

PRINCIPLES OF CORROSION

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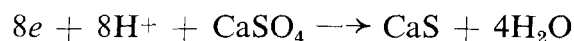
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WHY METALS CORRODE (*Art. 1 cont.*)

Underground Corrosion

If we approach the subject of underground corrosion in the light of what has already been said, we may expect to find some parallel with immersed corrosion. It is certain that metals in the ground can corrode only in so far as water is present ; and one may safely assume that any corrosion will be electro-chemical in character. In Britain, at least, it is exceptional for corrosion in service to be associated with an acid soil. This would seem to leave, therefore, only the oxygen absorption type of corrosion ; and this could occur only in pervious soils in which aeration from the surface is possible.

But the remarkable fact is that the most widespread and most dangerous form of underground corrosion is found in neutral water-logged clay, in which access of atmospheric oxygen to the metal surface is virtually prevented. Cast iron mains, for example, undergo characteristic 'graphitization' with ultimate failure. The explanation of this paradox (first advanced by the Dutch worker, von Wolzogen Kühr) lies in the action of anaerobic sulphate-reducing bacteria (*Desulphovibrio desulphuricans*) which, conjointly with sulphates present in the clay, provide an 'acceptor system' for cathodic hydrogen and so enable cathodic depolarization, and hence corrosion, to proceed in the absence of oxygen. The resultant cathodic reaction may be represented :—



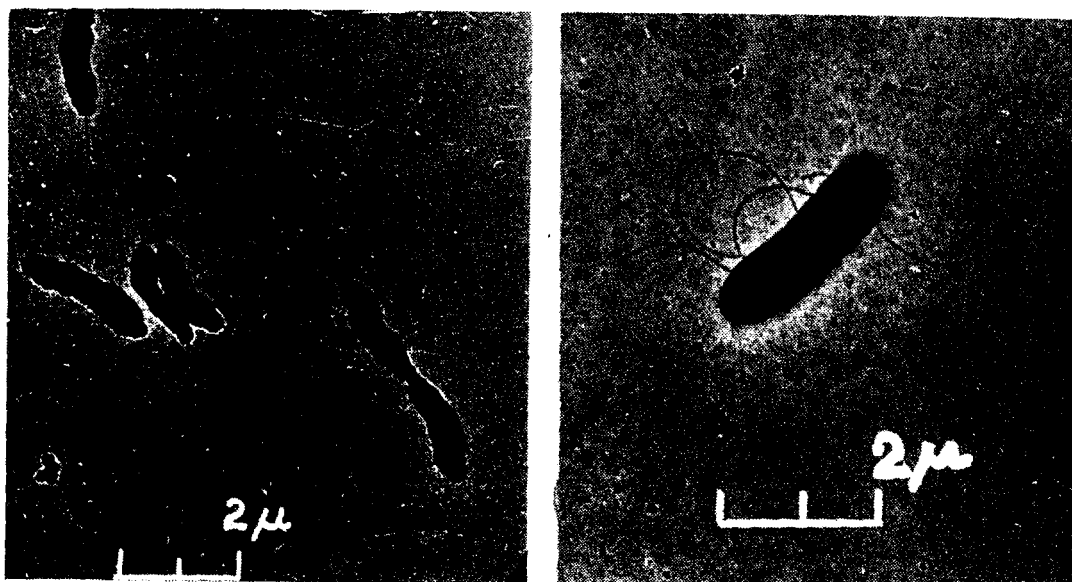


FIG. 5—ELECTRON-MICROGRAPHS OF SULPHATE-REDUCING BACTERIA, *Desulphovibrio desulphuricans*; (left) COMMON (MESOPHILIC) STRAIN; (right) THERMOPHILIC STRAIN (55°C.)

The reaction of calcium sulphide with water results in the liberation of hydrogen sulphide and the precipitation of black iron sulphide—the presence of which serves a useful diagnostic purpose in subsequent examination. Electron micrographs of the bacteria are shown in FIG. 5.

At the Chemical Research Laboratory of the Department of Scientific and Industrial Research*, anaerobic microbiological corrosion has been studied intensively over a number of years, both by laboratory experiments and by observations in the field. The characteristic corrosion of cast iron has been reproduced in the laboratory under strictly anaerobic conditions by inoculation of the oxygen-free medium with the sulphate-reducing organisms. Considerable light has been thrown on the mechanism of the process by the findings of this research: for example, the ability of the bacteria to utilize elemental hydrogen, the stimulative influence of iron, both free and combined, the influence of nutrients in the soil and, quite recently, the remarkable influence on corrosion of elemental sulphur. Attention was drawn to this factor by the common occurrence of free sulphur in the anaerobic corrosion products of iron. Investigation revealed that a simple aqueous suspension of elemental sulphur attacks iron with quite unexpected rapidity (T. W. Farrer and F. Wormwell, *Chem. and Ind.*, 1953, p. 106); e.g. the rate of attack of a 15 per cent aqueous suspension of sulphur is similar to that of a 3 per cent solution of hydrochloric acid.†

The importance of this discovery in relation to underground corrosion lies in the fact that, whereas periods of anaerobiosis are required for the production of sulphur (iron sulphide, the product of bacterial action, being oxidized to sulphur during periods of aeration), the attack of sulphur on iron can proceed independently of whether oxygen is present or not. Thus, a mechanism is

* *Annual Reports of the work of the Laboratory are published under the title of Chemistry Research (London: H.M.S.O.).*

† *The highly specific nature of this reaction (among the common metals iron is the only one attacked) has suggested its use for appraising the continuity of non-ferrous coatings on iron and steel (T. W. Farrer, *Chem. and Ind.*, 1954, p. 77). For the selective etching of iron and steel, the innocuousness of the reagent permits the use of a paper mask in place of wax or varnish, while the virtual absence of hydrogen evolution (as with acid etching) ensures clear-cut edges with deep and uniform etching.*

forthcoming for the continuous corrosion of buried iron throughout alternating periods—as frequently occurs in service—of anaerobic and aerobic conditions.

An extensive study has also been made at the Chemical Research Laboratory of possible inhibitors of the sulphate-reducing organisms. Interest attaches to the toxicity of certain metal ions (particularly in view of the fact, already noted, that iron ions favour the bacteria). For example, cobalt and cadmium are highly toxic, while copper is sufficiently toxic to give to copper-bearing steel (0.3 per cent Cu) a four-fold superiority over plain mild steel in resistance to microbiological corrosion. Investigations in the field have revealed the important fact that, although the great majority of clay soils are, as already mentioned, highly aggressive towards iron and steel, occasionally one finds a water-logged clay soil that is harmless, as shown by the satisfactorily long life of structures buried therein. Sometimes lack of either sulphate or of organic matter has resulted in low bacterial activity, while in other cases substances definitely toxic to the bacteria have been identified.

A remarkable example arose from the investigation of an archaeological site (T. W. Farrer, L. Biek and F. Wormwell, *J. Appl. Chem.*, 1953, p. 80), believed to be the centre of an ancient leather industry, in which iron articles, embedded at various depths in water-logged clay soil and extending in origin to Roman through medieval times, have been found in excellent preservation. Samples of the soil (as little as 0.5 per cent added to the medium used) were found to be toxic to the sulphate-reducing bacteria, and it was concluded that high concentrations of tannate in the soil had been mainly responsible for its non-aggressive properties. In laboratory experiments a concentration of 0.01 per cent tannic acid was found sufficient to render the bacteria incapable of sulphate reduction. The possibility of applying these findings as a method of preventing corrosion is now being examined by field experiments.

Some of the foregoing conclusions may appear a far cry from the simple postulates from which we started. But let us not forget the essentially electrochemical character of underground corrosion in whatever form it takes ; so far as basic principles are concerned we have not really moved very far from those of the simple voltaic cell, a matter to which we shall return when we come to discuss methods of prevention.

Atmospheric Corrosion

In the corrosion of metals exposed to the atmosphere, it is obvious that liquid water must frequently play a part, particularly when the metal surface is freely exposed to rain. One might indeed be inclined to think that the process is then the precise counterpart of immersed corrosion—naturally with the proviso that it will be of the oxygen absorption type. A little reflection will show that differences must exist even though the reactants may be essentially similar. As in immersed corrosion, we have the presence of an electrolyte, and again oxygen must be present if corrosion is to continue. What then, is the difference ?

We have seen that in immersed corrosion the most common controlling factor is the rate of supply of oxygen. Evidently this cannot be the controlling factor in atmospheric corrosion because, of necessity, there must always be excess of oxygen. Even if the surface is wet with rain, the film of water must already have taken up its full quota of atmospheric oxygen. To look at this question from another angle, let us consider the simpler—or apparently simpler—case of indoor corrosion.

We know that a clean iron specimen exposed to an apparently dry indoor atmosphere will rust ; it rusts, in fact, in a characteristically discontinuous

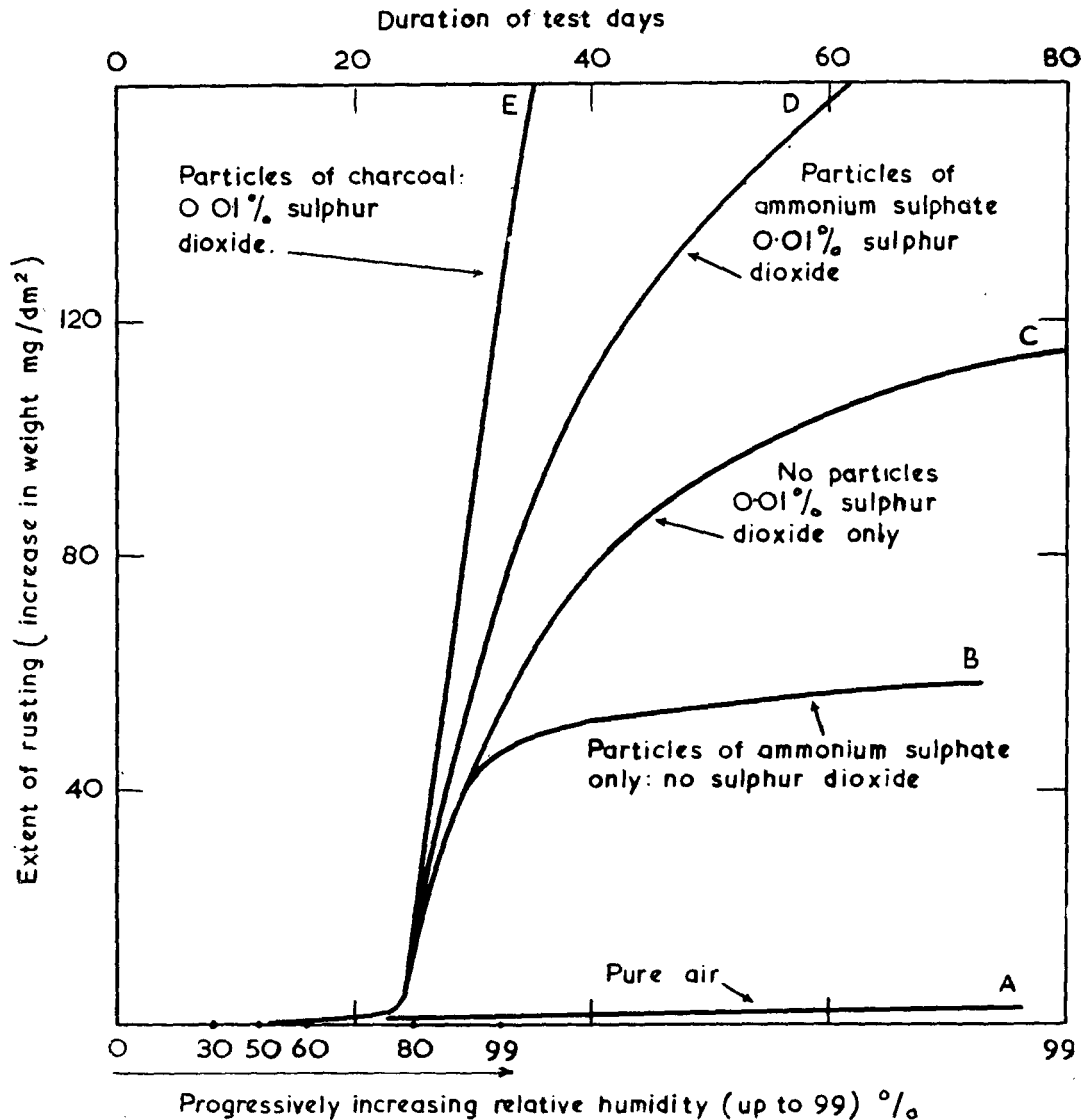


FIG. 6—INFLUENCE OF SOLID AND GASEOUS POLLUTION AND OF RELATIVE HUMIDITY ON RUSTING OF IRON IN AIR

manner, often showing thread-like forms, from a number of separate centres. Years ago, the experiment was tried of enclosing iron specimens within a muslin 'cage' in a room, the relative humidity of which was carefully observed. Outside the cage, specimens rusted freely; inside the cage they remained bright. Further, when specimens that had been previously exposed within the cage for some length of time were exposed outside the cage together with freshly cleaned specimens, the clean specimens proceeded to rust, while the previously exposed specimens remained bright for quite an appreciable time. Subsequently the discontinuous form of rust set in, but always there was a marked difference between the two sets of specimens. This was one of the earliest demonstrations of the formation and the protective properties of invisible air-formed films of oxide on metal surfaces. The experiment illustrates, in fact, the outstanding feature of atmospheric corrosion, namely that it is the resultant of film formation and film breakdown. At the same time, it was observed that the rate of rusting of specimens outside the cage depended profoundly upon the relative humidity of the air; at a critical humidity, in the region of 75 per cent relative humidity, there was a catastrophic increase in the rate of rusting.

Later, the matter was explored in greater detail, under strictly controlled conditions, in experiments at the Chemical Research Laboratory, Teddington. Some of the results are summarized in FIG. 6 which shows the effect of progressively increasing the relative humidity in purified air and in the presence of both solid and gaseous contamination. On the left hand side of the diagram we have the region of film formation (direct oxidation) ; on the right hand side, the region of film breakdown. The figure epitomizes the state of affairs under sheltered conditions of exposure and, in particular, illustrates the following points :—

- (i) The principle of critical humidity. Even in the presence of either gaseous or solid ' pollution ' (or of both), no rusting occurs below the critical humidity. Any attack is confined to the formation of the invisible oxide film, the magnitude of which cannot be shown on a scale which represents the corrosion resulting from its breakdown when the critical humidity is exceeded.
- (ii) The fact that the controlling factor is not (as in immersed corrosion) the rate of supply of oxygen. There are two cases : (a) In the presence of sufficient atmospheric pollution the controlling factor is provided by the relative humidity—i.e. by the rate of supply of water. (b) Since at high relative humidities corrosion is negligible in the absence of pollution, it follows that the controlling factor must then reside in the rate of supply of corrosion-sponsoring nuclei.
- (iii) For all atmospheres in which the critical humidity is, if only intermittently, exceeded : the profound influence of atmospheric pollution.
- (iv) In all locations in which atmospheric pollution is present : the importance of ensuring (as a measure of prevention in enclosed spaces) that the relative humidity does not exceed the critical value.
- (v) The profound stimulative effect of traces of sulphur dioxide on the atmospheric corrosion of iron, particularly in the presence of particles of solid salts, and outstandingly so in the presence of traces of substances of high adsorptive capacity (charcoal in the experiments). This is in marked contrast with the influence of carbon dioxide (formerly believed to be the major promoting factor in atmospheric corrosion) which, in another series of experiments, was found to have a definitely repressive influence, both in humid (unsaturated) atmospheres and under ' super-saturated ' conditions in which moisture is precipitated on the specimen.

The foregoing conclusions (derived from purely laboratory investigations) receive impressive verification from the extensive field tests of Dr. J. C. Hudson at home and abroad. (See J. C. Hudson and J. F. Stanners, *J. Appl. Chem.*, 1953, 3, 86). At overseas (non-marine) stations corrosion is generally low, corresponding with low degrees of atmospheric pollution, notwithstanding that temperatures range from sub-polar to tropical, and prevailing relative humidities from well below to well above the critical humidity. In dry climates, corrosion is negligible ; in tropical (humid) climates it is severe only when the atmosphere is polluted either by smoke or sea spray.*

* *Recent comprehensive reports of the Tropical Testing Establishment of the Ministry of Supply (Nigeria, British West Africa) have strikingly confirmed that under tropical conditions (contrary to the popular belief) corrosion is of no greater order than in temperate regions. Indeed, at jungle sites sufficiently remote from the sea it is (because of the absence of marine or industrial contamination) extraordinarily small—far smaller than in the most rural districts of the United Kingdom. These reports are as yet unpublished and the foregoing information is given by the courtesy of Dr. H. R. Ambler, O.B.E., Director of the Tropical Testing Establishment.*

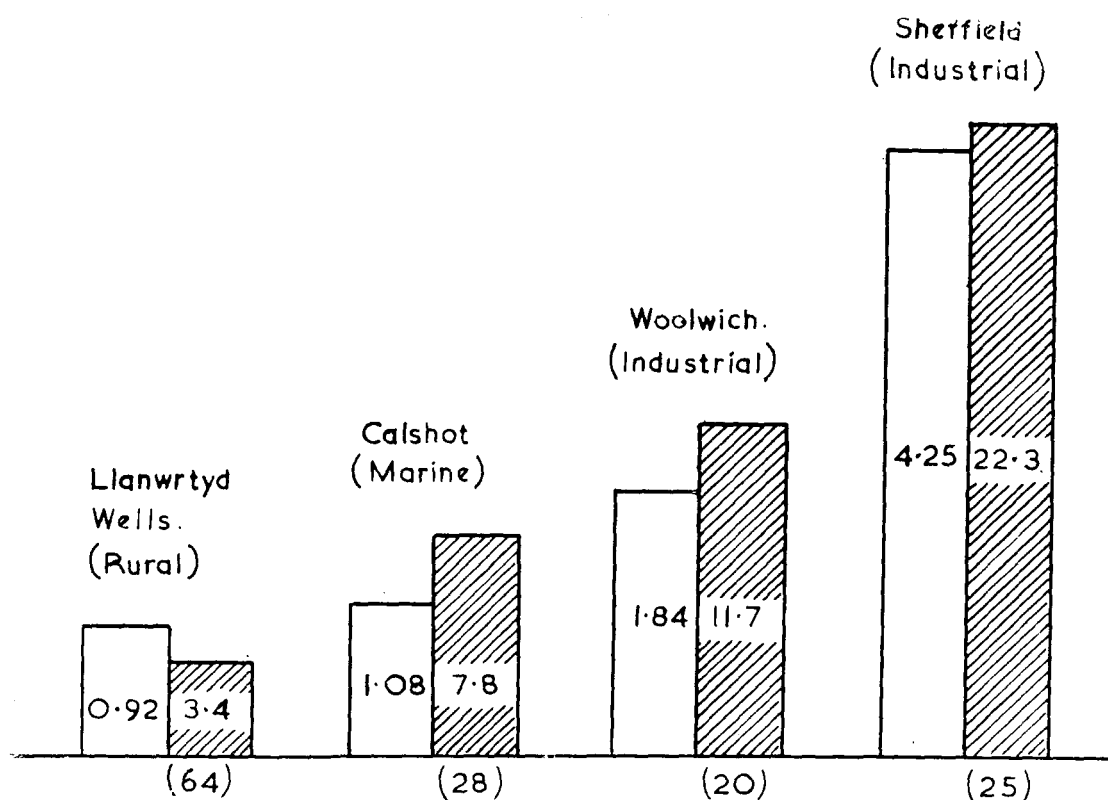


FIG. 7—CORRELATION OF RATE OF RUSTING OF MILD STEEL WITH ATMOSPHERIC POLLUTION. LEFT HAND BARS : RATE OF RUSTING (THOUSANDS OF AN INCH PER YEAR). RIGHT-HAND BARS : TOTAL SOLID DEPOSITS (GRAMS) PER SQ METRE PER MONTH. FIGURES IN BRACKETS ARE RAINFALL VALUES (INCHES PER YEAR). (J. C. Hudson)

At home stations a striking degree of correlation was observed between corrosion values and determinations of atmospheric pollution (total solid deposits), ranging from very small values at a station in Mid-Wales to very high values in an industrial district of Sheffield (FIG. 7). The corresponding rainfall figures, although showing no specific correlation with corrosion, do confirm (for example, rainfall was by far the highest at the Mid-Wales station), that the influence of rain is not, *per se*, adverse. It is, in fact, more usually beneficial, either by removing matter which stimulates corrosion (as with iron), or (as with copper) by assisting in the development of a product (the familiar 'green patina') having protective properties. Formerly believed to be a basic copper carbonate and a concomitant of unpolluted atmospheres, the patina has been found in the United Kingdom, even in the most rural atmospheres, to consist predominantly of basic copper sulphate—the result of attack by wind-borne sulphur dioxide. Near the sea coast, basic copper chloride appears and may then predominate, but only if urban districts are sufficiently remote. Copper is saved from destruction by its habit of forming insoluble basic compounds; iron, on the other hand, has virtually no such tendency, and the product of discontinuous rust must derive largely from hydrolysis of the initially-formed normal iron sulphate.

Direct Oxidation (Metal-Gas) Reactions

Metal-gas reactions proceed characteristically in the absence of water, or in atmospheres in which the critical humidity is not exceeded. They are revealed visually in the tarnishing of copper and silver at room temperatures in atmospheres carrying traces of sulphur compounds, the film of reaction product

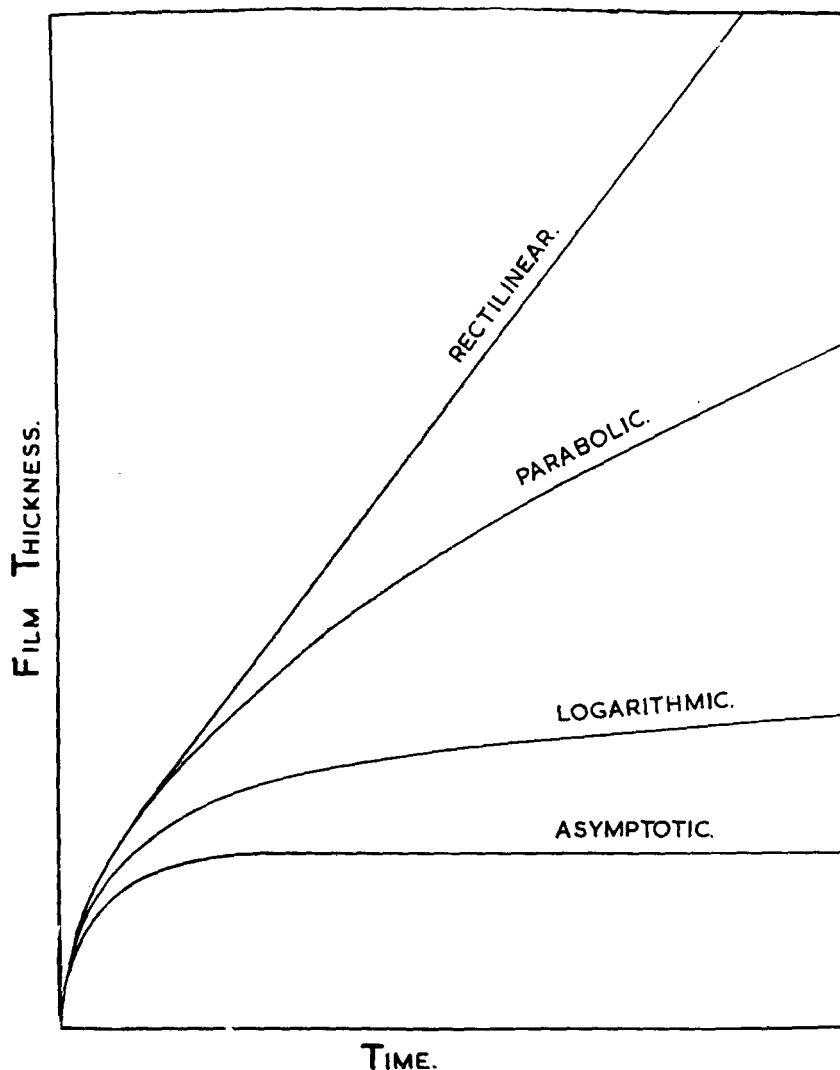


FIG. 8—TYPES OF OXIDATION/TIME CURVE (METAL-GAS REACTIONS)

reaching thicknesses sufficient for the development of interference colours. This, however, must be regarded as a special case since, although the presence of oxygen is essential, the relatively rapid growth is due either to the intrusion of sulphur atoms into the oxide lattice (as with copper), the film consisting mainly of oxide, or to their predominance in the lattice (as with silver), the film consisting essentially of sulphide. The low-temperature 'dry oxidation' of iron and steel (representing the more general case) produces superficial oxide which normally offers a greater order of resistance to further growth, and there is no visible change. The process is greatly stimulated by rise of temperature, however, leading to interference colours at an intermediate temperature range and to wastage of metal by scaling at still higher temperatures.

Unfortunately, space forbids more than a passing reference to the field of direct oxidation—in which much fundamental study has been made.

For the sake of continuity with what has gone before, we may note the four main types of film growth, as shown (FIG. 8) by the relationships between film thickness and time. (The figure assumes a common initial rate of attack; the middle curves become straight lines when film thickness is plotted respectively against the square root and a logarithmic function of time). When once established, a curve may often persist unchanged, even though the environmental

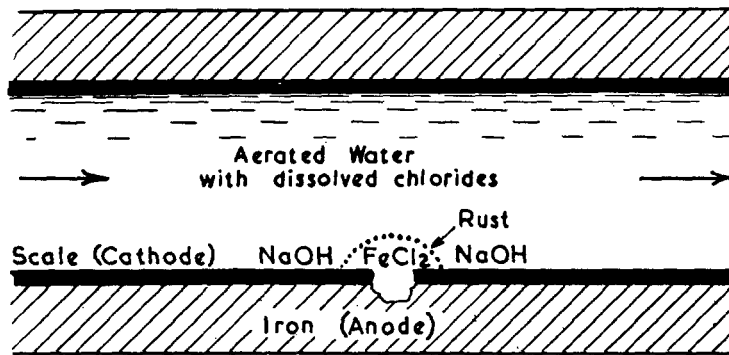


FIG. 9—TYPICAL MECHANISM OF PITTING (AT A BREAK IN AN OXIDE SCALE)

factor responsible for its initiation may vary within wide limits* ; clearly, this is of considerable significance as indicating a controlling factor that is associated with properties of the first-formed film.

Distribution of Corrosion

During this discussion we have referred to corrosion merely in terms of 'total corrosion'—i.e. without reference to the manner in which it is distributed either on or in the metal. This matter is obviously one of considerable practical importance on which at least some brief comment must be made.

General Corrosion

The simplest case is that of corrosion distributed uniformly over the surface with uniform depth of penetration into the metal. This is also the least dangerous case ; indeed, unless aesthetic considerations or dimensional changes are important, it rarely constitutes a serious problem in service.

Localized Corrosion or Pitting

Localized corrosion, particularly in natural waters or neutral solutions, may arise from the presence of a film or scale that is capable of functioning as a cathode when the underlying metal is exposed at any point. The dangerousness of the situation arises from the fact that oxygen reaching a large 'catchment' area of the metal surface that is functioning cathodically may directly contribute to the corrosion at the small anodic area (FIG. 9) ; the cathodic area is protected, but only at the expense of augmenting the attack elsewhere, the depth of penetration being correspondingly increased. This is the normal explanation of 'pitting', which, depending on the thickness of the section, may lead to more or less rapid perforation. It will be evident that the combination of a large cathode with a small anode provides conditions particularly favourable for such localized attack.

An important corollary is the part which the distribution of dissolved oxygen may play, either in determining the efficiency of the cathodes the position of which is decided by other causes, or influencing the actual distribution of anodes and cathodes. This is the basis of the well-known 'Differential Aeration Principle' associated with the name of Dr. U. R. Evans, by whose work it was largely established. As we have seen, in neutral solutions corrosion is essentially a function of oxygen supply, but this is required and used only at the cathodes. The differential aeration principle states that cathodic areas will be encouraged where the concentration of oxygen is greatest and paradoxically, anodic places (where metal is attacked) will tend to flourish where the

* Examples of this 'persistence' will be found in the *Second Report to the Atmospheric Corrosion Research Committee* (Trans. Faraday Soc., 1927, 23, 126, 128, 158).

oxygen concentration is least. As was shown, however, by Bengough and Wormwell, in solutions of alkali salts the effect of oxygen distribution is in fact exerted in virtue of its effect upon the distribution of cathodic alkali. Initial starting centres may be innumerable, but the lateral spreading of alkali determines which persist and which are 'stifled'.

Impingement Attack

Under certain conditions of service, associated with high speeds of water movement and turbulent flow—as may happen, for example, in condenser tubes and heat-exchangers—the impingement of the water stream (usually carrying entrained air) on the metal surface may dislodge the surface film and lead to a characteristic localized attack. From the work of R. May, F. LaQue and others, much knowledge of the mechanism and the control of this form of attack has been accumulated.

Stress Corrosion

In so far as the application of stress must increase the store of internal energy in the metal, any such stress must increase the general tendency to corrode. Normally, however, this effect is sufficiently small to be neglected. In practice the combination of a corrosive environment with the presence of static or internal stress in the metal is dangerous only in specific circumstances, associated either with the environment (e.g. cold-worked brass in presence of traces of ammonia, leading to 'season-cracking') or with the metal (e.g. precipitation of carbide at grain-boundaries in chromium nickel steels, leading to 'weld decay'). This type of failure is characteristically intercrystalline; but the amount of damage to the structure is quite disproportionate to the amount of corrosion, which may be very small indeed.

Corrosion Fatigue

In failure by 'corrosion fatigue' the stresses are external to the metal and alternating in nature. Here, corrosion may be regarded as a trespasser upon what is essentially the field of the mechanical engineer. As is well-known, the 'fatigue failure' of a metal is brought about by the prolonged application of alternating stresses, the maximum value of which may be well below the ultimate tensile strength of the metal. In the presence of a corrosive environment, failure may occur at stresses of still lower numerical value. In other words the 'corrosion fatigue limit' is less—sometimes very appreciably so—than the ordinary 'fatigue limit'. For our present purpose, we may note that the amount of corrosion required to produce this effect, which may be very serious in its consequences, may be quite extraordinarily—from any other viewpoint insignificantly—small. We may also note that the type of failure is, in general, transcrystalline—in contrast with that produced in (static) 'stress corrosion' which is characteristically intercrystalline.

'Metasomatic' Corrosion

At the other extreme in terms of alteration of material per unit volume, we have the case where penetration of corrosion affects the 'body' of the metal or alloy in a manner analogous with the geological process of 'metasomatosis'. Examples are provided by the so-called dezincification of brass and the graphitization of cast iron, under appropriate conditions of environment. In extreme cases, whilst the external form may not have been affected at all, the underlying material may have undergone a complete change of composition. With brass, the change is from brass to what is virtually copper; it was shown years ago

by Bengough and collaborators that the process normally consists of an attack on the copper-zinc solid solution as a whole, followed by re-deposition of copper *in situ* as pseudomorphs of the original crystals. The graphitic corrosion of cast iron is probably a true selective attack, favoured by the strong electrochemical action between iron and graphite. Much of the iron is leached out altogether ; the residue consists mainly of graphite with other insoluble constituents of the original metal and associated iron compounds which, when *in situ*, are characteristically in the ferrous condition. Again, the original shape is preserved, but the graphitized portions are correspondingly light in weight ; they may be cut with a penknife, and readily mark paper. This type of attack appears to be favoured by a local deficiency of oxygen in the ambient liquid.

Filiform Corrosion

We have already referred to the discontinuous (thread-like) nature of the rust which forms on iron or steel surfaces in the early stages of atmospheric corrosion. Recently much attention has been directed to the worm-like manner in which rust grows outwards from the initial nuclei. As these filiform tracks commonly develop under films of lacquer on fabricated surfaces, the matter is of some industrial importance. The phenomenon is associated with the presence of suitable nuclei and appropriately high humidity. The simplest explanation for the forward growth of a track and the suppression of lateral growth (and the apparent mutual repulsion when two tracks meet) would seem to be the formation of cathodic alkali on the more aerated flanks of the track, with consequent passivation of those areas ; much interest attaches to the active (presumably anodic) head of the growth. Results from further investigations in this field may be expected. Meanwhile, from the point of view of avoiding this trouble, reference may again be made to FIG. 6. It will be observed that the conjunction of suitable nuclei and a relative humidity above the critical value is necessary for growth to start at all ; moreover, if nuclei are present, growth may start at any time when appropriate humidities are reached. It must further be remembered that a freshly-prepared metal surface, imperfectly covered with its protective oxide skin, is normally in an extremely active condition ; indeed, the cleaner the surface the more active it must be. ' Finishing processes ' should be regarded as the beginning stages in the service life of a fabricated article ; all too often the influence of environment is overlooked, with the result that particles of workshop dust are allowed to settle on the surface and these are rendered visible only by the effects they subsequently produce. Clean air, as well as clean metal at the start, must be the best safeguard against this form of attack.
