CORROSION PHENOMENA – AN INTRODUCTION

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The objective of this talk is to provide broad-brush comments on a wide range of corrosion phenomena in order to provide a measure of common ground for the more detailed talks which follow, and also to discuss in slightly greater depth a few topics for which time does not allow individual coverage. The topics discussed are restricted to those included in the area commonly called “wet” corrosion; **atmospheric corrosion and corrosion at high temperatures will be treated separately**. At this stage, at least, the treatment will not be either deeply chemical or deeply mechanistic, but will be restricted to factual discussion of the ways in which corrosion may lead to materials problems in practice.

CORROSION PHENOMENA may be separated according to the following scheme, which also provides a layout for this talk.

Uniform Corrosion		
*Galvanic Corrosion	-	in which corrosion is localised by the coupling of dissimilar metals
Crevice Corrosion Pitting Corrosion Intergranular Corrosion	-	in which attack is localised by geometrical or chemical factors.
Stress Corrosion Hydrogen Embrittlement Corrosion Fatigue	-	in which attack is affected by mechanical factors to produce crack-type failures.
Selective Leaching	-	in which attack is modified by particular chemical effects.
Erosion Corrosion	-	in which attack is modified by flow effects.
*Microbiological Corrosion		

(a) UNIFORM CORROSION

Corrosion is an electrochemical process in which a metal reacts with its environment to form an oxide or other compound. The cell which causes this process has three essential constituents: an anode, a cathode and an electrically conducting solution. Simply, the anode is the site at which the metal is corroded; the electrolyte solution is the corrosion medium; and the cathode forms the other electrode of the cell and is not consumed in the corrosion process. At the anode the corroding metal passes into solution as positively-charged ions, releasing electrons which participate in the cathodic process. Thus the rate of corrosion is equivalent to the electron current flowing between anode and cathode of the corrosion cell. The distribution of anodic and cathodic areas is one of the most important factors determining the type of corrosion which occurs, but in the simplest case the corrosion cells are very small and numerous, and distributed in a random manner over the surface of the metal, and the effect is more or less uniform attack on the surface.

The overall rate of the process under these circumstances may depend on a number of factors but the important criterion is the balance between rates of anodic and cathodic reactions required to maintain electroneutrality, and the overall rate of corrosion is controlled by the rate of whichever reaction occurs least readily.

Although many metals display active corrosion behaviour when immersed in a corrosive solution, others including many engineering alloys carry a stable film of solid corrosion product, frequently an oxide. If this film has good cohesive strength and adhesion to the metal, and low ion conductivity, the rate of metal dissolution is limited to the rate at which metal ions can pass through the film, often a factor of $10^3 – 10^6$ times less than the rate of corrosion of unfilmed metals. This is the phenomenon of passivity, exhibited by stainless steels, nickel alloys, titanium and many similar materials and responsible for their utility as engineering materials in corrosive environments.

Although uniform corrosion is responsible for the greatest destruction of structural materials, it is not technically a major cause for concern. The rate of attack is measurable by relatively simple tests and the lifetime of plants and components can be predicted with confidence. It is the more complex forms of corrosion which present problems, in that they provide the means for localisation and acceleration of the attack, making possible plant failure with only little total metal loss, frequently through microscopic pits or cracks which may not be readily visible until failure has actually occurred.

(b) GALVANIC (BIMETALLIC) CORROSION

When two dissimilar metals are immersed in a conducting solution they usually develop different corrosion potentials. If the metals are in contact this potential difference provides the driving force for increased corrosion, the less noble of the two metals corroding more rapidly, while the more noble corrodes less.

An electrochemical series based on the standard thermodynamic data for the metals is frequently used as a basis for ranking metals under these conditions, but a more practical means of ranking is a galvanic series determined experimentally for particular corrosion elements.

Dissimilar metal contacts provide the first example of situations in which the anodic and cathodic areas of a corrosion couple can be separated and therefore the rates of the two reactions may be substantially different, while electroneutrality is still maintained.

Although tables of galvanic behaviour will show which alloy of a galvanic couple will become anodic and which cathodic, they give no indication of the rate of corrosion to be expected of the anodic material. For example, many active/passive materials which behave well in sea water and would be expected to be cathodic in many couples are in fact not very good cathodes and readily become polarised. Under these conditions acceleration of attack of the baser member of the couple is often less than might be expected. The prediction of rates is thus quite complex, and there is much qualitative tabular material available to provide assistance (e.g. BS PD6484:1979).

Base	Magnesium	
	Zinc	
	Aluminium (*commercial*)	
	Cadmium	
	Duralumin (*Al with 4½% Cu*)	
	Mild steel	
	Cast iron	
	Stainless steel (*Type 430; 18% Cr*)	ACTIVE
	Stainless steel (*Type 304; 18% Cr 10% Ni*)	ACTIVE
	Lead-tin solders	
	Lead	
	Tin	
	Nickel	
	Brasses	
	Copper	
	Bronze	
	Monel	
	Silver solders (*70% Ag 30% Cu*)	
	Nickel	PASSIVE
	Stainless steel (*Type 430*)	PASSIVE
	Stainless steel (*Type 304*)	PASSIVE
	Silver	
	Titanium	
	Graphite (*Carbon*) (*non-metal*)	
	Gold	
Noble	Platinum	

Galvanic series in sea-water. (Courtesy International Nickel Limited.)

Two further factors are of major importance, an environment/distance effect and the area ratio effect. The former is straightforward, simply that galvanic effects are reduced in proportion to the distance from the cathodic region and to the resistivity of the environment – the enhancement of attack at anodic regions is much reduced in poorly conducting solutions, where the resistance of the corrosion cell plays a major part in controlling the corrosion current. The area ratio effect is the key to the practical significance of galvanic coupling, for if a large cathodic area is coupled to a small anodic area (and ratios of hundreds and sometimes thousands of times occur in practice), then the rate of attack of the anodic material may become very high indeed. Conversely, large anodes coupled to small cathodes may not give problems even with unfavourable pairs of materials.

(c) CREVICE CORROSION

It is quite possible for corrosion to become localised on a single metal if environmental conditions are able to develop non-uniformly over the surface. The existence of crevices, either as a result of design or by development of deposits etc, can lead to occluded regions in which oxygen, the usual cathodic reactant, cannot be replenished. Whereas both anodic and cathodic reactions once occurred uniformly over the surface, after a short period the only reaction remaining in the crevice may be the anodic reaction, balanced by cathodic action outside the crevice. The resulting crevice corrosion is most serious in active/passive materials where a sequence of events may follow leading to significant and irreversible changes in the environment within the crevice. **This topic is to be explored in more detail elsewhere**.

(d) PITTING CORROSION

Pitting corrosion is another form of extremely localised attack by which plant can be seriously damaged while the overall metal loss is negligible. It occurs predominantly as a result of the action of chloride ions, although bromides, hypochlorites and a few other species are occasionally responsible, and it is particularly insidious because it frequently occurs in environments which are close to providing complete protection for the alloy except for occasional fluctuations in conditions. Again, the phenomenon is most serious in alloys which can cause major changes of the environment within the pit, when an autocatalytic increase in corrosion rate can occur. **More details are providing in the following talk**.

(e) INTERGRANULAR ATTACK

Grain boundaries are somewhat more reactive than the matrix of an alloy, but since the difference in reactivity is slight, grain boundary effects are usually of little consequence. However, there are a few alloy systems in which very severe attack can occur at grain boundaries, usually as a result of improper heat treatment. Austenitic stainless steels may become sensitised to intergranular attack if they are heated in the range 500-800 °C. Chromium carbide is precipitated at grain boundaries, and by removing large amounts of chromium is precipitated at grain boundaries, and by removing large amounts of chromium from solid solution renders the zone adjacent to the boundary particularly susceptible to attack. This effect may be found in the heat-affected zone adjacent to welds, if too great a heat input has held the temperature of the zone in the sensitising range for a sufficient period. The problem is avoided either by correct heat treatment or more commonly by lowering the carbon level of the steel below 0.03 per cent or stabilising the carbon by the addition of strong carbide-formers such as titanium or niobium so that the carbon is no longer available for chromium carbide precipitation.

High-strength aluminium alloys are also susceptible to intergranular corrosion if the heat treatment has been such as to cause the precipitation of the intermetallic phases, on which the alloys depend for their mechanical strength, in the grain boundary regions. The effect can again be avoided by proper alloy selection and careful heat treatment.

(f) STRESS CORROSION AND RELATED TOPICS

Stress corrosion is arguably the most serious of a number of phenomena involving the combination of mechanical factors and corrosive environments. The term refers to the apparently brittle (low macroscopic ductility) failure of a number of alloys in very specific environments, under tensile stresses which may be significantly lower than the tensile strength of the material and frequently lower than the yield strength. During stress-corrosion cracking the alloy is virtually unattacked over most of its surface, while fine cracks grow through it. Since it is extremely difficult to detect stress corrosion whilst it is occurring, the failure which occur are frequently unexpected and sometimes catastrophic.

The fracture paths may be intergranular or transgranular depending on the system, and although they may branch extensively they run generally normal to the tensile component of the stress. After an induction period, which may be very long, the crack growth rates can become extremely high. The variables involved include environment composition and temperature, metal composition and structure, and stress. A number of mechanisms have been proposed, including pre-existing chemically- or physically-active paths, yield assisted enhanced corrosion rates and film rupture mechanisms, and each probably has its validity in different alloy systems. A detailed analysis is not appropriate here.

(g) HYDROGEN EMBRITTLEMENT

It has become common for engineers to include hydrogen embrittlement under the blanket term stress-corrosion cracking, although the two processes are mechanistically quite distinct. Hydrogen embrittlement is a mode of low ductility fracture which may be induced in ferritic and martensitic steels at high strength levels and in titanium alloys by the introduction of hydrogen. Although it is relatively simple to demonstrate the distinction between hydrogen embrittlement and true stress corrosion in suitable laboratory tests it is by no means easy to separate the mechanisms in practical failure situations with high-strength materials. Thus for example much of the stress-corrosion cracking reported in alloy steels in hydrogen sulphide or cyanide environments is undoubtedly due to the effects of hydrogen rather than to anodic processes. The hydrogen may arise from a variety of sources including electroplating and welding, but the problem is of greater concern when the hydrogen is generated by corrosion. Not only is this continuously available while the alloy is exposed, but for sufficiently susceptible alloys the only environmental requirement is the presence of water in some form.

(h) CORROSION FATIGUE

Corrosion fatigue may be described as a reduction in fatigue resistance due to the action of a corrosive environment. Thus it is determined by the loss in mechanical properties rather than by a particular mechanism or failure appearance. In fact, the fatigue performance of most metals varies from in vacuo testing conditions through ambient laboratory conditions to obviously corrosive situations, but a measurable difference may be expected between ambient laboratory fatigue data and data obtained in corrosive environments. Some authors would consider corrosion fatigue to be a special case of stress corrosion cracking, but the mode of failure is usually closer to fatigue than to stress corrosion and the phenomenon occurs over a wider range of materials and environments.

(i) SELECTIVE LEACHING

In environments which are marginally aggressive a number of alloys can suffer a particular form of attack in which one element of the alloy is removed by corrosion. The most common example of this phenomenon is he dezincification of brass, but the selective removal of nickel from cupro-nickels, aluminium from aluminium bronzes and a number of rarer cases are known. Two types of mechanism have been proposed, continuous selective removal of the more active metal of the alloy, supported by solid state diffusion to maintain the supply of this metal at the metal/solution interface, or general dissolution of the alloy followed by redeposition of the more noble constituents. There is evidence to support both mechanisms and no doubt each applies in the appropriate circumstances but the precise details are not important here. The effect of the mechanism is to replace a region of solid alloy by a spongy mass with little mechanical strength. In plug-type dezincification for example this may occur in isolated regions completely penetrating tube walls, with the risk of blow-out and leakage. In layer type attack, the immediate problem is perhaps less severe, although in heat transfer situations the reduced thermal conductivity of the affected layer may give rise to problems, and in some situations the volume of the corrosion product is sufficiently great to give significant fluid flow problems.

(j) EROSION-CORROSION AND RELATED TOPICS

Erosion-corrosion is the acceleration of the rate of deterioration of a metal resulting from relative movement between the corrosive fluid and the metal surface. It is characterised by the development of a surface profile of grooves, gulleys, waves, rounded holes etc, which usually exhibits a directional pattern. These features are produced as a result of the flow velocity of the liquid and the mechanical removal either of corrosion product or in extreme cases of solid metal. Most metals and alloys are susceptible to erosion-corrosion damage including many which depend upon the formation of a surface oxide film for resistance to corrosion. Erosion-corrosion occurs when such protective films are damaged by the flow and the alloys are attacked at a rapid rate. In practice confusion frequently arises between erosion-corrosion and impingment attack, and in many cases the terms are used synonymously. More correctly, the latter is limited to cases of direct impingment by the corrosive fluid onto a metal surface, for example in areas of sharp change of direction, or when a jet of liquid is able to strike a metal surface disposed at right angles to the direction of flow.

Erosion-corrosion attack is rapid, and frequently quite unexpected, for unless an alloy has been tested under appropriate conditions this aspect of corrosion performance may never have been evaluated. Again, many such problems arise as a result of turbulence perhaps caused by quite unplanned crevices, ledges, deposits, obstructions or changes in cross section which disturb an otherwise laminar flow pattern. A further effect of erosion-corrosion is sometimes the modification of the galvanic behaviour of materials, in cases where an oxide film may be broken down locally by the fluid flow but maintained elsewhere. Similar arguments can be used to explain differences in the galvanic behaviour of pairs of materials inflowing environments.

The entrainment of solids in the flowing fluid markedly increases the erosion effects observed, although when the removal of material is primarily controlled by the solids, the phenomenon is strictly terms impact-erosion. A further, related form of attack is cavitation-erosion which is localised damaged as a result of exposure to a cavitating liquid. If the cavitation intensity is slight, the major effect may be removal of oxide films leading to more rapid corrosion of the metal (cavitation-corrosion), however at higher intensities the cavitation itself can lead to rapid removal of metal and this is the erosion process properly defined.

(k) MICROBIAL CORROSION

Microbial corrosion is not strictly a separate form of corrosion; it is the deterioration of an alloy by conventional corrosion processes which are stimulated or otherwise modified as a result of the activity of living organisms. Biological activity may influence corrosion in a variety of environments including soil, natural waters and sea water, natural petroleum products and in oil emulsion cutting fluids. Since evidence of microbial activity can be obtained from such a wide range of corrosive environments, it is important to be sure that problems which are diagnosed as microbial corrosion do, in fact, depend critically on the presence of the organisms, for it is very easy to be misled in situations in which the corrosion process is essentially a conventional one accompanied by a small amount of adventitious microbial activity which has little overall effect on the corrosion rate. Micro-organisms can affect corrosion behaviour in a number of ways:

1. by producing slimes and deposits which give rise to crevice corrosion;
2. by creating corrosive conditions through their metabolic products, or by destroying materials added to the system to provide corrosion inhibition;
3. by directly influencing the corrosion reactions.

Micro-organisms are usually classified according to their ability to grow in the presence or absence of oxygen. Those which require oxygen in their metabolic processes are termed aerobic; those which grow most favourably in environments containing no oxygen are called anaerobic. The most significant of the aerobic bacteria are the sulphur oxidisers and the iron bacteria. The sulphur oxidisers are capable of oxidising elemental sulphur or sulphur-bearing compounds to sulphuric acid. They thrive best in environments at low pH and can produce localised sulphuric acid concentrations up to 5 wt%. Thus they are capable of creating extremely corrosive conditions. However, since they require sulphur for their existence they are most frequently found in metalliferous mines, in oil fields and associated with sewage plants. Since the mechanism of corrosion is simply one of acid attack, the sulphur-oxidising bacteria are as much a problem with many non-metallic materials as with metals and alloys. The iron bacteria are a group of aerobic organisms which are able to assimilate ferrous iron from solution and oxidise it to ferric hydroxide which is precipitated in sheets surrounding the bacteria. They occur frequently in soil waters and supply waters and they result in the formation of tubercles on the steel surface of supply pipes. The tubercles can lead to crevice attack of the pipe wall, frequently with graphitic corrosion beneath, and can also provide a suitable habitat for the anaerobic bacteria in the region beneath the tubercle.

The most important anaerobic bacteria which influence the corrosion behaviour of steel structures are the sulphate-reducing bacteria. These reduce dissolved sulphate to sulphide, with the assimilation of hydrogen. Their involvement in the corrosion reaction can be twofold. By providing a ready means of removal of hydrogen from the metal surface, they can facilitate the cathodic reaction of the corrosion couple, and thus stimulate the corrosion rate; alternatively the sulphide films formed from their metabolic products can also stimulate the corrosion process, probably by providing a more active cathodic surface than that of the metal itself. Sulphate-reducing and sulphur-oxidising bacteria can operate in a cyclic fashion when soil conditions change. That is, sulphate-reducing bacteria can grow rapidly during rainy periods when the soil is wet and poorly aerated, while the sulphur oxidisers can thrive as the soil dries out, oxidising the sulphide metabolic products to sulphuric acid, which may cause extensive corrosion damage to buried metal structures.