TP 1 b Deposits a *hard* film, slow drying

TP 1 c Deposits a *hard* film, slow drying – *also displaces moisture from wet surfaces*

TP 2 a Deposits a *soft* film following solvent evaporation

TP 2 b Deposits a *soft* film – *also displaces moisture from wet surfaces*

Solvent-based fluids, which deposit a coating after the carrier solvent has evaporated, have been a traditional form of protection for some years. Usually they have a low viscosity, which together with appropriate additive treatment enables wet surfaces to be dewatered as part of the protective process. The periods of protection may range from a few days indoors, to over a year outdoors. Type TP 2 b fluids are widely used as automotive “damp start” sprays, for removing moisture from plug leads, and traditionally as dewatering fluids providing interstage protection for components directly after machining with water miscible cutting fluids.

Solvent based fluids are usually applied either from a dip tank, by spray system, or by brushing.

B. Soft Film, Grease-like, Non-solvent

The grease like protectives tend to be specified where consumers are seeking a soft heavy build film. They are particularly used for core protection of wire ropes, cables, and chains, where flexing will not result in breakage of the protective film; for these applications the protective also serves as a lubricant.

TP 3 Petroleum jelly, Vaseline™ or petrolatum based materials, frequently applied by hot-dip or by smearing or trowelling onto surfaces.

TP 4 a Mineral oil based greases, usually smeared or trowelled onto surfaces to give a thick film.

TP 4 b Synthetic or vegetable oil based greases, non-mineral oil, applied by smearing or trowelling, and applied in those applications where special compatibility with sealants or adhesives is necessary.

TP 5 Semi-fluid compounds, based on highly viscous oils, usually thixotropic to control flow, and applied by smearing, or by hot-dip. Application is by smearing or trowelling, although since they generally have fixed melting points, hot-dip application can be used to apply a lighter and more controlled coating weight. At temperatures above the melting point, they can also be pumped and sprayed with appropriate equipment to fill more inaccessible voids.

C. Protective oils, Soft film type, Non-solvent.

Protective oils are available in a wide variety of viscosity ranges, but all are designed to leave an oily soft film on surfaces without the use of a solvent, so avoiding some of the disadvantages of solvent-based materials. They range from very low viscosity, approximately 4 mm²/s at 40 °C, to highly viscous fluids

The protective coating oils are applied by dip, spray brush or circulation. For larger applications, such as for instance, application of protective oils to metal strip at steel mills, these fluids are applied by electrostatic spray, and therefore are designed to achieve the correct electrical characteristics.

D. Strippable coatings.

These coatings are resin or plastic in consistency, usually of a heavy build, and removable by mechanical stripping, usually by hand. Commonly used for protection of hand tools during storage.

TP 7 Hot dip, strippable coatings, generally based on hot-melt resins and plastics, and where the part is dipped into the hot melt

TP 8 Strippable coatings deposited from a solution of resins in rapidly drying solvents, spray, brush or dip applied

E. Volatile Corrosion Inhibitors:

Usually abbreviated to VPI or VCI, this type of protection showed considerable increase in use during the 1990s. Whilst originally mainly used for protecting steel surfaces, products are now available for protecting other metals, and for multi-metal situations. VCI products work by continuously releasing a vapour with powerful anticorrosion properties; on contact with metal the vapour is adsorbed onto the surface creating a film that will protect the metal from corrosion. The film is rehealing and self-replenishing through further vapour release.

Formulations are available that can function in the presence of trace acid residues, but their efficiency can be impaired for instance by acids exuding from wooden packaging. Enclosed systems are recommended for maximum performance of this type of product but treat rates usually allow for some leakage but the most important criteria are that the vapour has access to all the surfaces to be protected and that ingress of water is prevented. When selecting a VCI care should be taken to establish compatibility with paints, plastics and all the metals to be protected. Some inhibitors may attack paints and plastics, and actively corrode some non-ferrous metals (see notes below). Although these products are volatile it is recommended that they should be placed within 30 cm of the surface to be protected for best results. Methods for application are described below.

TP 9 Paper. Supplied as rolls or sheets Impregnated into various types, weights and grades of paper, used for wrapping parts and components. The paper may emit VCI from either one or from both faces. Polymer Film.

Supplied as rolls, sheets or usually bags tailored to the correct size, for later heat sealing. Suited not only for protection of small parts, but also for protection of individual large machine tools, vehicles, complex machinery, etc.

Powders. VCI Powders are used to protect pipe work and tank systems, box sections, etc. by blowing through the system using low pressure compressed air and then sealing the system. Powders may also be applied from a solvent such as alcohol.

Powder Sachets. Powder contained in perforated sachets, used in conjunction with other sealed packaging.

Tablets. Small tablets, incorporated into other forms of sealed packaging

VCI Oils Oil soluble VCI products are blended with mineral oils to produce oils that can be used in mothballing of power generators and hydraulic systems, and can also be used for protecting sealed spaces or box sections.

Water Soluble VCI Products. Normally based on water-soluble VCI powders and other water-soluble inhibitors these products are mainly used as hydro test additives and for enclosed cooling systems.

F. Contact Inhibitors

TP 10 Contact inhibitors, consisting of chemicals to inhibit corrosion when in DIRECT contact with metal surfaces

Papers may be impregnated with solutions of conventional non-volatile inhibitors. When parts, which are wrapped in papers with, contact inhibitors, they are activated when condensed or contaminating moisture leaches out the inhibitor.

G. Water Based and Emusifiable Protectives

Usually mixed with water prior to use, applied by dip, spray or brush, and depositing an oily or waxy film after drying.

TP 11 a Depositing oily film

TP 11 b Depositing wax film

Use of temporary protectives which are mixed with water prior to use have been preferred in some areas over solvent based fluids, particularly to eliminate the safety related problems of use. They are successful in some but not all areas of use.

H. Desiccators and Dehumidifiers.

Corrosion of ferrous materials usually only takes place in the presence of water, and susceptible parts should always be protected from aqueous contamination. Storage indoors, under cover or in areas where condensation cannot occur are therefore recommended.

One way to remove moisture from a sealed environment, bag, box, container, etc., is to incorporate sufficient solid desiccant such as silica gel within the container or to use a dehumidifier.

J. Inert Atmosphere.

Oxygen from the atmosphere is invariably required for corrosion to occur. Replacement of air by a dry inert gas such as nitrogen or carbon dioxide either in a sealed environment, or one where a small positive pressure can be maintained may be suitable for temporary corrosion control of some components or equipment. Note that nitrogen may be preferred, since some alloys show potential for corrosion under carbon dioxide.

K. Barrier Foil

The performance of temporary corrosion inhibitors can be enhanced or replaced by the use of a barrier foil. These are usually laminates consisting of three layers. An aluminium layer, which has very low moisture transmission rate, is sandwiched between a polyester layer, which gives the foil strength, and a polyethylene layer, which facilitates a good seal. This foil will have moisture transmission rates in the region of 0.05 g/m² per day of moisture vapour compared to up to 4g/m²/day for polyethylene under the same conditions. Using barrier foil and either a VCI or desiccant can provide a very effective anticorrosion package for long-term storage.

8.4 MULTIFUNCTIONAL CORROSION PROTECTIVES.

Mention has already been made, see above, of temporary corrosion protectives that also provide other functions. There has been a trend to multifunctional fluids, which has been quite marked in recent years.

Prime examples are:

Mill oils and prelubes. Protectives for sheet steel and aluminium, or mill oils, which are required particularly when the steel strip is intended for the automotive industries, need to serve not only as corrosion protective but also as presswork lubricant. Such oils are applied at the mill at low coating weight; they provide protection during storage at the mill, shipping to the press shop, and storage both before and after pressing into body panels. Specifications raised by the motor industry now refer to these as “prelubes”, requiring a high level of press performance, and subsequent compatibility during the assembly operation. The same prelubes also need to provide protection from corrosion and staining of cold rolled and hot rolled steel, galvanised, galvannealed and strip that has been electro-coated with zinc and zinc nickel alloys, as well as aluminium.

Metalworking and corrosion protectives for machined parts. It has been accepted for many years that cross-contamination exists from one chemical to another during machining operations. Light oils which are formulated to contain additives both for metalworking and for corrosion protection are now specified for certain machining operations, and the same fluid may also provide the final protection during storage and shipment. In some cases, the same fluid may also be used for lubrication of various parts of the machine tools themselves.

Wash fluids. Wash fluids used following metalworking operations may cause cross contamination of subsequent corrosion protectives. In new trends, light corrosion preventive oils are often also used as wash fluids, thereby reducing problems of cross contamination with one multifunctional fluid.

8.5 ENVIRONMENTAL CONSIDERATIONS

The area or environment in which a Temporary Corrosion Protective is used may dictate or require special considerations in terms of toxicity, emissions to atmosphere, potential for pollution of earth or water, or for contact with food. Examples are:

a) **Incidental Food Contact.** Special products are available which comply with requirements for incidental food contact. In most parts of the world including the UK, products that are listed by the US NSF (National Sanitary Foundation) are accepted where incidental food contact may occur. This registration was previously carried out by the US Department of Agriculture.

b) **Rapidly Biodegradable Protectives.** Where products are used in sensitive applications, and where potential contamination of earth or watercourses may occur, products which exhibit rapid biodegradability are available. Whilst these products give satisfactory performance in protection of metal surfaces, they are based on renewable resources and designed to degrade rapidly when accidentally spilled onto land, triggered by exposure to high levels of micro-organisms.

Suppliers will be able to advise on selection of the most appropriate product for special applications.

8.6 PRECLEANING AND REMOVAL

It is generally accepted that the performance of a coating system is improved by good surface preparation before application. This is particularly true with permanent coatings and BS 7773: 1995, Code of Practice for Cleaning and Preparation of Metal Surfaces, covers this in some detail. For temporary protectives the requirements are less onerous and will depend on the component being protected and its surface condition. In general surfaces must be free from contaminants that are corrosive, or may impair adhesion or continuity of coating, or restrict access of inhibiting vapours. The contaminant will normally dictate the choice of preparation. Solvent degreasing, an alkali wash or steam cleaning would remove oil or grease for example and mechanical, acid and electrolytic techniques may be employed to remove scale or rust. In some cases a simple water wash may be sufficient but others may require a combination of more than one treatment.

Removal of temporary protectives is normally achieved using the same techniques employed for precleaning although the standard of cleanliness required will be dictated by any further process the part may undergo. In many cases the protective system may be left in place. Manufacturers will give their recommended method of removal on the technical data sheet for each product.

8.7 HOW TO SELECT A TEMPORARY PROTECTIVE

Answers to a number of questions can help in selection of the correct temporary protective system, and for most appropriate selection the user is advised to consult suppliers for specific recommendations. He should give answers to the following questions:

1. what metal or metals, and how complex
2. how contaminated is the surface,
3. what preparation can be carried out,
4. is it water-wet,
5. what length of protection required,
6. what methods are available for application,
7. if necessary how will it be removed,
8. what is the atmosphere and does the atmosphere vary, is it in a marine or industrial area
9. what temperatures and temperature changes are involved over the lifetime of the protection.

The conditions and period of exposure, the shape of the component or assembly, quantity of items to be treated, and the method of application govern the final choice. Generally speaking there are **four environments**.

Controlled atmospheres: In principle no protective is needed inside an oxygen free or desiccated package but a light oil or grease is often applied as a fail safe before and after packing and in the event of a temporary control failure.

Dry indoor storage or sealed packages: Components stored in heated indoor rooms or sealed packages should be coated with oil or grease or if preferred packed with a volatile corrosion inhibitor.

Covered out door storage: The period of storage will dictate the choice of product. For protection periods of one to two years soft hot dip or solvent deposited types are typical. In some cases over wrapping may be necessary.

Unsheltered outdoor storage. When cover against the elements cannot be provided soft hot dip or solvent deposited films with increased thickness or hard films are recommended. Secondary wrapping may be recommended

8.8 APPLICATION NOTES

8.8.1 Solvent Based Coatings

Combustion: The solvents used are usually light hydrocarbons, kerosene or white spirit fractions. Even lighter and sometimes more combustible solvents tend to be used for those products requiring a faster dry time. Hydrocarbon solvents present risk of combustion. A continuing trend has been to use solvents that possess a higher flash point, and therefore reduced risk of combustion.

Health Hazards: Use of solvent based fluids in confined areas, and contact with the skin, can present health hazards.

Volatile Organic Compounds: The solvents used in these fluids can be classed as Volatile Organic Compounds, and may cause photochemical smog. Legislation is in place to control the use of VOCs, and government is actively promoting elimination or reduction.

Removal/ Degreasing: Removal of the softer and lighter films is usually by conventional solvent or water based degreasing fluids. Hard, particularly heavy film coatings are usually removed by solvent based fluids. Sometimes the use of heat and/ or forced air circulation may be is required to speed up the process.

Dip Tanks – Solvent Evaporation: If applied by dip tank, users must be aware that the solvent in the tank system will gradually evaporate away, leaving a richer, more concentrated fluid which will tend to deposit an increasingly heavier coating. Large users should check the additive concentrations regularly, seeking advice from their supplier on any rectification required.

Spray Systems – Seal Compatibility and Nozzle Blockage. Check that all parts of the spray are compatible: the drying solvent may affect elastomer seals or coatings. With heavier-build coating system, particularly the hard film materials, check that nozzles remain clear. Nozzles on sprayers that are used only intermittently are best cleaned after use with solvent, or blown through to clear.

8.8.2 Protective Oils:

Thixotropic oils. Some oils behave in a thixotropic manner, i.e. whilst pumped, sprayed or agitated, they behave as a normal liquid. However, whilst at rest (for instance after spray droplets alight on a vertical surface) they behave almost as a solid, inhibiting flow and drain from the surface. For this reason, thixotropic oils can offer advantages above and beyond those of a conventional oil, helping to maintain film thickness, even on vertical surfaces, and therefore maintaining design anti-corrosion characteristics, as well as reducing spillage onto surrounding floor areas.

Protective oils for sumps. Many oils are designed to be multifunctional, and to serve as a lubricant. For instance Type 6 b fluids are available as storage oils for the sumps and lubrication systems of compressors, gearboxes, engines, etc., and many such products are designed to be compatible with the usual lubricant used in the equipment at a later stage. In some cases they may also be suitable for lubrication of the equipment for longer term

“Prelubes”. A special type of multifunctional oil. Prelubes are a type of corrosion preventive oil designed for electrostatic application to steel strip at the mill, and that same coating is designed to provide the lubricant capabilities in the press, for forming steel strip into car and truck body panels, under body parts, etc. The protective coating is also designed to be fully compatible in the later auto assembly process, so that the material may be compatible with process cleaners, paint coating processes, as well as adhesives and sealants used in assembly.

Wash fluids. Some of the low viscosity protective oils are also designed as wash fluids for parts during manufacture, to remove metalworking fluids, and to provide a light protective film in storage.

TP 6 a Protective, non-solvent oils, leaving a soft oily film. Applied by spray, dipping, etc. May be thixotropic.

TP 6 b Oils for filling into sumps of equipment, engines, gearboxes, compressors, etc., for protection whilst in storage or shipping

8.8.3 Strippable Coatings

Physical protection. This type of heavier build coating has attractions in also protecting parts against physical damage.

Solvents. Type TP 8 may give the same combustion and safety hazards outlined for solvent-based materials, see above.

Costs. In view of the heavy coating weight, higher costs are frequently encountered, although coating finally stripped off can often be re-used

Hot dip baths. Suppliers of strippable coatings are also able to give guidance on suitable thermostatically controlled baths for applying products of Type TP

8.8.4 Vapour Phase Inhibitors.

VCI chemicals can be used to enhance the performance of the other types of temporary protective coatings that have been described earlier, and are frequently used in conjunction with other types of protection.

Protection period. Provided that the component to be protected is in a sealed environment, and the correct weight of VCI is introduced, the protection period can be almost indefinite. Conversely, when the seal is breached the volatile inhibitor will be lost to atmosphere, leaving the surfaces potentially open to corrosion.

Metals: The VCI products used can be specific for the various metal types. A VCI recommended for ferrous materials may not provide protection for other metals, and parts constructed of a combination of metals will need to be protected by VCI products designed to protect all the metals used.

Controlled emission: In addition to supply of the chemical as sachets or tablets, special “emitters” are available which allow controlled emission of the VCI chemical into the atmosphere. This may be used for large sealed areas, such as machine rooms that may not require access by personnel over long periods, or the mothballing of electrical and other equipment in sealed rooms. These emitters may be sponge impregnated with a VCI Powder or plastic containers holding powder that have a breathable surface allowing the VCI to function.

8.8.5 Contact Inhibitors.

Contact Inhibitors Metal-Specific. As with VCIs, the inhibitors are usually selective to only one metal type.

No Sealing. The system does not require to be sealed.

Water Leaching. Repeated or prolonged wetting of the paper will leach out all inhibitor, reducing efficiency.

Trends have been away from use of conventional contact inhibitors, and towards use of VCI impregnated papers, etc.

8.8.6 Water Miscible Protectives.

Concentration. Usual concentrations vary from 5 – 25% by volume of the protective in water, users are advised to check recommended ratio, and to control carefully and regularly.

Concentration Measurement – can frequently be carried out at the tank side by use of refractometer. Seek advice from supplier.

Temperature. Some water-based fluids are designed for use at ambient temperatures, some at elevated temperatures, typically 60 – 70 C. Use by dip at higher temperatures helps water

to dry out more rapidly after coating – correct corrosion protection can only be achieved after allowing parts to be fully dried.

Water loss from diluted fluid. Use particularly at higher temperatures causes water loss from the system, a mix that starts at 10% may quickly over-concentrate to 25%, and this over-concentration may affect film formation.

Hard water. High water hardness may affect mix stability, leading to separation and scumming; seek advice from supplier.

Microbial degradation. As with water miscible cutting fluids, such water mixes may suffer from growth of micro-organisms.

Note that until the diluting water has been driven off from the coating, the correct level of corrosion protection will not be achieved.

8.8.7 Desiccants and dehumidifiers

Removes moisture only. Note that desiccants/dehumidifiers do not themselves control corrosion, only removing one of the potential corrosive elements.

Volume of solid desiccant required. Consult suppliers and other guides for details of quantity of desiccant required for particular volumes and conditions. Failure to use correct threshold levels will result in corrosion.

Timber. Note that other packing materials such as timber pallets, bearers, dunnage, etc., can hold considerable quantities of water, and may be a significant potential cause of corrosion.

Condensation. During shipping, a container may be subjected to travel through a number of climate changes. This can result in formation of condensation on the metal surfaces. A number of specialist manufacturers produce suitably packaged desiccants to maintain humidity levels at about 30%RH to prevent spoilage of the cargoes carried in these containers.

APPENDIX A: CORROSION CONTROL CHECKLIST

Factors Affecting Corrosion Control

Edited by Bill Nimmo from the work of John Newman

A1.1 Factors that can influence corrosion:

Environment

Chemical

Natural

Storage, transit

Stress

Residual stress from fabrication

Static, variable and alternating operating stresses

Shape

Joints and flanges

Crevices and deposits

Trapped and contained liquid

Compatibility

Metals with metals

Metals with other materials

Quality control of materials

Movement

Flowing fluids

Parts moving in fluids

Two- and three-phase flow

Entrained solids

Vibration and pulsing

Temperature

Oxidation, scales and tarnishes

Heat-transfer effects

Molten deposits

Condensation and dewpoints

Control

Surface cleaning and preparation

Coatings

Cathodic protection

Inhibitors

Data logging

Inspection

Planned maintenance

A1.2 Environment

The type of environment to which a material is exposed is a major factor in determining the type and severity of corrosion undergone. Minor constituents of the surroundings can be critical, aggravating or suppressing corrosive attack. Geographical location is also important, as is the influence of weather and season.

Natural environments

Air

Rural (farming, fertilisers, ammonia); Coastal, marine (chloride); Industrial, urban (sulphur dioxide, soot and acid rain).

Waters

Rivers, lakes, wells, water pipelines, dams; sea water (tidal, “splash zone”), estuaries, harbours (in most of these, chlorides are significant contaminants, as well as a variety of corrosive biological agents).

Soils

Clays, chalk, loam; drainage; acidity; access of air; bacterial action (sulphate reducing bacteria).

Chemical environments

Urban and industrial atmospheres; Environmental pollutants creating aggressive mists; Interior of reaction and storage vessels in chemical plant.

Other environments

Embedded metals may react with non-metallic materials such as wood, plastics, and concrete. The porosity of some of these media allow contact with stagnant water.

Temperature

Increasing temperature usually causes increased rates of corrosion. A notable exception is when temperature increase reduces relative humidity or dries out the environment completely.

Incident radiation

Sunlight, ultraviolet light and thermal radiation, can activate short-lived reactive chemical species from contaminants in the environment, aggravating corrosion.

A1.3 Stress

General or uniform corrosion causes progressive loss of cross-section and increased stress levels, while uneven and localised corrosion causes high stress concentrations. Design should control extremes of stress and environment arising at any time in the life-cycle of the structure.

Think about the following ...

- Residual and thermal stresses arising from fabrication

- Transportation shocks and vibration
- Installation
- Performance and pressure testing, leading to overstressing, test fluids corrosion
- Operating and fault conditions
- Maintenance, including effects of modifications and repairs

Static stresses

The environment both inside and outside a structure can affect the strengths of the materials specified. For each alloy, *Stress Corrosion Cracking (SCC)* requires specific environmental corrosive conditions, with the alloy subjected to a critical tensile stress (residual or applied).

Fluctuating stresses and corrosion fatigue

In a corrosive environment the stress level at which it could be assumed a material has infinite life is lowered or removed completely. Corrosion fatigue and fretting are both in this class. Much lower failure stresses and much shorter failure times can occur in a corrosive environment compared to a situation where the alternating stress is in a non-corrosive environment.

Hydrogen effects and stress

Atomic hydrogen released by cathodic reactions during corrosion can enter metals, causing several significant types of damage. Hydrogen has a strong tendency to travel along stress gradients and accumulate where there are high tensional stresses. By several mechanisms, this can cause cracking in steels. Hydrogen may also be introduced during welding or due to cathodic protection.

A1.4 Shape

"Trap" geometry is poor geometry. Corrosion may be fostered by retention of liquids or contact of the metal surface with a local environment differing from that expected by the designer. Features shown opposite encourage poor drainage, possibilities for solution concentration, differential aeration and poor access for inspection, repairs or maintenance.

Think about the effect of the following ...

Access

Inspection and maintenance requires adequate access to all parts of a structure. Design must allow for easy replacement of material where the risk of corrosion and the consequences of failure are significant.

Joints, flanges

Crevice let stagnant liquid accumulate, causing locally accelerated corrosion from differential aeration. There can also be contact between dissimilar metals. Slower drying at joints can increase concentration of aggressive salts. Consider the use of appropriate and safe solvents.

Welds

Poor weld profile, lack of fusion and stitch welding can all lead to crevices and stress raisers.

Deposits

Debris on horizontal surfaces can give shielding corrosion (differential aeration corrosion). Corrosion products and water forming scales can affect heat transfer and cause temperature differentials that can lead to corrosion.

Liquid traps

Poorly draining areas can result in increased corrosion generally. Increased corrosion may also occur at the water line zone.

A1.5 Compatibility of materials

From the point of view of corrosion, metals may be incompatible with each other or with other materials they contact. The relative areas of two different metals in electrical contact can affect their corrosion rates. This is particularly damaging if the more “active” (anodic) metal has a smaller area.

Think about the following sources of incompatibility ...

Within the metal

Fabrication may create differences in metallurgical structure or alloy composition, allowing local attack, such as:

- End-grain attack on exposed cross-sections of susceptible wrought metals
- Weld decay
- Knife-line attack (intergranular corrosion) near welds, especially in some stainless steels
- Selective corrosion (or dealloying) of some materials.

Dezincification is loss of zinc from brass.

Within the environment

A fluid may contain active metallic species that can lead to local corrosion. For instance, dissolved copper in contact with metallic aluminium can cause pitting.

Contact with other materials

Care may be necessary when a metal is in contact with non-metallics, such as plastics, wood, concrete and some electrically conductive mineral species, such as magnetite (magnetic iron oxide) and iron sulphide.

Welds

Changes in weld metal and base metal composition and structure result in galvanic corrosion or intergranular effects, such as weld decay in unstabilised stainless steel.

A1.6 Movement

Movement of the corrosive environmental agent and the movement of parts can seriously affect the corrosion rates and mechanisms.

Think about the following ...

Flowing fluids

The flow of fluids relative to a metal can increase the corrosion rate. Erosion corrosion may become significant at high rates of flow when the flow changes from laminar to turbulent.

Impingement Caused when liquids impact on a metal surface. Damage can arise due to:

- free-falling droplets
- mist droplet impingement in pipe vapour flow at changes of flow direction or internal irregularities
- jetting of droplet-laden vapours
- dripping of liquids onto surfaces
- agitation
- damage due to impingement of solids (erosion).

Cavitation Damage can occur in regions associated with steep liquid velocity gradients, where vapour-filled voids may form and collapse supersonically, causing shock waves that damage the metal surface by severe localised attack through massive momentum transfer to the metal. Areas subject to local boiling, and dead-end locations can be prone to similar damage.

Parts moving in the fluid

Care is needed when considering metals for moving components such as pump impellers or stirrers, which are susceptible to erosion, impingement and cavitation.

Two-phase and multi-phase fluids

Bubbles, particles and immiscible liquids (e.g. oil and water) in moving fluids can increase the corrosion rate. Differentially wettable solids tend to partition into the most highly wetting liquid phase, increasing its apparent density and tendency to sink.

A1.7 Temperature

Higher temperatures generally increase corrosion rates. However, corrosion needs a liquid phase and, if drying occurs, higher temperatures may be beneficial. If operating temperatures are too high a material will oxidise, forming scale. Thick scales and metal loss result in overheating, from loss of water cooling or absence of insulation. Heat transfer will be progressively impeded as scales or deposits thicken.

Think about the following ...

Environmental factors

Polluted gases can accelerate attack and are often accompanied by heat. Examples are, sulphurous flue gases such as sulphur dioxide and sulphur trioxide, halogens such as chlorine compounds, nitrogen oxides, carbon particles such as soot and hydrolysable organic compounds.

Source of heat

Heat sources include:

- electrical heating elements
- steam heating
- friction and wear
- solar radiation
- processes such as drying
- engines and motors

Remember, some sources of heat can be very localised such as electrical contacts or heaters of any type. In many cases thermal cycling occurs, this can accelerate the corrosion rate and introduce combined effects. Small temperature changes can produce marked changes in corrosion resistance.

Condensation – dewpoint effects

When hot combustion gases cool, condensation may give rise to acid dewpoint conditions. This can occur with chimneys, vehicle exhausts, power and process plant and certain horticultural environments.

A1.8 Glossary

Anion A negatively charged ion.

Anode The electrode of a cell where reacting elements lose electrons (become oxidised).

Bimetallic corrosion (galvanic corrosion) Corrosion of two different electrically contacting metals immersed in the same electrolyte.

Biocide A chemical additive that kills life forms.

Calcareous scale (chalky scale) A scale precipitated from salts dissolved in hard waters.

Corrosion allowance Sufficient additional metal thickness above that required for design code load requirements, to compensate for loss of metal thickness.

Cathode The electrode where the reacting cations gain electrons.

Cathodic protection (CP) Deliberate decrease of the corrosion rate by making the potential of a metal structure immersed in an electrolyte more negative (more cathodic).

Cation A positively charged ion.

Corrosion current The electric current flowing in the metal between the electrodes of a corrosion cell due to the corrosion reaction.

Corrosion-erosion (erosion-corrosion) Combined action of corrosion and erosion that removes any inherent or applied protective film, causing localised material loss.

Corrosion fatigue Localised corrosion cracking from fluctuating stresses where the corrosive environment eliminates the classical fatigue endurance limit.

Corrosion monitoring Any method used to observe or measure the progress of corrosion.

Corrosion potential The overall potential of a metal due to a corrosion reaction.

Crevice corrosion Localised corrosion at, and resulting from, corrosive conditions within a fine crevice formed between two opposing surfaces, of which at least one is a metal.

De-aeration (de-oxygenation) The removal of oxygen either from gases or aqueous liquids.

Deposit attack A form of crevice corrosion due to solids deposited on a surface.

De-alloying (selective dissolution) Preferential corrosive removal of an alloy component, creating mechanically weak areas.

Differential aeration The variation in dissolved oxygen concentration in the solution contacting the metal surface enhancing corrosion.

Electrode In an electrochemical cell, the location at which electric charge enters or leaves a metallic surface (see also anode and cathode).

Electrode potential The difference in electrical potential between an electrode and the electrolyte it is contacting.

Electron The electrically charged particle liberated from neutral atoms that carries electric current through the metallic path in an electrochemical cell.

Electrolyte (electrically conductive solution) A solution in which the passage of electrical charge occurs.

EMF (electromotive force) series of metals The tabulation of standardised metallic electrode potentials

Filiform corrosion Corrosion with the appearance of filaments that progress across a metal surface leaving a meandering track.

Fretting corrosion Deterioration by corrosion or oxidation at the contact area between metals subjected to small repeated displacements under load.

Galvanic series A listing of metals and alloys showing the order of corrosion potential in a specific environment, commonly sea water.

Galvanising The coating of iron and steels with a layer of zinc and iron-zinc compounds, by immersion in a bath of molten zinc.

Graphitic corrosion A form of de-alloying corrosion of grey cast iron in which the strong metallic constituents are removed leaving a mechanically weak residue of corrosion inducing graphite.

Half-cell (electrode) One of the electrodes, and its immediate environment, in an electrochemical cell.

Hydrogen electrode (standard hydrogen electrode) An electrode at which the equilibrium $H^+ + e^- \rightleftharpoons 1/2H_2$ is established on a platinum surface. At specified standard conditions this electrode is assigned an arbitrary reference potential of 0.00 volts, against which to make all other potential measurements, including the calibration of more practical secondary reference electrodes.

Hydrogen embrittlement Embrittlement caused by the entry of atomic hydrogen into a metal.

Impingement attack A form of localised corrosion-erosion caused by impinging flow.

Intergranular attack Preferential corrosion at grain boundaries.

Inhibitor A substance added to an environment in small concentrations to reduce the corrosion rate to an economic or safe level.

Knife-line attack Severe highly localised attack, resembling a sharp cut into the metal, close to the fusion line of a weld in a stabilised austenitic stainless steel.

Millscale Thick oxide layer produced on metals during hot rolling. The term is usually applied to scale on steels.

Passivity Decrease in the corrosion rate of a metal in solution resulting from the formation of a thin and generally non-visible protective film of metal corrosion products.

pH value A number that indicates the acidity or alkalinity of a solution. A pH of 7 is neutral, a pH greater than 7 is alkaline and a pH less than 7 is acidic.

Pitting (pitting corrosion) Highly localised corrosion in which penetration into the metal occurs, with consequent danger of perforation.

Potential (electrode potential) Potential difference at an electrode-solution interface defined with reference to another specified electrode. See **reference electrode**.

Reference electrode (standard electrode) A half-cell of reproducible and known potential by means of which an unknown electrode potential may be determined.

Scale Thick visible oxide film formed during the high temperature oxidation of a metal.

Sensitisation Increased susceptibility to attack, in a corrosive environment resulting from heating, such as from welding usually in stainless steels.

Stress-corrosion cracking Cracking due to the combined action of corrosion and an essentially static internal or applied tensile stress. See also *corrosion fatigue*

Tarnish (patina) Dulling, staining or discoloration due to formation of thin films of corrosion or oxidation.