

Corrosion Control in Engineering Design

Contents

CHAPTER 1.....	2
INTRODUCTION AND THE SIGNIFICANCE OF CORROSION.....	2
CHAPTER 2.....	10
RELATION TO DESIGN.....	10
STATIC SITUATIONS.....	10
DYNAMIC SITUATIONS.....	14
THE METAL AS PART OF A DESIGN.....	21
CHAPTER 3.....	24
PREVENTIVE MEASURES.....	24
CHAPTER 4.....	30
CONCLUSIONS.....	30
SOME INTERESTING READING.....	Error! Bookmark not defined.

CHAPTER 1

INTRODUCTION AND THE SIGNIFICANCE OF CORROSION

Corrosion involves the reaction of a metallic material with its environment and is a natural process in the sense that the metal is attempting to revert to the chemically combined state in which it is almost invariably found in the earth's crust. Whilst it is, therefore, a process that may be expected to occur, it should not be regarded as inevitable and its control or prevention is possible through a variety of means. The latter have their origins in electrochemistry, since the reactions involved in causing corrosion are electrochemical in nature, but corrosion control is as much in the hands of the engineering designer as it is the province of the corrosion prevention specialist. To the engineer, corrosion may be regarded as resulting in a variety of changes in the geometry of structures or components that invariably lead, eventually, to a loss of engineering function e.g. general wastage leading to decrease in section, pitting leading to perforation, cracking leading to fracture.

The rusting of ordinary steel is the most common form of corrosion and overall adds up to a high proportion of the total cost attributed to corrosion. General corrosion, in which the whole of the exposed metal surface is attacked, may lead to failure in the engineering sense, but this is usually avoided by the application of suitable control measures. All corrosion, however, is not of the general type and localised effects may pose more complex problems, especially in the engineering context. It is important to realise that corrosion characteristics are not inherent properties of alloys, as are yield strength, electrical conductivity and the like, since they relate to a combination of alloy and environment. Consequently, an alloy may be very resistant to corrosion in a particular environment, yet perform poorly in another, and even in a given environment factors like temperature, rate of flow and geometrical aspects may be critical. In any event, the significance of corrosion to the engineer is that it leads to loss of engineering function and the following examples have been chosen to illustrate this in a variety of the branches of engineering. They also serve to define some of the commoner forms of aqueous corrosion and their various consequences.

FAILURE OF A CHEMICAL REACTOR

The catastrophic explosion at Flixborough in June 1974 has been traced to the failure of a bypass assembly introduced into a train of six cyclohexane oxidation reactors after one of the reactors was removed owing to the development of a leak. The leaking reactor, like the others, was constructed of 12.3 mm mild steel plate with 3 mm stainless steel bonded to it, and it developed a vertical crack in the mild steel outer layer of the reactor from which cyclohexane leaked leading to the removal of the reactor. One of the factors contributing to the crack was stress corrosion, resulting from the presence of nitrates that had contaminated river water being used to cool a leaking flange. Mild steel exposed to hot nitrate solution and to stresses which in extreme cases may be well below the yield strength, and may remain in the structure from the fabrication procedure or may derive from operating stresses, especially if intensified by a defect, can develop intergranular cracks. Such stress corrosion cracking results from the conjoint action of stress, of an appropriate magnitude, and a corrosive environment, of specific composition, upon steel having a wide range of compositions or structures. Different types of steel are not equally susceptible to cracking as measured by the minimum stress to promote cracking or the concentration of the salt responsible for the corrosion reactions that cause crack propagation.

Stress corrosion cracks propagate over a range of velocities from about 10^{-3} to 10 mm/h, depending upon the combination of alloy and environment involved. Their geometry is such that if they grow to appropriate lengths they may reach a critical size that results in a transition from the relatively slow crack growth rates associated with stress corrosion to the fast crack propagation rates associated with purely mechanical failure. This transition occurs when the stress intensity, which is a function of the geometry of the component, including the crack size, reaches the fracture toughness value for the material concerned i.e. when:

$$K_c^2 = \sigma^2 (c + r_y), \quad (1)$$

where K_c = fracture toughness, σ = stress, c = crack length and r_y = length of the plastic zone associated with the crack. In practice, because of the relaxation and the dimensions of the component, stress intensity equations are somewhat more complex than (1), but the principle is not altered. Thus, (1) leads to the concept of a critical crack length, C_{cr} , in terms of the stress intensity, K_{scc} , below which stress corrosion crack propagation does not occur, such that:

$$C_{cr} = X \left(\frac{K_{scc}}{\sigma_y} \right)^2 \quad (2)$$

where X = a factor dependent upon geometry, and σ_y = yield strength.

Whether or not a stress corrosion crack will grow to reach the critical size for fast mechanical fracture will depend, among other factors, upon the source of the stress that initiates cracking. If this is a fabrication stress, such as a residual welding stress, or if it derives from misalignment of fastener holes, crack propagation may well result in stress relief and the crack may cease to propagate if the crack tip stress intensity falls below K_{scc} before K_c is reached. On the other hand, if the source of the stress that drives the slow stress corrosion crack is derived from the operating conditions, the crack tip stress is not likely to relax and catastrophic failure eventually will occur. Fortunately, operating stresses are frequently below the minimum stress required for stress corrosion cracking and most instances of stress corrosion failure arise from the presence of stresses of yield stress magnitude left in structures as the result of fabrication procedures. The exceptions are usually pressure vessels, such as chemical reactors, high pressure gas transmission lines and steam boilers, and it is probably not insignificant that the incidence of stress corrosion failure has increased considerably over the last two decades as engineering design efficiency has improved, involving higher operating stresses and higher yield strength materials, and as the problems of corrosion spread relatively uniformly over exposed surfaces have been largely overcome, resulting in the possibility of more localised forms of corrosion.

In this latter respect the specificity of environments that will promote stress corrosion cracking is significant. It is important to realise that not all corrosive environments promote the formation of stress corrosion cracks. Those that do will usually be those that do not promote widespread corrosion in the sense of the attack being spread fairly uniformly over all exposed surfaces, since, if for no other reason, this is not likely to lead to the geometry of a crack, which requires that the crack sides remain relatively inactive whilst the tip remains active to maintain propagation into the metal. Consequently those environments, such as sea water, that normally promote general corrosion of mild steel, are not likely to promote stress

corrosion, whilst those chemicals sometimes used to control corrosion by addition to an otherwise corrosive environment, a field touched upon later, may result in a borderline condition, between general corrosion and no corrosion, wherein the attack can be localised. Thus, the addition of caustic soda to boiler feed waters to reduce the corrosiveness of the latter towards mild steel can result in the form of stress corrosion frequently referred to as 'caustic cracking'. The important general point is that those environments that cause stress corrosion are frequently highly specific to the particular alloy involved and a list of some environments that have been shown to promote stress corrosion in various materials is given in Table 1.

Table 1
Combinations of some alloys and environments that have
been shown to promote stress corrosion cracking.

Material	Environments
Al alloys	Chlorides, moist air
Mg alloys	Chloride-chromate mixtures, moist air Nitric acid, fluorides. Sodium hydroxide
Cu alloys	Ammonia, moist air, moist sulphur dioxide
C steels	Nitrates, hydroxides, carbonates Anhydrous ammonia
Austenitic steels	Chlorides, sulphur acid
High strength steels	Moist air, water, chlorides, sulphates, sulphides
Ni alloys	Hydroxides
Ti alloys	Halides, methanol

Although this list of environments that have been shown to promote stress corrosion cracking may appear extensive it is by no means exhaustive. For a given alloy however there are many more environments that do not cause stress corrosion than those that so act. It is possible, by appropriate electrochemical measurements or by laboratory stress corrosion tests properly conducted, to identify potent environments for a given material, although failures continue to occur in circumstances that may not reasonably have been expected, as the following example indicates.

STEAM TURBINE FAILURE AT A POWER STATION

Extensive damage to a turbine-generator, occurred as the result of the spontaneous brittle fracture of a shrunk-on l.p. turbine disc, initiated by stress corrosion cracking in the crown of a keyway in the disc bore. Stress corrosion cracking of disc bores and keyways was also found on a number of other discs.

The maximum size of keyway crack sectioned was 4.5 mm, although many smaller cracks were observed. The application of fracture mechanics to the geometry of the discs for the fracture toughness of the steel involved showed that in the presence of such stress corrosion cracks spontaneous initiation of a catastrophic brittle fracture would occur, when the speed of the turbine-generator reached 3200 rev/min, the speed achieved during a proving test of the overspeed protection when the failure occurred. Similar proving tests, at approximately monthly intervals over the 4½ years of service prior to the failure, had involved maximum speeds of 3450 rev/min, indicative of the absence or slow growth of the stress corrosion

cracks over that period. The fact that failure occurred during an overspeed test is probably of secondary importance, since if the stress corrosion cracks had continued to grow they would have reached the critical size for catastrophic failure at the operating speed (3,000 rev/min). Similarly, due to temper embrittlement, the fracture toughness of the steel was lower than would otherwise have been the case and a material of higher fracture toughness would have tolerated larger stress corrosion cracks without succumbing to their unstable propagation, and the failure would have been postponed if not avoided. It is frequently difficult with such failures to identify with certainty the specific corrosive environment responsible for cracking.

The chemical composition of the steam at the inlet to the l.p. turbines at Hinkley Point 'A' was not abnormal, although it did contain very low concentrations of hydroxide, ammonia and acetate ions. According to the published work available at the time of the failures, such low concentrations as were involved (below 1 part per million) would not be expected to promote the formation of stress corrosion cracks, but the generation of concentrated solutions from much more dilute solutions is always a possibility where heat transfer occurs, as between steam and metal in the 'wet' zone of an l.p. turbine. The condensation of steam at the entry to a given keyway on a disc would produce a dilute solution normally containing less than 1 ppm of dissolved impurities. Subsequent evaporation of this condensate in the downstream portion of the keyway would result in a concentration of the non-volatile substances in the solution. The degree of concentration will depend upon the relationships between condensate film flow rate, heat transfer to the film and mass transfer of steam from the evaporating film. The maximum concentration that can be formed depends on the degree of surface superheat of say 2 °C, a concentrated solution could contain 10 per cent of sodium hydroxide, which would certainly cause stress corrosion cracking of low alloy disc steels. After completion of the initial investigations of this failure it was thought most likely that the concentration of some species present in minute quantity in the steam was involved in the failure mechanism. Indeed laboratory experiments at realistic initial stress intensities on samples of the Cr-Mo disc steel produced stress corrosion crack velocities in the range 5×10^{-5} to 2.5×10^{-3} mm/h, depending upon whether the tests were performed in steam or concentrated sodium hydroxide solutions. It is possible that other salts may have been involved in the failure, e.g. ammonium acetate which may also promote stress corrosion cracking in some steels. But even the lowest crack growth rates claimed in the tests mentioned could account for the crack sizes in the keyways within the operational lifetime of the Hinkley Point turbines, while the highest rate would produce critical size cracks within one month, well able to explain the absence of failure during the overspeed test one month prior to that which caused the catastrophic failure.

However, since the Hinkley Point failure investigation work has continued in an attempt to obtain a better understanding of the environment responsible for the cracking of steam turbine discs, since exhaustive analyses of steam samples, under a variety of boiler operating conditions, indicated that the chemical quality of the steam was very high, with impurities well within the normal range associated with power plant operations. This suggested that stress corrosion cracks could be initiated and propagated during normal turbine operations simply due to the action of high purity wet steam upon highly stressed steels of appropriate composition. Laboratory tests and tests upon rigs in power stations have now shown that relevant low alloy steels will indeed undergo stress corrosion cracking in high purity wet steam and that the crack growth rates in these experiments agree closely with those observed in service. Non-metallic inclusions in the steel may play a significant role in the failure mechanism, and minor changes in the composition of the steel and its structure, influencing its strength parameters, also influence cracking susceptibility. Preventative action to avoid

such failures could include the use of different steels (3.5 per cent Ni steel discs were not found to crack, whereas 3 per cent Cr Mo and 3.5 per cent Ni Cr Mo steels did fail), preferably with better control of non-metallic inclusions and the elimination of keyways from discs.

FAILURE OF A VEHICLE BRAKING SYSTEM

Not all corrosion induced failures result in the formation of geometrically sharp defects such as stress corrosion cracks, but even where corrosion results in the commoner form of pits, i.e. defects having depth to width ratios in the region of 1, the consequences in terms of loss of engineering function can be disastrous. Pitting corrosion, like stress corrosion, is a localised form of attack usually resulting in appreciable depthwise penetration of the metal and the formation of a cavity or the complete perforation of the metal to the surface opposite to that upon which the pit initiates. Like other forms of localised corrosion, the total amount of metal destroyed may be relatively small, but because of its distribution the consequences in terms of loss of function may be very markedly greater than would have been the case had the same amount of metal destruction been uniformly spread over the whole of the exposed surface. This is particularly true in the case of the corrosion of tubes conveying the fluid in the hydraulic braking systems for road vehicles, where a small corrosion pit, involving relatively little metal destruction, can lead to loss of fluid with disastrous effects.

FAILURE OF CONDENSER TUBES NEAR BAFFLE PLATES

The localisation of corrosion does not invariably have its origins in either chemical heterogeneity in the metal, resulting in the concentration of attack upon some structurally identifiable features, or in some borderline condition between overall surface attack and complete immunity from reaction, related to the composition of the environment for the particular metal concerned. Most metals of engineering significance owe their corrosion resistance to the formation of a protective, adherent, film upon the metal e.g. the stainless steels and aluminium alloys. Such films are frequently extremely thin, so much so as to be invisible, and are often formed by initial reaction with the environment to which the metal is exposed. The continued protection of the metal depends upon the film remaining intact, but it may suffer chemical breakdown, by some change in the environmental conditions, or it may suffer physical damage whereby the underlying metal is exposed and then corroded. The commonest form of physical damage occurs through relative motion of the metal and environment, with the subsequent metal destruction referred to as erosion-corrosion. The latter may result from impingement upon the metal surface of solid particles suspended in the environment, of gas bubbles or vapour-filled cavities caused by sudden changes in pressure, or simply by turbulence alone. With such a mode of failure it is usually possible to relate the distribution of the attack to some detailed aspect of the flow conditions and this is apparent in the following example. This concerns the failure of brass heat exchange tubes, having cooling water flowing over their outer surfaces to cool a fluid contained within the tubes. Most of the surfaces exposed to the cooling water were free of visible signs of corrosion, but in sharply defined zones, a series of overlapping, rounded pits indicated regions of attack that in some zones had resulted in perforation of the tubes and the escape of process products.

The zones of attack invariably coincided with where the tubes passed through loosely-fitting baffles plates, incorporated to distribute the flow of cooling water. Where the tubes passed through the oversize holes in the baffle plates, allowing the coolant to short-circuit the intended path, the water velocity would reflect the turbulent conditions in the restricted space,

resulting in the destruction of the protective film that was clearly effective at those surfaces remote from the baffle plates and where the water velocity would be much lower.

CORROSION FAILURE OF AIRCRAFT

Pitting and stress corrosion cracking, the forms of localised corrosion mentioned above, may sometimes be observed in juxtaposition in the same structure. This may be the result of a series of closely spaced pits reducing the effective section to the point where the remaining metal fractures under the influence of the operating load or it may be the result of stress corrosion cracks being initiated at the bottom of pits, because of local environmental changes within the pit or because of stress concentration. Pitting and cracking in aluminium alloys, constituting part of the pressure bulkhead of a Vanguard aircraft, contributed to the rupture of the rear pressure bulkhead, and the resultant loss of the major portion of both horizontal tail surfaces in cruising flight when the corrosion initiated crack exceeded the critical length.

In this particular instance corrosion was initiated in regions that were not readily accessible for inspection, a situation that not infrequently arises in many different structures. Inspection for corrosion, either by visual examination or other methods, has implications for the designer in that facilities which allow inspection should be incorporated, or at least considered from the point of view of feasibility, at the design stage and not as an afterthought.

CORROSION PREVENTION AND ITS ECONOMIC OVERTONES

In the avoidance of these, and other, forms of corrosion the designer is not usually presented with a simple, precise, answer to the problem, in the sense that may be believed of, say, his stress calculations. Thus, it is rarely the case in tackling a corrosion problem that the solution arises from manipulating an equation to provide a single valued answer, and more often than not a number of possible alternative approaches will be available. From a purely technical standpoint, corrosion can be prevented in a number of ways; (i) by using a corrosion resistant materials, possibly as a protective coating covering an inherently reactive material for the environment concerned; (ii) by controlling the environment, through manipulation of its composition; (iii) by changing those electrochemical factors that control the corrosion reactions. Technical considerations may preclude the use of some possible solutions to a corrosion problem, such as when a chemical process is involved and the reactants or products constitute the corrosive environment but which cannot be modified to avoid corrosion since this would adversely affect the process reactions or the quality of the product produced. However, even when there are no such technical limitations upon the solution to a corrosion problem, economic considerations should impose further boundary conditions that will usually assist in making a choice between the possible alternative approaches to the avoidance of corrosion. Of course, despite their numerate form, cost calculations involve elements of uncertainty. For example, assumptions must be made regarding the relative installed costs of alternatives and of the corrosion rates that will occur in the conditions to be met in the future and which will determine the extent to which maintenance is required and production lost. These are difficult to estimate correctly, because factors unknown at the time of the calculations may become important, and these uncertainties are made worse by the problem of allowing for inflation, especially over long periods. Normally a subjective assessment is required, guided by the apparently numerate cost analysis. It is important to realise that the approach to a particular problem will not be confined only by technical or economic factors of the types mentioned above, since the availability of materials at the

relevant time can exert a marked influence. This is not a peculiarity of corrosion prevention, of course, and in general terms it is clear that if the choice of a particular material of construction involves a considerable delay in its supply, the use of a technically inferior, but readily available, material may well be a more attractive solution viewed from an economic standpoint.

The economic argument in relation to corrosion control is really concerned with the conflict between capital costs and maintenance costs. Assuming intelligent technical decisions the final choice that will usually need to be made will be between a high capital cost, long life, structure and one involving lower initial but higher maintenance costs. The deciding factor may even be the ready availability of the resources needed for maintenance – it can be better to accept a shorter life with a material that can be repaired by local labour than to use a better material which requires specialists to be imported whenever maintenance is needed. The continuing debate as to the detailed accounting techniques to be employed in setting-up the equations to solve this, apparently, simple arithmetical exercise, arises partly because of the unknowns, i.e. the changes in the cost of money, taxation procedures etc, over the lifetime of a structure. It is sustained by the difficulties in allowing for the costs of downtime, whilst corroded components are replaced, or for the reduced operating efficiency of plant that has deteriorated in service. It is clear that it would be difficult, especially in the present context, to give a generalised approach to the economics of corrosion control, but its significance is such that some points need to be underlined and these are possibly best made with specific examples.

The first of these concerns the construction of three tidal openings on the Manchester Ship Canal System, in which the water changes from reasonably well aerated tidal sea water at the sea-end to anaerobic polluted stagnant ‘fresh’ water in the docks. Superimposed upon this is seasonal fresh water flooding from canals and rivers and sea-water intrusion by tidal overflow and the passage of ships through locks. The variability in the environment is therefore considerable and measurement of corrosion rates for mild steel showed that the appropriate general wastage rate could be taken as 0.0075 mm/year. The tidal openings were of sheet piled construction, with some 50 per cent of the thickness could be lost before the stresses in the remaining metal exceeded safe limits. At the time of the following assessment, the steel for the first opening had already been supplied with a thickness of 9.65 mm, giving a predicted lifetime of 32 years, assuming the general wastage rate mentioned above was relevant to both surfaces. The required life was 50 years, indicating the necessity for a reduction in the corrosion rate. In order to achieve the latter three alternatives were considered (a) the use of either a hot applied asphalt coating or a cold applied coal tar epoxy system, (b) power impressed cathodic protection with or without the coating system, or (c) the use of thicker steel in the second and third openings. (The technical aspects of coatings and cathodic protection are considered later.) The assumptions made in arriving at a comparison of the costs were that the hot applied asphalt would extend the life before corrosion commenced to 8-10 years; the equivalent figure for the epoxy coating was 12-15 years. The costs (1964 figures) are shown in the Table 2 for the main alternatives.

Table 2
Cost comparisons for alternative approaches to extending
lifetime of tidal openings on Manchester Ship Canal⁽⁷⁾

Steel thickness mm	9.65	9.65	9.65	11.7	11.7
Coating	None	None	Epoxy	None	Asphalt
Cathodic protection	None	For at least first 20 years	For first 7 years at least	None	None
Life-years	32	50	50	45	50
Capital cost of CP system	-	£20K	£3K	-	-
Operating costs for CP system	-	£48K	£4K	-	-
Coating cost	-	-	£16K	-	£8K
Additional steel cost	-	-	-	£6K	£6K
Fifty year cost	Replacement	£68K	£23K	Replacement	£14K

The obvious conclusion from these comparative figures, despite the fact that they do not include values for the cost of replacement after 50 years, is that an increased steel section with the asphalt coating would provide the most advantageous course of action. The application of the coating also had the technical advantages of dealing with corrosion in the region of the waterline and above and would allow the later application of cathodic protection if necessary. For the tidal opening for which the steel had already been delivered at the time of this analysis, the asphalt coating was also applied together with cathodic protection.

Although the direct costs of corrosion, involving replacement or maintenance of components, can be considerable, the indirect costs, involving loss of output from Magnox nuclear power stations, amounting to about 15 per cent or 400 megawatts over all the reactors involved and a cost to the industry of some £140m between 1968 and 1975, is a case in point. The problem involved an excessive corrosion rate of certain, very cheap, mild steel fasteners at the hot end of the reactors, the corrosive environment not being aqueous but gaseous. The corrosion of metals at elevated temperatures by gaseous atmospheres has many similarities to wet corrosion, but is met less frequently since the vast majority of engineering structures operate at the ambient temperature.

Carbon dioxide, the high pressure gas used as a heat transfer medium in Magnox reactors, becomes heated to temperatures of about 400 °C in the latter when, it is now appreciated, it attacks mild steel at unacceptably high rates in relation to the lifetime of a reactor. The corrosion rate is markedly sensitive to temperature and by reducing the gas output temperature below about 350 °C the corrosion is reduced to acceptable levels. However, the penalty for reducing the temperature is a reduced efficiency and hence output, unless the gas throughput can be increased, involving the replacement of the gas blowers and/or the fuel elements with ones of different design. Other solutions are still being sought for this problem, which if ignored could result in small components becoming detached and hampering the movement of fuel elements, but even if a simple solution is found now the costs already incurred by the corrosion of a few cheap fasteners is already very considerable.

CHAPTER 2

RELATION TO DESIGN

The primary objective of this section is to indicate how some of the parameters with which the design engineer is normally concerned, e.g. geometry, stress, fluid and heat transfer, can themselves influence corrosion. In the present context total design is implied i.e. not only the shape of the component or structure, but the material, its fabrication and the relation of these to the environment in which it is to be used. It is also convenient to distinguish between static and dynamic situations especially in order to emphasise some of the problems unique to the latter.

STATIC SITUATIONS

Use of dissimilar metals in electrical contact

It is well known that in cells or batteries two dissimilar substances immersed in an appropriate electrolyte will provide a source of electrical energy. The generation of the latter in, for example, the Daniel cell involves the dissolution of the zinc electrode whilst copper is deposited from the electrolyte on to the copper electrode. If the two electrodes are not electrically coupled then the rate of dissolution of the zinc or the deposition of the copper will be very markedly reduced whilst immersed in the same electrolyte. Any two metals, providing they are sufficiently dissimilar in the electrochemical sense, in electrical contact will undergo essentially similar responses in that the dissolution, or corrosion, of one of the metals will be accelerated by contact with the other metal. The extent of such **galvanic or bimetallic corrosion** depends upon a number of factors but, as Table 3 shows, it depends critically upon the metals coupled, reflecting their different electrochemical characteristics.

Table 3
Weight losses for iron and coupled metals of the same relative surface
areas immersed in a 1 per cent chloride solution
(O Bauer and O Vogel, Mitt, Mat Prnf Amt Berl. 1918, 36, 114)

Metals coupled to iron	Wt loss of iron (mg)	Wt loss of coupled metal (mg)
Copper	183.1	0.0
Nickel	181.1	0.2
Tin	171.1	2.5
Lead	183.2	3.6
Aluminium	9.8	105.9
Cadnium	0.4	307.9
Zinc	0.4	688
Magnesium	0.0	310.4

It is clear from Table 3 that the effects of coupling copper or magnesium to iron are very different, and indeed that the corrosion of iron can be prevented by coupling it to magnesium. (The Table does not include a comparative figure for the amount of the corrosion of iron in 1 per cent sodium chloride in the absence of it being coupled to another metal, but the amount

would be appreciable, although less than when it is coupled to, say, copper.) Whilst the corrosion of iron, in the conditions to which Table 3 refers, can be prevented by coupling to magnesium the corrosion of the latter would be increased beyond that which would be observed in the absence of coupling. In such circumstances the magnesium is referred to as a sacrificial electrode and the prevention of the corrosion of the iron results from cathodic protection, a subject referred to later.

The extent to which corrosion of a given metal is aggravated or mitigated by coupling to a dissimilar metal depends not only upon the relative electrochemical characteristics of the two metals concerned, but also upon other factors, such as their relative exposed surface areas, the nature of the electrolyte and the temperature. Copper rivets inserted into a steel joint of relatively larger surface areas have caused only a slight increase in corrosion of the steel, whereas steel rivets in contact with a large area of copper have suffered severe corrosion. The distribution of corrosion in the vicinity of bimetallic joints is a complex subject, depending upon factors such as the conductivity of the electrolyte, whereby the corrosion is localised very close to the joint or more evenly distributed according to whether the resistive path is high or low, respectively. Changes in temperature can produce variable effects. Table 3 indicates that zinc acts as a sacrificial anode when connected to iron under those exposure conditions. However, the zinc-iron couple can reverse its polarity, with the iron becoming anodic to zinc in certain fresh waters when the temperature exceeds about 60 °C. Clearly this could be a problem of significant practical importance in such components as galvanised steel domestic water heaters. Notwithstanding these various potential problems it would be incorrect to assume that corrosion is the invariable result of coupling dissimilar metals and therefore that bimetallic couples must always be avoided in any engineering design. It is a matter of common observation that dissimilar metals can often be coupled without adverse effect and guidance is available for those couples that are likely to result in corrosion. Where other considerations result in the necessity for coupling dissimilar metals despite the corrosion hazard the latter can often be avoided by suitable metallic or paint coatings on the metals or by the use of electrical insulation at the joint.

Soldering and brazing are methods of joining metals that will more frequently involve bimetallic junctions than will welding or the use of mechanical fasteners. Because of the relative area effect, it is usually preferable for the solder or brazing alloy, which frequently has a relatively small exposed area, to be more electropositive (or cathodic) than the parent metal. Joints between steel components are therefore likely to suffer less serious corrosion if prepared with a silver solder than if a zinc-rich alloy is used. Possibly the greatest corrosion hazard arising from the presence of soldered joints relates not so much to the bimetallic coupling but to the flex that may be allowed to remain upon exposed surfaces. Fluxes containing chlorides are particularly liable to promote subsequent corrosion, if not thoroughly washed away following the making of the joint, and it is preferable to use one of the non-corrosive fluxes now available. In welded joints, the difference in the electrochemical characteristics of the weld and parent metals are usually much less marked than with soldered or brazed joints, but problems can arise.

Welded joints are more likely to result in stress corrosion cracking, if the residual stresses introduced by welding are not subsequently relieved, also structural changes in the heat-affected zone of the parent metal may lead to certain localised forms of corrosion involving selective leaching that is essentially galvanic in origin.

The 18 Cr 8 Ni austenitic stainless steels are particularly prone to this form of corrosion, known as weld decay, and which involves intergranular corrosion along the austenitic grain boundaries in certain environments. The heating cycle to which the parent metal is subjected adjacent to the weld can result in the precipitation of chromium carbide in the grain boundaries where, because the carbide contains much more than 18 per cent chromium, a zone of metal impoverished in chromium is formed. Since the corrosion resistance of the steel derives from the formation of a chromium-rich protective film, the corrosion resistance of the chromium depleted grain boundary regions is diminished and preferential attack occurs.

The solution to this problem is either to use a stabilised steel containing titanium or niobium, which have stronger affinities for carbon than has chromium so that chromium depletion does not occur, to use a stainless steel with a carbon content restricted to a maximum of 0.03 per cent, or to heat the whole of the welded assembly to a temperature high enough to take the carbides back into solution and cool fairly rapidly to prevent their reprecipitation. Both stabilised and low carbon steel are readily available, but they must be specified where required. A common mistake is to assume that it is sufficient to order 'stainless steel'. In fact there are a considerable number of alloys commonly known as stainless steel and, except where the conditions are relatively mild, the individual alloys can be very different in corrosion behaviour. While the weld decay problem is well understood and the precautions reasonably well known, other similar examples exist where this is less than the case. The corrosion resistance of the high nickel alloys (Hastelloys and high nickel austenitic steels) can also be impaired if the initial heat treatment is not correct or if they encounter a dangerous heating cycle during welding or hot working operations. In some cases the impaired corrosion resistance is confined to a narrow zone on either side of the weld. An example is with some austenitic steels in hot strong nitric acid, which from its morphology is known as knife line attack. Like weld decay, this form of corrosion is due to precipitation reactions during the heating cycle – it can be minimised by the use of a low carbon or a niobium stabilised steel, but under extreme conditions the best course is to use a completely different material, such as titanium. This is another example of the extent to which localised corrosion, involving relatively little metal dissolution, can result in the deterioration of an engineering structure to a markedly greater degree than would have been the case had the same amount of metal dissolution been spread uniformly over the whole of the exposed surfaces.

Intergranular corrosion along sensitised grain boundaries is not a peculiarity of stainless steels, since some of the high strength aluminium alloys, for example, can show similar effects. Nor is selective leaching only found along structurally-distinct features such as grain boundaries. The types of corrosion frequently referred to as dezincification, when referring to the preferential leaching of zinc from brasses, as graphitisation, when relating to the selective attack upon the metallic components of grey cast irons, or as dealloying, when a generic term is required, have features in common with the forms of corrosion mentioned above. Dezincification can occur uniformly over an exposed surface or it may take a more localised form, known, respectively, as layer-type and plug-type. The environmental conditions that favour dezincification of brasses are stagnant or slowly running water, elevated temperatures, poor aeration and extremes of acidity or alkalinity. The selective removal of the zinc leaves a porous film of copper adhering to the component and therefore associated, in the absence of other deposits, with a change of colour from the characteristic yellow of brass to the red of copper. More importantly, there is a marked deterioration in strength associated with these changes, which are best avoided by the use of alloys less susceptible or

immune from this type of failure. Thus, lowering the zinc content of the brass or adding a small amount of arsenic in its preparation will be beneficial, or, for the more severely corrosive conditions, the use of cupronickels may be advisable. The graphitisation of grey cast iron pipes buried in certain soils involves selective leaching of the metallic phases and leaves a weak mass of graphite and corrosion products that retain the shape of the pipe, until some relatively small pressure change, frequently associated with ground movement, causes a fracture. Its avoidance sometimes lies in the use of spheroidal, rather than flake, irons or the application of other corrosion prevention methods, such as cathodic protection.

Many of these and other examples of selective leaching have their origins in the same galvanic processes as are readily understood when dissimilar metals are placed in electrical contact whilst immersed in an electrolyte. They help make the essential point that corrosion is not prevented simply by avoiding contact between dissimilar metals, important though that is in its own right, and that galvanic cells may be generated at chemical heterogeneities distributed on a micro scale and indeed, as indicated below, by the operation of additional agencies.

The importance of geometrical factors in corrosion

One of the commonest causes of corrosion, especially in static structures such as frameworks, is poor geometrical detail that results in the entrapment of a corrosive environment. Detail should be such that moisture and dirt are not trapped, involving the use of adequate drainage holes if necessary. Nor is this simple point relevant only to such structures, since tanks and other containers frequently need to have their contents removed and if this is not carried to completion the consequence can be severe corrosion.

Possibly of even greater significance, if only because they are more likely to be overlooked in design, are crevices or smaller geometrical discontinuities frequently related to the method of fabrication. It is obvious that poorly fitting joints are likely to retain any corrosion substance with which they come into contact, but even when the preparation of the joint is sound its detailed design can have a marked influence upon the incidence of corrosion. Thus, upward facing ledges, from overlapping plates or protruding welds, allow the collection of debris that will aggravate corrosion at the underlying surfaces. This is because corrosion reactions may frequently involve oxygen dissolved in the aqueous phase and those surfaces to which oxygen does not have ready access will undergo marked attack, in contrast to those regions to which a plentiful supply of oxygen is available. The differential aeration of surfaces, one of the commonest causes of corrosion, is not a peculiarity of details such as are shown in Fig 18, but it can occur over large distances as, for example, with a buried pipeline passing through soils of varying oxygen content in regions displaced by distances measured in miles. Nevertheless, corrosion resulting from variations in the oxygen available for electrochemical reaction most frequently involves local changes arising from deposits that shield parts of exposed surfaces and crevice corrosion provides an obvious instance. In fact crevice corrosion, although frequently involving oxygen, can also arise from local changes in the concentration of other substances involved in some corrosion reactions. It is important to remember that crevices are not just created at metal-metal joints. Special care must be taken when bolting metals to moisture retaining materials like wood, which may itself release corrosive substances. Something akin to the localised conditions involved in crevice corrosion can occur due to the collection of condensation on downward facing members, causing particularly damaging corrosion to load bearing joints.

DYNAMIC SITUATIONS

In dynamic situations a number of additional physical factors may become important because of their effects upon the breakdown of the protective film that would otherwise form by reaction between the metal and environment. These may involve relative motion of the metal and environment, changes in stress or heat transfer leading to a variety of forms of corrosion failure but upon all of which the design engineer may exercise influence.

Relative motion of metal and environment

An example was given earlier of erosion-corrosion of brass condenser tubes due to high velocity, turbulent, cooling water impinging upon the surfaces of the tubes where they passed through poorly fitting baffle plates. This problem, involving the destruction of what would otherwise be a protective film is of widespread occurrence and severity, depending upon the metal and its environment, their relative velocities, the presence or otherwise of suspended matter and so on. However, since both corrosion and its prevention are frequently dependent upon the rate of supply of chemical species to a metal surface, the effect of increased velocity of an environment with respect to the metal with which it is in contact is not invariably to aggravate corrosion. Thus, the shielding of surfaces by deposits, already mentioned as a cause of corrosion, is less likely in high velocity solutions than when the latter are stagnant. By the same token, where the rate of corrosion is controlled by the rate of supply of some substance, e.g. oxygen, to a metal surface, it is to be expected that the corrosion rate will increase with flow rate, simply because the rate of supply of the critical species controlling the overall reaction rate is increased. This is readily apparent in the results of Mahato et al for corrosion in steel pipes conveying natural water, where the controlling parameter is the transfer of oxygen to the metal surface. The semi-empirical equation developed from this work to give the amount of corrosion, W , in mg/dm^2 , is:

$$W = 5.21 \text{ Re}^{0.535} [(0.96t + 0.31)^{0.5} - 0.56], \quad (3)$$

where Re is the Reynolds Number based on the initial pipe diameter and t is the time in days. This, and like expressions for other systems of metal and environment, are only valid for the particular controlling conditions to which they refer, but it makes the general point that increases in flow velocity, proportional to Re , can significantly increase the amount of metal corroded in unit time. Of course, in the same way, when corrosion prevention is achieved by the addition of inhibitors to the environment, a subject discussed later, the effectiveness of the inhibitor is related to its supply to the metal surface and so it can be more efficient in flowing than in stagnant conditions.

Nevertheless, it is most frequently the case that the high velocity impingement of liquids upon metal surfaces, the turbulence that can be created at geometrical features causing a change in flow direction or the cavitation that occurs in liquids due to sharp pressure changes, may all promote a degree of corrosion in excess of that which would be observed in the absence of such aspects in a design. The scouring action by solid particles suspended in a fluid which disrupts an otherwise inactive surface is an obvious possible cause of enhanced corrosion that will increase with relative velocity. But gaseous bubbles, created by sudden rarification of pressure or the entrainment of air, can have essentially similar effects if they are large enough and collapse at the metal-liquid interface imparting 'hammer blows' or shock waves to damage the metal surface. This mechanical damage may be sufficient to erode a surface in the absence of any corrosive reaction, but if the damage exposes metal that

is reactive to the environment concerned then corrosion will further enhance the surface deterioration. The problem may be particularly acute in ships' propellers, water turbines, pump impellers and the like, if the design and material of construction are inadequate.

Marked variations in the extent of attack over adjacent parts of a surface exposed to the same environment are observed where pipework fails by erosion-corrosion due to changes in velocity at a bend. A detailed examination of the shape of pits resulting from such velocity effects will usually indicate undercutting of the metal on the downstream side. Where turbulence results from small protrusions, e.g. deposited matter, weld spatter, the pitting frequently takes the horse-shoe shape. Such features of the pitting associated with the various types of erosion-corrosion together with the fact that the pits are usually clean and devoid of corrosion products, allow this mechanism of failure to be distinguished from pitting corrosion in stagnant or low velocity conditions.

A significant contribution to the avoidance or diminution of erosion-corrosion can be made by the designer in view of the influence of shape or geometry upon this mode of failure. In general, design features that decrease fluid velocities and streamline the flow will be beneficial, as will increase in section thickness at vulnerable areas if the problem cannot be completely overcome. The incorporation into the design of readily replaceable parts is sometimes necessary, as are baffle plates to avoid impingement of fluids on to critical parts if inlet ports cannot be located to avoid the problem. Although all of the methods of corrosion prevention are, in principle, available for controlling erosion-corrosion, the selection of resistant alloys coupled with attention to design details is one of the commonest ways of alleviating the problem. A resistant alloy can only be defined in relation to its conditions of exposure, i.e. the composition, temperature and velocity of the environment, and so on, but the significant improvements that can result from alloying are indicated by the following maximum sea water velocities that can be tolerated by different copper alloys used as tubes in heat exchangers.

Alloy	Max Velocity, m/sec
Copper	1
70 Copper 29 Zinc 1 Tin	2
76 Copper 22 Zinc 2 Aluminium	2.5
70 Copper 30 Nickel (0.5 Iron)	5

It should be remembered however, that whilst for some systems of metal and environment corrosion rates may increase virtually linearly with flow rate, this is not invariably the case. Thus, in some cases the corrosion rate may decrease with increasing velocity, as for example when 17-19 per cent Chromium 9-13 per Nickel stabilised stainless steel is in contact with white fuming nitric acid at about 40 °C, due to the dispersion of otherwise aggressive corrosion products that enhance corrosion in stagnant conditions. In other cases, the corrosion rate may initially increase with fluid velocity later passing through a maximum and falling to a relatively low rate at high velocities, as is observed for a number of materials immersed in relatively pure waters free from aggressive ions. Clearly, in view of these variable effects, it is especially important to recognise any potential problems arising from fluid velocity effects at the design stage, so that the material selection can be made in the context of the details of the service condition.

An example that illustrates the need for attention to detail during design is the use of mild steel for storage of sulphuric acid. Corrosion is rapid in weak acid, but in strong (70 per cent

or above) acid a protective layer of ferrous sulphate is formed that reduces the corrosion rate under static conditions to an acceptable level. The corrosion rate is however increased by liquid velocity or increase in temperature. Hence while mild steel is the accepted material for acid storage tanks problems can arise. One problem associated with the effect of the strength of the sulphuric acid is related to the affinity of strong acid for water. The film of acid left on the side of the tank as it is emptied tends to become corrosive because it picks up moisture from air sucked into the tank, and if the tank is not to be refilled within a few days it is common practice to include a drying agent in the tank vent. For the same reason, the outlet pipe should be positioned to facilitate complete draining of the tank when this is required. The position of the acid inlet is also critical, as if acid enters near the tank wall the local turbulence causes locally increased corrosion. Experience has shown that local thinning due to this cause can extend from top to bottom of the tank (because the liquid level varied as the tank was filled and emptied) and in one case a full 3,000 ton tank split from top to bottom in this locally thinned region, causing serious damage. In large tanks the inlet should be arranged at least 2 m from the tank wall; in smaller tanks good practice is to introduce wear plates in the vicinity of the inlet. Another phenomenon occasionally encountered is deep grooving caused by hydrogen gas bubbles continually following the same path and accelerating corrosion by virtue of the local movement of the acid. This can be particularly dangerous in horizontal tanks, or in manholes on the side of vertical tanks.

Mild steel is, despite the problems mentioned, generally a satisfactory material for sulphuric acid tanks. A relatively recent development is the use of anodic protection, which prevents all of the above types of corrosion; as it allows the metal thickness to be reduced, an anodically protected tank can actually be cheaper and has the additional bonus that the acid remains purer because it contains less dissolved iron.

Stresses and corrosive effects

If a normally protective film overlying a metal surface is disrupted by plastic deformation in the underlying metal then reactive metal may be brought into contact with an aggressive environment and corrosion, in one form or another, will ensure. The instances of stress corrosion cracking mentioned earlier are examples of corrosion resulting from the conjoint action of stress and a reactive environment upon metals, but such conjoint action can take other forms. Thus, if the corrosive reaction is not sufficiently localised to retain the geometry of a crack, by the rate of attack being essentially the same in the depth and width direction, then pits or fissures, rather than cracks, will result. Alternatively, if stress is applied in a cyclic manner, so that rupture at a protective film, corrosion and reforming of a film occur in a repetitive fashion, then failure may occur by corrosion fatigue. The latter is one of the commonest modes of material failure, involving crack initiation and growth under the influence of a repetitively applied stress of appropriate amplitude and frequency, as with fatigue in the absence of any environmental interaction, but with the crack initiation and/or propagation stages facilitated by corrosion. From the engineering viewpoint the most significant effects of the corrosive reactions are that, comparatively, they lower the minimum stresses above which such failure occurs and they also usually increase the crack velocity, either of which will result in a reduced life for components.

For initially plain specimens, corrosion fatigue is often assessed in laboratory tests by varying the initial stress amplitude (S) and observing the number of stress cycles (N) necessary to produce total failure, resulting in an S-N curve that is compared, when produced in the presence of a corrosive substance, with a similar curve produced with the specimens in

contact with air. (The implicit assumption that laboratory air is not corrosive frequently may not be valid.)

The application of linear elastic analysis to crack growth problems in general has involved corrosion fatigue, the essential difference from the older approach of deriving S-N curves being that a pre-cracked specimen is employed to determine the crack extension per stress cycle (da/dN) as a function of the maximum stress intensity (K_{max}) or the stress intensity range per cycle (ΔK). The results indicate that in the absence of corrosion there is a limiting value of K , K_{TN} , below which fatigue crack growth does not occur, and that in the presence of a corrosive substance this is lowered to K_{CF} and the crack growth rate is increased above that observed in the inert condition for the same stress intensity. For a wide variety of materials, the limiting stress intensity range for corrosion fatigue

$$\Delta K_{CF} = (2.7 \pm 0.3) 10^{-5}.E.$$

where ΔK is measured in $MN.m^{-3/2}$ and the modulus E is in MN/m^2 . For steels, with moduli of about $2.10^5 MN/m^2$, ΔK_{CF} is in the region of only 5 to 6 $MN/m^{-3/2}$, indicating the importance of geometrical discontinuities in facilitating corrosion fatigue crack growth. The importance of avoiding notches, especially with sharp profiles, in structures subjected to cyclic loading is well known if fatigue is to be avoided, but in the presence of a corrosive environment this is frequently even more important. The significance of crevices from the corrosion viewpoint has already been mentioned, but such geometrical features are not only important in relation to their influence upon oxygen distribution, since there are many other electrochemical reactions that can be stimulated by localised changes in ion concentration, and geometrical discontinuities in general will frequently facilitate localised concentration changes.

Although the corrosion fatigue properties of materials vary with the environmental conditions, the latter are much less specific for corrosion fatigue than they are for stress corrosion, especially in relation to their influence upon ΔK_{CF} . Crack growth rates at stress intensity range above ΔK_{CF} are sensitive to the composition of the environment, as is apparent from the results for a Titanium – 6 per cent Aluminium – 4 per cent Vanadium alloy immersed in various environments, but the ΔK_{CF} values do not appear to be particularly influenced by the nature of the test solution. However, for initially plain surfaces, fatigue properties as measured by the stress below which total failure is not observed can be markedly influenced by changes in the environment. S-N curves for a mild steel in various aqueous solutions and shows the deleterious effect of chloride addition to water, especially in the presence of oxygen. The difference between the behaviour of plain and notched surfaces is probably largely related to the varying effects of different environments in producing pitting on initially plain specimens. Where the environment promotes pitting it will produce an increase in the stress intensity for the same loading conditions, as well as allowing local electrochemical changes within the confines of the pits that could not occur at a plain surface, either of which mechanisms would facilitate corrosion fatigue crack growth.

In a somewhat similar fashion the frequency of stress cycling and the stress wave form may influence corrosion fatigue, in ways that are not apparent in fatigue in the absence of environmental reaction. Metal dissolution is, of course, time dependent, so that the longer the period of a stress cycle the greater is the extent to which dissolution can occur during that cycle. It may be expected therefore that, in general, the effects of corrosion upon crack growth will be greater the lower the frequency, and this is frequently found to be the case.

Similarly, prior exposure of a structure to corrosive influences in the absence of stress cycling can influence subsequent behaviour when repetitive stresses are applied, if pitting occurs during the prior exposure period.

There are similarities between certain aspects of failure by corrosion fatigue and by stress corrosion. Thus, particularly at very low stress cycle frequencies ($< \sim 0.01$ Hz), failure by these two modes can be indistinguishable and some of the effects upon corrosion fatigue of corrosion reactions leading to pitting, mentioned above, are also observed in stress corrosion. At first sight it may appear odd that failure resulting from fluctuating or dynamic stresses can have similarities to failure under the static stress situation that is assumed to exist in relation to stress corrosion failure, and indeed with the latter it may be difficult to understand why crack propagation should occur at all, when the stress may be appreciably below the yield stress or the stress intensity well below the fracture toughness value. It should be remembered however that corrosion, even in the absence of stress, can be sufficiently localised to produce the geometry of a crack, so long as dissolution is concentrated at the advancing front and there is relatively little dissolution on the sides of the discontinuity. The presence of stress will help to concentrate the dissolution at the crack tip, since it is there that the stress intensity will be maximal and where plastic deformation, resulting in the disruption of otherwise protective films, will be concentrated. The influence of a pre-existing sharp discontinuity (notch or crack) in facilitating stress corrosion crack propagation therefore may be expected to be dramatic, as it is in corrosion fatigue, and this is found to be so. For example, certain titanium alloys can be made to fail by stress corrosion when immersed in sea water if the specimens are pre-cracked, but the same alloys in the same environment will not crack if statically loaded as plain specimens. Clearly, in relation to alleviating both stress corrosion and corrosion fatigue failure it is important to avoid sharp changes in section, whether these relate to design features or to surface defects in a structure.

Whilst this will invariably be beneficial it will not ensure immunity from such failures, since stress corrosion or corrosion fatigue cracks can be started at initially plain surfaces. Where the stresses are high enough to promote even a small amount of plastic deformation in the metal the attendant disruption of a protective surface film to expose bare metal frequently will be sufficient to initiate the dissolution reactions. This may be particularly important at start-up or shut-down of plant where, although the design stresses maybe well below any stress thought likely to induce plastic deformation, thermal stresses may operate in this way. The significance of residual fabrication stresses, if not previously relieved, should not be overlooked in this respect, since they will normally be of yield stress magnitude if produced by welding. Even if such stresses are static, in the sense of being associated only with elastic strains at the relevant time, subsequent localised corrosion by pitting or intergranular penetration will initiate plastic deformation due to the enhanced stress level at the tip of the discontinuity and this can sustain the corrosive attack. Obviously for any stresses below the level that will initiate localised corrosion at an initially plain surface, the local stress intensity can be raised to a dangerous value if corrosion penetrates the metal to a sufficient extent, and the problem in service is the same as that at the design stage, namely to avoid significant changes in section. The various protective treatments discussed later can be employed to this end, but it is also sometimes possible to introduce compressive stresses into the surfaces of components, by shot or hammer peening or surface rolling, that will at least delay the incidence of stress corrosion or corrosion fatigue cracks, because such cracks will form only in the presence of tensile stresses of appropriate magnitude. However, surface compressive stresses will only remain effective so long as the deformed layer that constitutes the inhomogeneous deformation which introduces the stresses in the first place remains intact.

Pitting or general corrosion leading to removal of this layer, usually not much thicker than about 0.1 mm, will relieve the compressive stresses and so remove the protection with consequent failure.

Situations can arise, both in relation to stress corrosion and corrosion fatigue, where slow crack growth by either of these mechanisms will occur during service and questions then arise as to the point in time when the structure should be regarded as unsafe. The approach then used is based essentially upon Equation (2), as is that concerned with defining the maximum allowable defect size in a structure to avoid any crack growth. For comparison between materials it is convenient to consider 'design stresses', to allow for the different properties of the different materials, and, since the designer is usually interested in the residual strength of a cracked structure, it is convenient also to convert the fracture toughness values to critical crack lengths.

Apart from the more obvious ways of tackling the problems of stress corrosion and corrosion fatigue, through appropriate material selection, the specification of resistant surface coatings or control of the environment, the designer can markedly influence the incidence of such modes of failure by other devices. Attention to the details of manufacturing methods, to minimise residual stresses resulting from grinding, joining, interference fits or misfits in assembly usually will be worthwhile, as will relief of fabrication stresses by thermal treatment where possible or the introduction of surface compressive stresses by peening or rolling. Finally the avoidance of sharp changes in section, that may relate either to some aspect of the design or to some surface defect arising in manufacture, will invariably be beneficial, as will any measures taken to avoid the incidence of geometrical discontinuities, such as pits, during service.

Temperature and heat transfer in relation to corrosion

Most electrochemical reactions proceed at faster rates with increasing temperature, approximating to a doubling of rate for each 10 °C rise in temperature whether the corrosion process involves dissolution leading to general attack or to a more localised form such as cracking. In general therefore lower temperatures will be beneficial, but there are exceptions. The reversal of polarity of the iron-zinc bimetallic couple with increasing temperature has already been mentioned and there are other instances of equally sharp changes in the nature or extent of corrosion as temperature is increased. It is a matter of common experience that bare steel immersed in tap water at room temperature will corrode at a relatively high rate producing the familiar orange-brown rust as a corrosion product. An identical piece of steel immersed in the same tap water but at the boiling point of the latter will develop a black, adherent, film of corrosion product that is sufficiently protective to reduce the corrosion rate very considerably. This change in the nature of the corrosion products and their degree of protectiveness is not peculiar to the system mentioned nor indeed should it be assumed that where there is such a change it will be invariably beneficial. Thus, for example, the stress corrosion cracking of mild steels in nitrate solutions is unlikely at 20 °C but occurs with alarming ease at 100 °C, and this largely related to the effect of temperature upon the nature of the corrosion products involved, rather than its influence upon crack tip dissolution rate and hence crack velocity. The earlier statement that corrosion rates will approximately double for each 10 °C rise in temperature is only valid providing the details of any part of all of the reactions involved do not change, which will usually mean that the statement is valid only over restricted range of temperature change.

The above assumes isothermal conditions but in many practical situations heat transfer occurs across the metal-solution interface and although in many such cases it is still the temperature at the interface that is critical, rather than the fact that heat transfer occurs across it, nevertheless there are circumstances in which the latter can be important. These circumstances will arise when concentration changes occur in the solution in contact with the metal at the interface across which heat transfer occurs. Crevices, such as are formed when heat exchanger tubes are not fully expanded into a tubeplate, are particularly likely to facilitate solution concentration, and hence corrosion in many cases, under heat transfer conditions due to local boiling and evaporation. The stress corrosion cracking of riveted seams in boilers (caustic cracking) is a particular instances. Feed waters to boilers have additives made to them to render them less corrosion, the additions making the boiler water distinctly alkaline. If the latter can enter a riveted seam, due to inadequate caulking, evaporation of the water will lead to concentration of the caustic alkali which, if it exceeds an appropriate level and there are tensile stresses present due to misfits in fabrication, can result in stress corrosion cracking.

However, even in the absence of crevices it is possible for marked concentration changes to occur at surfaces where heat transfer conditions exist. Heat is transferred through a thin layer of superheated liquid on a metal surface, the temperature gradient rising to about 10 °C as the heat transfer rate increases and the boiling point of the liquid is approached. Convection currents then transfer the heat from this thin film to the bulk liquid. When the heat flux rises to a sufficiently high value, bubbles of vapour begin to nucleate at points on the metal surface and the liquid starts to boil, with the bubbles becoming detached and, by stirring, further assisting in the transfer of heat. Further increase in the temperature of the metal surface causes the rate of boiling to increase and the bubbles become so numerous that they coalesce to form a continuous film of water vapour between the metal and bulk liquid. The vapour film acts as a thermal insulator, so that the heat flux initially falls as the temperature difference across it increases, but later rises again as the latter continues to increase and film boiling occurs. The more important aspects of these events from the corrosion viewpoint are that, by the stirring effects involved, the transport of material to and from the metal surface will differ from that which occurs in stagnant conditions, with the implications mentioned in the context of relative motion of metal and environment, and that, by evaporation into a bubble, concentration of dissolved solids in the film of water between the bubble and metal surface may occur. Some of the solids dissolved in boiler water, e.g. sodium hydroxide, produce a protective film on mild steel at low concentrations but can be corrosive if sufficiently concentrated, or if the concentrated substance is not itself corrosive, it can deposit on the metal surface reducing heat transfer and raising the metal temperature so that steam, produced from water penetrating the deposit or scale, may react with the steel, if the temperature achieves values in the region of 400 °C.

The effects of scales and/or corrosion products in reducing thermal conduction leading to higher temperatures in the underlying metal can lead to other modes of failure. Thus, if local hot spots are developed in a tube wall, thermal stresses will be generated and these can result in plastic deformation, apparent as bulges. (The temperature differences required to produce such effects in a mild steel tube are in the region of only 100 °C.) If the local stress and temperatures are high enough and sustained then the tube may fail by creep, i.e. by the formation of intergranular voids and their coalescence into cracks. Evidence of such local hot spots is usually apparent in the microstructure of the steel, the pearlite becoming divorced or spheroidised.

There is an additional way in which thermal gradients over a metal surface immersed in an electrolyte can induced failure and this arises because of the possibility of a thermogalvanic cell being generated between the hot zone, acting as anode, and the colder regions acting cathodically. The detailed mechanisms involved in thermogalvanic cells are complex and it should not be assumed that temperature variations over a metal surface will result invariably in corrosion from such a source, which is just as well in view of the impossibility of designing any heat exchanger without some temperature gradients. However the problem does arise in some of the commonly used metals in certain environments, especially if the hot, anodic area is small in comparison with the colder, cathodic area.

The concentration of corrosive substances at metal interfaces through which heat transfer occurs can take place in circumstances that are not always easily recognised. Thermal insulation used for lagging pipework would not usually be regarded as a particularly hazardous material from the corrosion viewpoint, but it can contain a few parts per million of chloride and the ingress of water can leach this chloride transporting it to the covered metal surface where concentration can occur due to the heat transfer. If the chloride reaches an appropriate concentration and the material being lagged is an austenitic stainless steel then stress corrosion cracking can occur, and there have been many such failures in service.

To the engineering designer the lesson to be learned from these various examples is that corrosion usually will be lessened or prevented by avoiding unnecessarily high temperatures, especially if these are variable over a surface. Perhaps most importantly where heat transfer conditions are involved consideration should be given to the possibilities of solution concentration, especially in crevices and under scales or other thermal insulation whether present by accident or design or as the result of the service conditions.

THE METAL AS PART OF A DESIGN

In the totality of an engineering design the metal and its fabrication are important parts, but the detailed choices may be determined by considerations other than those involving corrosion. Thus the strength/weight ratio, elastic modulus, electrical or thermal conductivity or other considerations may determine the nature of the metal or alloy to be used in a particular application. Similarly the physical properties of the alloy, the size of the structure, the number of components and so on, will usually determine the mode of fabrication, with economic considerations applied overall. Where likely corrosion problems may only be considered as part of the design after these primary requirements have been met, the freedom of action in relation to corrosion prevention will necessarily be somewhat restricted. But even where likely corrosion problems are of primary concern in material selection it is important to realise that, say, the use of a stainless steel instead of a mild steel will not always diminish corrosion problems, because the modes and rates of corrosion are not constant for a given material, but rather they are dependent upon the environment to which it is exposed. The following figures⁽¹⁴⁾ refer to the corrosion rates, expressed in terms of depth of metal removed in unit time, for mild steel and various stainless steels in different acids.

Table 4
Penetration rates (mm/year) for various steels in different acids

Steel	70% Nitric Acid 60 °C	20% Hydrochloric Acid 20 °C	80% Sulphuric Acid 20 °C
Mild Steel	Very high	38	0.4
13% Chromium	0.15	120	4.5
12% Chromium 12% Nickel	0.05	5	0.5
17% Chromium	0.1	35	0.7
18% Chromium 8% Nickel	Nil	25	1.5

Clearly any of the stainless steels would provide better life than mild steel in hot concentrated nitric acid, but in hydrochloric acid only the 12 per cent Chromium 12 per cent Nickel steel is significantly better than the mild steel, which in the sulphuric acid is better than any of the stainless steels, which in the sulphuric acid is better than any of the stainless steels, costing about an order of magnitude more per unit weight. These differences are largely related to the differing oxidising characteristics of the acids, the corrosion resistance of stainless steels mainly depending upon the formation of a protective chromium oxide film upon their surfaces, so that in the absence of an adequate supply of oxygen, as with the hydrochloric acids, the chromium addition is of little benefit. Essentially the same point can be seen in relation to the atmospheric corrosion of metals, that good corrosion resistance in a particular atmosphere is no guarantee of good resistance in other circumstances, as the following figures indicate.

Table 5
Penetration rates (mm × 10⁻³ per year after 10 year exposure)
of various metals exposed to different atmospheric conditions

Metal	Atmosphere		
	Industrial	Marine	Rural
Aluminium	0.81	0.71	0.0025
Copper	1.19	1.32	0.58
Lead	0.43	0.41	0.48
Zinc	5.13	1.60	0.86
Mild Steel	13.72	6.35	5.08
'Cor-Ten' Steel (0.4% Copper 1% Chromium 0.1% Phosphorus)	2.54	3.81	1.27

('Cor-Ten' is a proprietary material developed by United States Steel Company, and is one of a series of low alloy steels known as 'weathering steels'.)

The weathering steel, 'Cor-Ten', owes its improved corrosion resistance over mild steel in industrial and rural atmospheres to the development of an adherent rust film due to the incorporation of low-concentrations of certain alloying elements, but the relative improvement in those atmospheres is not nearly so marked in a marine atmosphere. When immersed in sea water 'Cor-Ten' is not significantly better than mild steel and its use is not

recommended in such conditions, although there are examples of it having been so used, no doubt because of its corrosion resistance in other situations and the assumption that this will be good irrespective of the environment.

The same point can be made in relation to other forms of corrosion; thus molybdenum additions to ferritic steels are beneficial with respect to stress corrosion cracking resistance in carbonate environments, but are detrimental in hydroxide solutions, and so on. The general point to be grasped is that in specifying the operating conditions for a component or structure it is vital that the environmental conditions be defined with as much precision as any other parameters, such as stress, temperature etc. Only by so doing can the selection of a material from the corrosion resistance viewpoint be made satisfactorily.

CHAPTER 3

PREVENTIVE MEASURES

Just as in earlier sections it has been shown that the incidence of corrosion is related to engineering design parameters so also is the prevention of corrosion a design responsibility. The dangers in divorcing the engineering design from the corrosion protection design can be illustrated in a variety of ways, but a few examples involving the use of protective coatings will suffice. The electrodeposition of metallic coatings for corrosion protective purposes is widely practised and usually results in layers of between 5 and 50 μm in thickness. The accommodation of these thickness changes on closely fitting parts needs to be taken into account in defining the dimensional tolerances. In the case of screw threads adjustment to the normal tolerances are possible or the plating thickness has to be accommodated within the standard clearance. The latter on small size threaded parts is itself small so that the coating thickness needs to be small, providing a reduced degree of protection. If the latter is not acceptable then the clearances need appropriately specifying in the initial design. Other coating processes, producing metallic or inorganic films, yield different thickness increases.

Clearly the method of coating formation should be decided at a reasonably early stage in the design so that tolerances appropriate to the selected method can be laid down. Moreover, if components are to be produced to very fine tolerances some of the above methods will be less desirable than others, for example metal spraying or hot dipping, with their relatively thick and variable thickness coatings, may be less acceptable than electroplating, again with obvious implications for designs. The latter, in terms of shape detail, also has implications in relation to variations in thickness of coatings. Complete uniformity of thickness over a surface is not easy to achieve by electrodeposition, since it is determined by the current density and this varies even over a flat plate. Corners and edges will usually receive more current than flat surfaces, whilst recesses will usually receive least, unless the anodes in the plating bath can be located to change the current distribution. Clearly once the decision has been made to use electrodeposition to produce a protective coating the design should aim at avoiding sharp corners, especially in recesses, if dimensional tolerances are likely to be tight. Although the same points could be made with other examples, these should suffice to underline the interplay between engineering design in the shape sense so frequently assumed in the context of that expression, and the corrosion protection system adopted, and hence point to the necessity for corrosion control being considered throughout the design of a project.

APPROACHES TO CORROSION PREVENTION

The metal selected for a particular structure or component may be stable in the environment to which it is exposed without any further protective scheme. Clearly this is the ideal situation, but it is only likely to be achieved in very mild environments or by the use of expensive materials, and usually will be due to the formation of a protective film by reaction between the metal and environment. Thus it is rarely the case that a metal is completely inert in an environment in which it does not appear to corrode, but rather is there some initial reaction that produces an inert corrosion product, often invisible to the eye, and which adheres to the metal surface effectively separating the latter from the environment. Whilst economic considerations or other requirements such as strength level, may determine that the

metal employed in a given structure is reactive to the environment to which it is to be exposed, it should be remembered that corrosion is a surface phenomenon and that if the surface can be rendered resistant the nature of the bulk of the metal is of little consequence; this is, of course, the idea behind the use of metallic coatings. The latter can be applied in a variety of ways, with varying implications for the design, including fabrication, of structures. Some of them have been mentioned already in relation to the electrodeposition of metallic coatings, but there are others.

Metal spraying, involving the feeding of metal through a flame to produce a finely divided form which is then projected by a gas stream on to the surface to be coated, is best suited to relatively large structures, such as structural steelwork, whilst metal coatings produced by dipping objects into baths of molten metal are restricted to components capable of immersion in the size of bath available.

Cladding is a method of attaching sheets of corrosion resistant metal to an underlying core, by bonding a sandwich of the relevant materials by rolling or by detonation of an explosive charge, and is widely used to produce aluminium-clad aluminium alloys and stainless steel-clad mild steel. The fabrication of structures from such materials in plate or sheet form can raise problems at joints, where sectioning of the composite plate can expose the less corrosion resistant core metal; more complicated geometries can sometimes be clad by explosive forming.

The primary objective of metallic coatings is to provide a layer of metal resistant to corrosion by the environment concerned, such coatings may acquire defects resulting in the exposure of the underlying metal and the establishment of a bimetallic couple. In such circumstances the nature of the metal coating is no longer of importance only in relation to the environment involved, but also from the viewpoint of its electrochemical properties relative to those of the metal exposed at the coating defect. Thus, a defect in a tin coating applied to mild steel will result in enhanced corrosion of the exposed steel, due to the bimetallic coupling, whilst mild steel exposed at a defect in a zinc coating will be protected from corrosion by the same environment which, in the absence of the zinc, would be markedly reactive towards the steel. The latter is said to be cathodically protected by the zinc acting as a sacrificial anode and the protection arises because the electrode potential of the steel in the galvanic cell is reduced to a value where the steel is immune, i.e. it acts as the cathode in the galvanic cell. For such protective action the zinc does not need to be in physical contact with the steel, so long as there is electrical contact between the two metals and the resistance of the circuit is not too high, since the essential feature of cathodic protection is that the electrode potential of the steel is lowered to a value where the steel is immune from corrosion.

This is the form in which cathodic protection is applied to structures as diverse as the hull of a ship or a buried pipeline, with sacrificial anodes of zinc (or of aluminium or magnesium for the protection of steel) dispersed to ensure that the whole of the surface to be protected is below the protection potential. The same result can be achieved without the use of sacrificial anodes, which themselves generate the current necessary for the protection but are thereby consumed and need to be replaced at appropriate intervals of time. Inert anodes, which may be of a variety of conducting materials, can be used for cathodic protection in conjunction with a source of direct current, i.e. a battery, rectifier or generator. The principles are essentially the same as with sacrificial electrodes, each system having its advantages for particular applications but sometimes with both being used to protect the same structure e.g. a

buried pipeline can be protected at river crossings with sacrificial electrodes and elsewhere with an inert electrode system.

All the above refers to modifying the metal in one way or another, i.e. by changing its composition to a more corrosion resistant one or by altering its electrode potential, but in so far as corrosion involved an environment as well as a metal it also may be possible to control corrosion through modification of the environment. The complete removal of a corrosive environment from contact with a metal will not frequently be possible, especially where the environment constitutes part of the process for which the plant was constructed or where the environment is extensive. But in the same way as a change in metal may result in the formation of a protective film by reaction with an environment, so an appropriate change in the latter to produce a favourable reaction upon a given metal should be possible. This is the principle involved in chemical inhibition, i.e. the addition of chemicals to an environment to inhibit corrosion that would otherwise occur. The nature of the additions will need to vary according to the metal and environment concerned, but in general, they are substances that react with one or other of the products of the corrosive reactions, or they are absorbed onto the metal surface, to produce an insoluble protective film.

The addition of caustic alkali to boiler feed waters to render them non-corrosive to mild steel has already been mentioned and is a typical example of the application of inhibition, operating in this case by the formation of thin adherent films of iron oxides. Chromate additions to water will achieve the same result, but by the formation of a chromium oxide film, as with stainless steels where the chromium is derived from the alloying addition made to the steel. Such inhibitors, and there are many others in addition to those just mentioned, are not only effective in preventing general or pitting corrosion, but can be equally effective in preventing or retarding other forms of corrosion, such as stress corrosion or corrosion fatigue.

The formation of chemically resistant films can be achieved by means other than the incorporation of inhibitors into corrosive environments, i.e. they can be formed, usually by immersion in concentrated solutions, before exposure. Thus, phosphate and chromate films can be formed on a variety of metals, whilst a black oxide film can be developed to give some protection to steels by immersion in nitrate-hydroxide solutions. Such chemical conversion films will not provide indefinite protection in all environments and the advantage of the formation of such films by incorporating inhibitors into the environment is that there will be a supply of inhibitors present for further reaction should the initially formed film be impaired for any reason. The formation of some films, including many of those that are most efficient in their inhibitive action, is associated with an increase in the electrode potential of the metal over that which would prevail for the same environment without inhibitor present. In the same way as cathodic protection can be related to a lowering of potential, involving the use of externally applied cathodic current, so the observation that chemical inhibition is sometimes associated with an increase of potential suggests that it may be possible to form protective films by the application of anodic current from an external source. (The possible conflict here that corrosion can be prevented by adequately lowering or raising the electrode potential of the metal is countered by the observation that corrosion in many systems of metal and environment only occurs over a restricted range of potentials.) The anodic formation of protective films is indeed possible and the best known example is probably that involving the anodising of aluminium products, to produce a very stable oxide film sometimes used as a decorative, as well as corrosion resistant film. But there are some combinations of metal and environment, such as stainless steels and titanium alloys in oxidising media, which can be

anodically protected in situ, in the same way as protective films are formed by the presence of an inhibitor in an environment. This technique of anodic protection has been applied mostly in chemical process plant, but it has also been applied in the transportation of dangerous chemicals that would otherwise involve the use of costly metals for containing vessels.

There may appear to be little connection between the chemical inhibition of corrosion and the most widely employed of all corrosion control procedures, namely the use of organic coatings in the form of paints, but in fact there is a very strong connection. The popular conception of how paints protect a coated metal is that the paint film physically prevents contact between the metal and environment, but this is demonstrably not the case. The corrosion of unpainted mild steel in a typical industrial atmosphere to form rust consumes 0.11g of water for each square centimetre of surface exposed per year of exposure, together with 0.03g of oxygen. Now if the permeabilities to water and oxygen of a typical thickness of a film of linseed oil based paint are measured it will be found that about 0.2g of both water and oxygen will pass through 1 cm² of the film in 1 year. Thus the permeability of the film is such that it will permit more water and oxygen to pass than would be required to account for the observed corrosion rate of even bare steel and so the paint cannot be acting simply as a physical barrier. In which case its function must be essentially chemical and it is not accidental that those paints which are most effective in preventing corrosion contain inhibitive pigments, sometimes identical with those substances added to aqueous solutions as inhibitors.

The formulation of paints and the design of painting schemes must be related to the conditions of use, i.e. to the metal to be protected and the conditions of exposure. Although painting is one of the oldest methods of corrosion control, it is only relatively recently that the mechanism of its protective action has begun to be understood, leading to the design of much improved painting schemes and typified by schemes employed on the Forth Rail Bridge and the relatively new Forth Road Bridge. The proximity of these indicates the similarities in their exposure conditions but the painting schemes are very different indeed. The Rail Bridge has a red lead priming coat followed by a linseed oil based paint and has a life cycle of about 2.5 years. The modern Road Bridge has a much more sophisticated scheme involving the cleaning of the steel surfaces by grit blasting, followed by a layer of sprayed metallic zinc, an etch primer, a coating of phenolic resin containing zinc chromate and finally two coats of a phenolic paint containing dispersed iron oxide. Thus the chemistry and electrochemistry of the system have been designed to combat the potential corrosion problems and the life cycle should be about 15 years. The correct formulation of paints will not provide maximum benefits unless the metal surface to be painted is correctly prepared in the first instance; indeed adequate surface preparation is vital for any of the methods of corrosion control involving the deposition of surface films. Accessibility to surfaces is clearly vital for both operations and whilst this is usually recognised in the general sense it is frequently forgotten in terms of detail. Riveted or bolted joints and other relatively sharp changes in profile frequently provide contours that are not easily cleaned nor adequately coated, with the inevitable early breakdown of a protective system.

Sharp edges or corners also present problems, since the surface tension of the liquid paint and the shrinkage that occurs during its drying both tend to produce marked thinning of the paint film at sharp corners. Clearly, as with so many aspects of design, smooth contours and the avoidance of sharp details should be the aims, and where these cannot be achieved fillers, such as jointing compounds, mastic and plastisols, should be used. The latter are particularly useful also in protecting the inaccessible parts of riveted joints and are extensively used in

aircraft construction, because of the inadequate elasticity of paint films applied over some joints and the almost inevitable ready ingress of corrosive media once the paint film is broken.

IMPLICATIONS OF TOTAL DESIGN

Some of the implications of the various corrosion control techniques for certain aspects of design detail have been mentioned in passing, but there are other aspects of this interplay particularly concerned with the choice of preventive procedures in relation to the totality of a design. It is obvious that chemical inhibition of corrosion is not an economically feasible proposition, even though technically viable, when the corrosive environment is extensive, e.g. the sea, rivers or the general atmosphere. Indeed the cost of inhibitors is such that they are usually only applicable in closed systems, as when they are incorporated into paint films and the corrosive environment is confined, or in recirculating systems, as with many heat exchangers, where it is important to maintain an adequate supply of inhibitor even after it has formed a protective film to allow for subsequent film breakdown. Essentially similar economic agents will usually preclude the use of inherently more corrosion resistant alloys in large structures. For example, the stress corrosion cracking of high pressure gas transmission lines by substances generated on the soil side probably could be prevented by adding about 1.5 per cent titanium to pipeline steel, but in so doing the price of the steel would be increased by about 100 per cent and when this is applied over the hundreds of thousands of tons of steel used throughout the world for this purpose each year, the total cost increase is formidable and alternative approaches to the solution of the problem are desirable.

It not infrequently happens that the solution to the corrosion problems likely to be experienced with a particular structure involves more than one of the preventative measures outlined in early pages. The protection of a buried pipeline is most readily achieved by the application of cathodic protection, since ideally this should involve no maintenance on the line and therefore no costly examination such as would be necessary if, say, a paint coating was used to control corrosion. The current consumption by a bare steel pipeline for adequate corrosion protection can vary between about 5 and 500 mA/m², depending upon the type of soil through which the line passes. Such high current densities would involve relatively high capital and maintenance costs, but if an appropriate organic coating is applied to the line the current requirement can be reduced to about 0.01 mA/m² with significant cost reductions, simply because the area of steel to be protected, at defects in the coating, is dramatically reduced.

The attraction of the dual approaches to corrosion control of using a weathering steel or a metal coating and a paint coating are obvious.

The interplay between corrosion prevention and design in its totality can involve factors other than the technico-economic ones mentioned above. The siting of structures, especially in relation to adjacent process plant, can have significant effects upon their subsequent performance. For example, the location of a metal structure down-wind of a battery of coke ovens, with the high sulphur content of the fumes emitted from such, is likely to create problems that would be markedly reduced if the structure were located on the windward side of the ovens. Nor should it be forgotten that corrosion is not limited to the time when a component is in service. It should not be necessary to mention that a pipeline not passing a fluid, a boiler not raising steam or a ship that is 'laid-up', still require protection from corrosion, but they are mentioned because such apparently obvious points are forgotten.

Similarly, parts of structures delivered to a site for erection need protecting from environmental influences if they are to be stored for any significant time; there is little point in attempting to facilitate the building of, say, a pipeline by ordering the steel well in advance of its requirement if it is then stored under conditions where it deteriorates to the point of uselessness before its time for consumption arrives.

CHAPTER 4

CONCLUSIONS

Rigorous solutions to corrosion problems are not always available, even where the circumstances that cause them can be defined and there is information or experience available to indicate the likely outcome. Codes of practice, specifications and the experience of manufacturers are available for tackling many corrosion problems and the designer should be aware of these and use them appropriately. There are particular problems in finding data for corrosion rates of metals in hitherto unexperienced environments, especially in relation to chemical processes, and it is thus necessary to obtain, usually short term, laboratory data before proceeding with a design. Where the corrosion rates are regarded as not excessive and the corrosion is spread reasonably uniformly over the exposed surfaces, even involving some degree of pitting, it should be possible to make an allowance for the reduction in metal thickness over the expected lifetime of the structure, so that it will remain safe throughout this period. The allowance made is commonly that which would give twice the desired life.

Where uncertainty or the lack of a technical means of controlling corrosion render a problem insoluble it may be necessary to live with it whilst monitoring the corrosion rate as the plant operates, so that appropriate action may be taken if the rate reaches unacceptably high levels. There are a number of ways of assessing on-line corrosion, involving electrochemical measurements or more direct assessments of effective section, but inspection visual or otherwise, for all systems that may corrode has ramifications for the designer in ensuring that it is possible. In some installations this may involve the incorporation of probes, coupons or test specimens exposed to the same environment as the plant and therefore simulating the corrosion of the latter, but in a form which allows easier assessment of the extent of corrosion. In other cases inspection holes may be necessary to allow access to those parts of the structure judged to be most vulnerable to corrosion. Where the latter is likely to reach unacceptable limits before the working life of the plant is reached and components need replacing the design should facilitate this, pumps and valves being components most likely to need replacement.

The implications for the designer of the various points that have been made in earlier pages can be summarised in the suggestion that the aims of design from a corrosion control viewpoint should be uniformity. In particular uniformity of contour to avoid sharp changes in section with their implications for fluid flow, (including the draining of containers) stress concentration, solution concentration, temperature distribution and the problems that they create in relation to the application of surface coatings for corrosion control. The effects of fabrication methods also should be considered in this context, welded, brazed or soldered joints, where applicable and providing any dissimilar metal contact problems are taken into account, usually providing less risk of crevices than mechanical fastening methods, although whatever method of joining is employed only careful attention to detail can ensure satisfactory performance. Finally, but as an integral part of the total design and not as an afterthought, the means of corrosion control, by material modification or by chemical or electrochemical treatment, should be considered with as much care as is put into any other aspect of the design process.

As an illustration of what can be achieved by appropriate detailing of corrosion control procedures, the light alloy undercarriage axle beam of an aircraft affords an excellent example. Originally protected only with a hydraulic fluid resisting paint, the anodised aluminium alloy forging suffered intergranular corrosion, as well as attack between the steel pins and housing within some two years of service, corrosion also occurring because of chafing by brake hoses that removed the protective coating. The structure is now shot peened to introduce compressive stresses into the surfaces, improving fatigue behaviour and reducing the risk of intergranular corrosion. After anodising, all the surfaces are coated with a chromated, chemically resistant epoxy primer, and with an epoxy finishing coat for appearance. The steel is treated with anti-fretting materials and the joints sealed with inhibited elastomeric jointing compound, to prevent the ingress of moisture, and anti-chafe protection, has been provided in the form of a locally applied elastomeric coating, to prevent abrasion by brake hoses. Such a sophisticated system of corrosion control is highly effective and is the standard necessary as airline operators call for 20 year first line service assuming adequate scheduled maintenance, instead of the previous 10 years, without extensive overhaul and re-building that would ground the aircraft for long periods.