

Treatments for the Protection for Metal Parts of Service Stores and Equipment Against Corrosion

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Foreword

NOTICE

This document has been taken directly from the Ministry of Defence of the United Kingdom's Defence Standard (Def Stan) 03-30 Issue 3 dated 4 February 2005 (last reviewed on 2 November 2009), "Treatments for the Protection for Metal Parts of Service Stores and Equipment against Corrosion" and contains only minor editorial and format changes to conform with the publishing requirements of AMPP standards. This is a word-for-word conversion of the Def Stan to ensure technical equivalency. There are several instances where question marks "?" appear in the original Def Stan within Equation 4 and Clauses 21, 22, 23, 27, and 29 (including subparagraphs). AMPP believes these to be erroneous but will not be incorporating changes to the original document for this publication.

The original Def Stan was adopted as an AMPP standard under the provisions of the AMPP Standards Committees Operating Manual Procedures for Conversion of Government Agency Standards.

- a. This standard is a guide to corrosion protection against atmospheric corrosion and covers all aspects from the basic mechanisms of aqueous corrosion, through a summary of the differing types to a detailed review of aspects of atmospheric corrosion. It concludes with a detailed survey of the methods of control against corrosion and a focused description of the particular methods of corrosion protection for different metals and alloys.
- b. This standard was originally produced on behalf of the Standardization Advisory Group (SAG) by the Corrosion Prevention and Metallic Materials Standards Production Group (E3).
- c. This standard has been agreed by the authorities concerned with its use and is intended to be used whenever relevant in all future designs, contracts, orders etc. and whenever practicable by amendment to those already in existence. If any difficulty arises which prevents application of the Defence Standard, U.K. Defence Standardization (DStan) shall be informed so that a remedy may be sought.
- d. Any enquiries regarding this standard in relation to an invitation to tender or a contract in which it is incorporated are to be addressed to the responsible technical or supervising authority named in the invitation to tender or contract.
- e. Compliance with this Defence Standard shall not in itself relieve any person from any legal obligations imposed upon them.
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In AMPP standards, the terms *shall* and *must* are used to state requirements and are considered mandatory. The term *should* is used to state something that is recommended, but is not considered mandatory. The term *may* is used to state something considered optional.

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Section 1: General Requirements

0: Introduction

- 0.1** This standard has been written as a guide, it contains information assembled from various specifications for the protection of metals against atmospheric corrosion and its prevention. It aims to give advice to designers on corrosion and its prevention. It may be used in conjunction with existing design documents.
- 0.2** This standard covers the protection of ferrous and non-ferrous metals by metallic, conversion, paint, varnish and lacquer coatings, corrosion preventatives and electrochemical processes which assist in combating metal corrosion. It also discusses design factors which can also play an important part in preventing corrosion and makes reference to the cleaning and pre-treatment of metals prior to the application of a surface finish.
- 0.3** The advice and recommendations are primarily for the designer of equipment exposed to the atmosphere. Corrosion and protection problems in components immersed in aqueous streams are touched on but lightly; for these other specialised sources of information should be consulted.

1: Scope

This document is a guide to corrosion protection against atmospheric corrosion and is written in several sections. It starts with a description of the basic mechanisms of aqueous corrosion since atmospheric attack on metallic components involves such mechanisms. It goes on to provide a summary of the different types of aqueous corrosion including those forms of deterioration where mechanical stress, as well as corrosion mechanisms, is involved. There is then a section that focuses on detailed aspects of atmospheric corrosion and includes a discussion of the crucial environmental factors that influence the phenomenon together with descriptions of some particular problems of atmospheric corrosion. This is followed by a detailed survey of all the methods of control against corrosion with emphasis on those approaches, materials performance, design and particularly protective coatings that are most relevant to the protection of components and equipment in atmospheric conditions. The final section provides a focused description of the particular methods of corrosion protection for different metals and alloys.

2: Warning

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3: Related Documents

BS EN ISO 4042	Fasteners—Electroplated Coatings
BS EN ISO 12944.5	Paints and Varnishes—Corrosion Protection of Steel Structures by Protective Paint Systems—Part 5: Protective Paint Systems
BS EN ISO 14713	Protection against Corrosion of Iron and Steel in Structures – Zinc and Aluminium Coatings – Guidelines
ISO 9223	Corrosion of Metals and Alloys—Corrosivity of Atmospheres – Classification
BS PD 6484	Commentary on Corrosion of Bimetallic Contacts and its Alleviation
DEF STAN 81-41	Packaging of Defence Materiel (Parts 1 to 6)
DEF STAN 03-36	The Use of Cadmium Alternatives in the Protective Coating of Defence Equipment
DEF STAN 03-38	The Use of Chromium Alternatives in the Protective Coating of Defence Equipment

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Section 2: Basic Mechanisms of Aqueous Corrosion

4: Electrochemical Mechanism of Aqueous Corrosion

4.1 When metals corrode in any environment containing liquid water whether it is freshwater, seawater, damp atmospheric conditions (in which H₂O can form a condensed film on equipment surfaces), wet soil or even within concrete, the deterioration process is in fact an electrochemical process. That is, the corrosion mechanism involves transfer of electrical charge and is not simply a chemical reaction.

4.1.1 The electrochemical nature of aqueous corrosion can be most easily appreciated by considering one particular type of corrosion involving the immersion in water of two different metals, which are also in electrical contact. This situation can be examined using as an example iron and copper as two metals immersed in the same aqueous liquid. The set-up is shown in Fig 1 where the electrical contact between the metals is a wire but in engineering practice is likely to be a weld or bolted joint between two different materials.

4.1.2 If an experiment is conducted with the arrangement in Fig 1a, what would be noticed immediately the experiment commenced would be the flow of electrical current in the connecting wire—indicated by a reading on the ammeter, “A”. Moreover, with the passage of time it would also be seen that this flow of current is accompanied by visible corrosion of the piece of iron as shown in Fig 1b. However, the surface of the copper would remain unaffected.

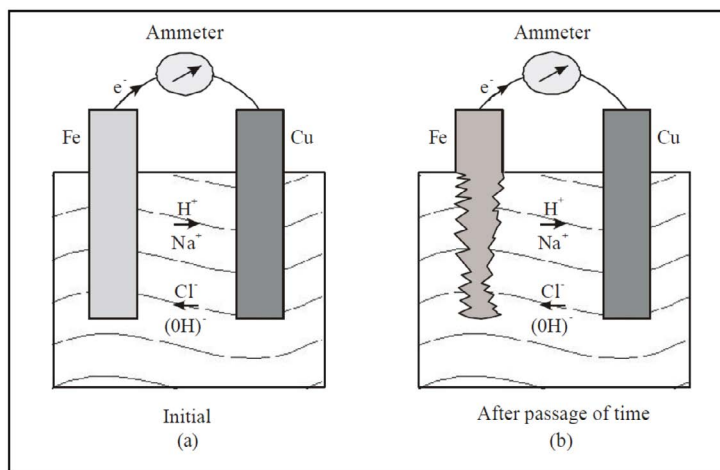


Figure 1: Electrochemical mechanism of Aqueous Corrosion in Bimetallic Cell

4.1.3 Thus it would be reasonable to conclude from this experiment that the iron in the set-up shown in Fig 1 is corroding by a mechanism that involves the flow of electrical current from the sites (the piece of iron) that are corroding. This sort of process, in which both chemical mechanisms (loss of iron from the solid into the water) and transfer of electrical charge (the current flowing) are involved, is called an “electrochemical process” and Fig 1 in fact represents the simplest type of electrochemical cell.

4.1.4 In detail in the set-up shown in Fig 1, it can be deduced that the flow of current in the connecting wire comprises flow of electrons which are being produced by the occurrence of the following reaction on the surface of the iron:-



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- 4.1.5** In Equation 1a, the subscripts (s) and (aq) are used to emphasise that solid iron is “dissolving” to yield Fe^{2+} ions which enter the aqueous liquid. However, in the general formulation of Equation 1a, these subscripts are not normally employed and equation 1a is conventionally written:-



- 4.1.6** Equation 1b also illustrates the electrochemical nature of the iron corrosion process since the reaction clearly involves the transfer of mass and charge (i.e., Fe^{2+} ions) from metal to water. The reaction represented by Equation 1b is called an “anodic reaction”—the name given in any electrochemical cell to a reaction that “releases” electrons. The surface upon which an anodic reaction occurs is termed the “anode”.

- 4.1.7** Actually the full description of the events taking place in the electrochemical cell shown in [Fig 1](#) is not yet complete. The electrons arriving at the piece of copper via the connecting wire are consumed by reacting on the surface of the copper with appropriate substances present in the water. In an electrochemical cell, reactions that consume electrons are called “cathodic reactions” and the surface upon which they occur is termed the “cathode”. Possible cathodic reactions occurring on the surface of the copper in the cell in [Fig 1](#) are:-



which is called the “hydrogen production” or “hydrogen evolution” reaction. and



which is called the “oxygen reduction” reaction.

- 4.1.8** Again the subscripts (aq) in Equations 2 and 3 are used to signify that the substance is present dissolved in the aqueous environment but these subscripts are normally omitted from the equations. The cathodic reactions (Equations 2 and 3) are very important in corrosion processes generally.

- 4.1.9** For completeness, it should be added that other possible cathodic reactions may occur on the copper in the cell shown in [Fig 1](#) depending upon the detailed composition of the aqueous environment but it is the reactions represented by Equations 2 and 3 which are of most interest in corrosion processes.

- 4.1.10** Further points of relevance in relation to the electrochemical cell shown in [Fig 1](#) are:-

- Electrical current also flows in the water between the pieces of iron (anode) and copper (cathode) by the systematic (and opposite) movement of positively-charged ions (e.g., H^+ , Na^+) and negatively-charged ions (e.g., OH^- , Cl^-);
- The solid surfaces (iron and copper) upon which the anodic and cathodic reactions occur, are called “electrodes” and hence the reactions summarised by Equations 1-3 are termed “electrode reactions”.

- 4.1.11** So, to conclude, the aqueous corrosion of a piece of iron, when in contact with a piece of copper as involving an electrochemical cell, has been described as a process involving flow of electric current and the occurrence of a so-called “anodic reaction” ([Equation 1](#)) with the electrons so released being consumed by “cathodic reactions” ([Equations 2 or 3](#)) on the connected piece of copper.

4.2 Corrosion Mechanism on a Single Component

- 4.2.1** The corrosion process described above represents one important type of corrosion (so-called “bimetallic corrosion” or “galvanic corrosion”—see 9.2) but of course numerous circumstances involve the corrosion of a component comprising a single metal or alloy. In fact it is possible to demonstrate practically (though not as simply as for the set-up in Fig 1) that the electrochemical mechanism of aqueous corrosion also applies to the corrosion of a single piece of metal.
- 4.2.2** Actually it is quite simple to adapt the electrochemical mechanism of aqueous corrosion depicted in Fig 1 to represent a valid representation of the corrosion of a single metal by considering that the cathodic reactions also occur (in addition to the anodic ones) on the surface of the single corroding component. Such a scheme is shown in Fig 2 for the case of any specific metal, M.
- 4.2.3** The “picture” in Fig 2 invites the impression that the anodic and cathodic sites are permanently separated and, when this is the case, corrosion is localised to the sites acting as anodes. There are several ways in which this situation of localised attack can arise (see clause 9). However when, as in many practical circumstances, a metallic component undergoes corrosion over the entire surface, it is necessary to envisage the anodic and cathodic reactions occurring simultaneously over the entire surface via an infinite number of microscopic, short-circuited cells.
- 4.2.4** A major consequence of this electrochemical mechanism of corrosion is that the rate of metal loss (in say mm of thickness lost per year) is directly proportional (via Faraday’s Laws of electrolysis) to the magnitude of the electrical current, I_{corr} , flowing in the surface of a corroding metal:-

$$\text{Corrosion rate} \propto I_{\text{corr}} \quad \text{Equation 4}$$

This relationship provides a powerful means of monitoring the corrosion rates of components.

- 4.2.5** Whilst on the subject of current flows in aqueous-corrosion electrochemical cells, it is worth emphasising that, for a single isolated piece of metal, the maintenance of charge neutrality requires that the total rate of production of electrons by the anodic reaction must be exactly balanced by the total rate of their consumption by the cathodic reaction. This, in turn, means that any factor which restrains the cathodic reaction will automatically reduce the rate of anodic dissolution (i.e., the corrosion rate).

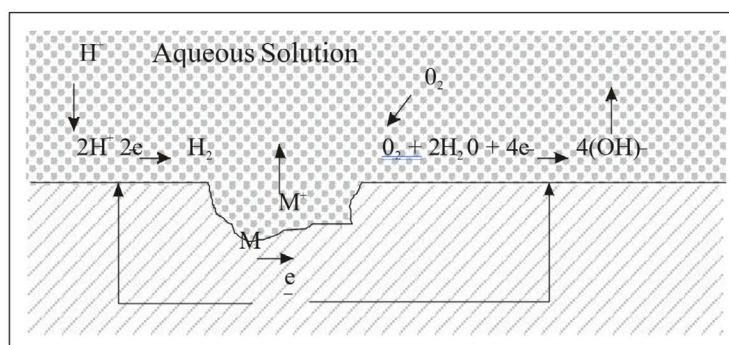


Figure 2: Electrochemical Mechanism of Corrosion of a Single Component

5: Electrode Potential

5.1 Basis of Electrode Potential and its Measurement:

- 5.1.1 Clearly, during aqueous corrosion, charge is being transferred across the metal surface at anodic and cathodic sites and this is obviously associated with a charge separation across the metal surface. This is illustrated in Fig 3 for a site at which the anodic reaction is occurring:



- 5.1.2 The charge separation or potential difference, illustrated in Fig 3, is called the “electrode potential” and can be easily measured to yield useful information about corroding metals. The measurement involves connecting the metal whose electrode potential is required via an high-impedance voltmeter to a “reference electrode” (Fig 4). The value shown on the voltmeter is quoted as the electrode potential measured using a stated reference electrode (e.g., the “saturated calomel reference electrode”, or the “silver/silver chloride reference electrode”).

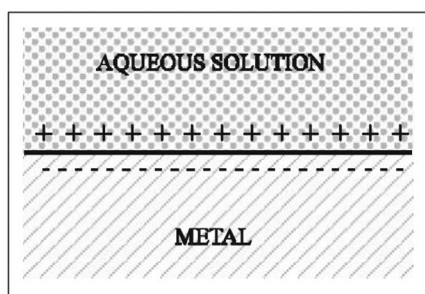


Figure 3: Potential Difference across Electrode Surface Associated with Electrode Reaction Represented by Equation 5

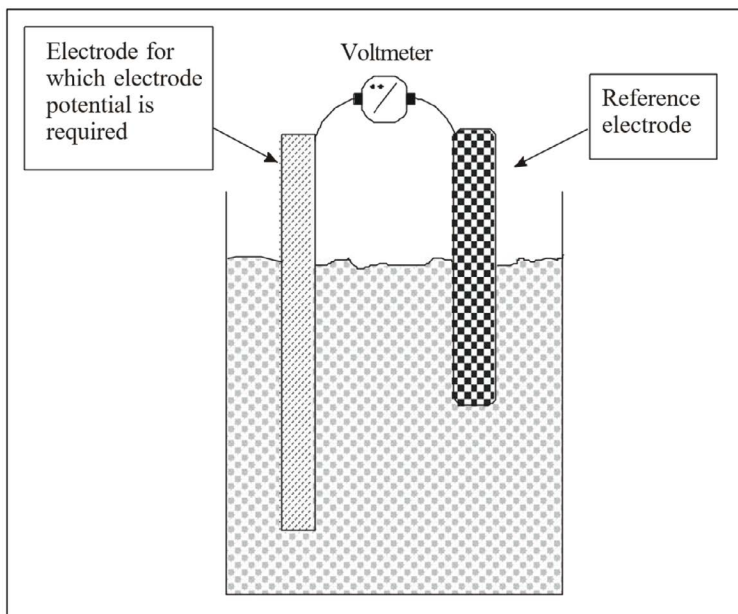


Figure 4: Measurement of Electrode Potential

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- 5.1.3** It is possible for a particular metal exposed to an aqueous environment to exhibit a range of electrode potential values depending upon the conditions. The relevance of the value of electrode potential can be recognised by considering in more detail the situation of a pure metal, M, exposed to an aqueous environment and the electrode reaction:-



- 5.1.4** The expression of the electrode reaction with an equals sign in Equation 6 rather than an arrow as in [Equation 5](#), is an acknowledgement that, in principle, the above reaction can occur in either direction. That is, it is necessary to envisage the reaction proceeding either to the right (metal dissolution) or, if there are any metal ions dissolved in the surrounding solution, to the left (metal deposition) or indeed being “in equilibrium”—showing no tendency for a net reaction in either direction. Which of these three eventualities occurs depends upon the value of the electrode potential existing across the metal interface.

5.2 Equilibrium Electrode Potential

- 5.2.1** Concentrating for the moment on the equilibrium situation, this is characterised by the existence of a particular value of potential difference across the metal surface which is called the “equilibrium electrode potential”, E_o .
- 5.2.2** As might be intuitively assumed, different electrode reactions (e.g., [Equations 1–3](#)) exhibit different values of equilibrium electrode potentials. For a particular reaction, the value of E_o depends upon the temperature and on the concentrations of the chemical substances taking part in the reaction and, for the specific case in which the participating substances are in their so-called “standard states”, the value of the equilibrium electrode potential is called the “standard equilibrium electrode potential”, E_o° .
- 5.2.3** A list of standard equilibrium electrode potentials for a number of reactions is given in Table 1; the values quoted relate to the Standard Hydrogen reference electrode (SHE). The table is sometimes referred to in textbooks as the “Electrochemical Series” and is often used as an approximate indicator of the relative reactivities of metals.

5.3 Electrode Potential and Direction of Electrode Reactions

- 5.3.1** It can be shown, with appropriate detailed arguments, that, in relation to a certain electrode reaction, say Equation 6:-

if the value of the existing electrode potential, E, across the metal surface (measured with the set-up in Fig 4) is more positive than the equilibrium value, E_o , then the reaction is driven spontaneously in the anodic direction:



- b. if the existing electrode potential, E, across the metal surface is less positive than the equilibrium value, E_o , for the electrode reaction, then the reaction is driven spontaneously in the cathodic direction:



and corrosion does not occur. These relationships are summarised in [Fig 5](#).

Table 1
Standard Electrode Potentials (Electrochemical series)

Electrode reaction	Equilibrium electrode potential, E_o° at 25°C and at unit activity of substances, volt (SHE)
$\text{Au}^{3+} + 3\text{e}^- = \text{Au}$	+ 1.43 [Noble-metal end]
$\text{Cl}_{2(\text{g})} = 2\text{e}^- = 2\text{Cl}^-$	+ 1.36
$\text{O}_{2(\text{g})} + 4\text{H}^+ + 4\text{e}^- = 2\text{H}_2\text{O}$	+ 1.23
$\text{Ag}^+ + \text{e}^- = \text{Ag}$	+ 0.80
$\text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^- = 4(\text{OH})^-$	+ 0.40
$\text{Cu}^{2+} + 2\text{e}^- = \text{Cu}$	+ 0.34
$2\text{H}^+ + 2\text{e}^- = \text{H}_{2(\text{g})}$	0.00
$\text{Pb}^{2+} + 2\text{e}^- = \text{Pb}$	- 0.13
$\text{Sn}^{2+} + 2\text{e}^- = \text{Sn}$	- 0.14
$\text{Ni}^{2+} + 2\text{e}^- = \text{Ni}$	- 0.25
$\text{Cd}^{2+} + 2\text{e}^- = \text{Cd}$	- 0.40
$\text{Fe}^{2+} + 2\text{e}^- = \text{Fe}$	- 0.44
$\text{Cr}^{3+} + 3\text{e}^- = \text{Cr}$	- 0.74
$\text{Zn}^{2+} + 2\text{e}^- = \text{Zn}$	- 0.76
$\text{Ti}^{2+} + 2\text{e}^- = \text{Ti}$	- 1.63
$\text{Al}^{3+} + 3\text{e}^- = \text{Al}$	- 1.66
$\text{Mg}^{2+} + 2\text{e}^- = \text{Mg}$	- 2.40
$\text{Na}^+ + \text{e}^- = \text{Na}$	- 2.71 [Base ("reactive") metal end]

5.3.2 The reason corrosion is so ubiquitous is because metals so often exist in aqueous environments at electrode potentials positive to the equilibrium electrode potential for the metal dissolution/deposition reaction. Indeed, as discussed in [SECTION 4](#), one method of controlling corrosion (cathodic protection) is based on shifting the electrode potential of a corroding component to the E_o value shown in Fig 5.

6: Polarisation of Electrode Reactions

- 6.1** The rate of corrosion of any particular metal in a certain aqueous environment clearly depends upon the rates of the constituent anodic and cathodic reactions, e.g., [Equations 1 & 3](#).
- 6.2** The rates of electrode reactions are controlled either by resistance to charge transfer at the metal interface or by the restricted rates of transfer of reactants or products of the electrode reaction towards, or away from, the electrode surface. These rate-controlling processes are usually referred to as "polarisation phenomena" and a specific electrode reaction which is subject to a high degree of polarisation will exhibit a slow reaction rate whilst a reaction which is "depolarised" can proceed at a relatively fast rate.

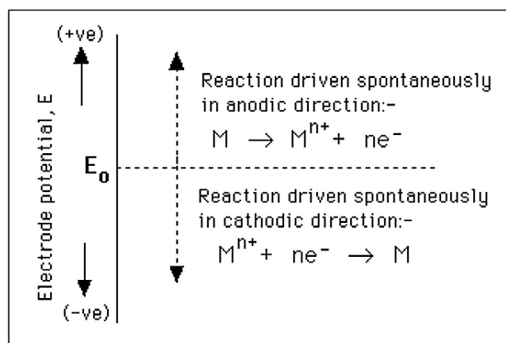


Figure 5: Relationship between Electrode Potential and Direction of Spontaneous Electrode Reaction

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7: Initial Consideration of the Different Types of Corrosion

- 7.1 Having examined the basic mechanisms of aqueous corrosion, the most obvious initial approach to classifying corrosion processes is as shown in Fig 6.
- 7.2 In addition, it is possible for components to deteriorate in service by mechanisms that involve both electro-chemical corrosion processes and some form of mechanical stress. The various manifestations of this situation are summarised in Fig 7.
- 7.3 The various types of corrosion and corrosion/stress degradation processes are covered in more detail in [SECTION 3](#).

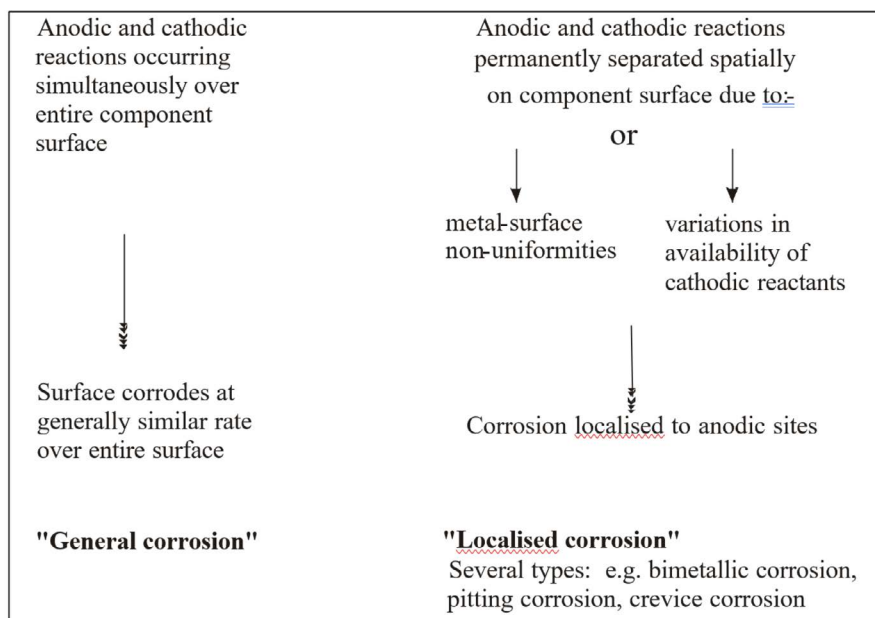


Figure 6: Basic Classification of Corrosion Processes

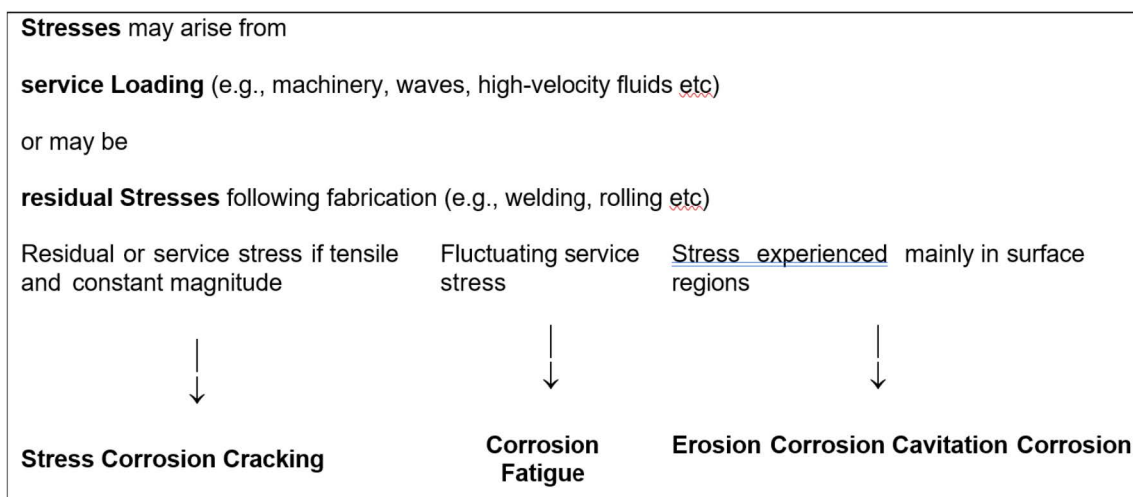


Figure 7: Modes of Deterioration of Components under Combined Action of Corrosion and Stress

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Section 3: Different Types of Corrosion

8: General Surface Corrosion

8.1 In [clause 7](#), a differentiation was made between corrosion that involves general attack at a more or less uniform rate over large areas of the surface of a component and various types of localised corrosion. The latter group is considered later in [clause 9](#). At this juncture attention will focus on general corrosion.

8.1.1 The rates of this type of corrosion can vary over very wide ranges. If the products (say Mn^{+} ions) of the anodic reaction, $M \rightarrow M^{n+} + ne^{-}$, go into solution in the immediately-adjacent environment, then the rate of metal loss may be high—thus leading to serious operational problems. The products of the corrosion reaction may in fact combine to form a loose precipitate, e.g., rust on carbon steel, but this does not cause any significant stifling of continued corrosion.

8.1.2 On the other hand, there may become established on the metal surface an insoluble film (often an oxide or hydroxide). This may be an air-formed film or it may be produced upon exposure to the aqueous environment and, if it is protective, i.e., if it forms as an adherent, non-porous film on the metal surface, it can protect the metal from rapid corrosion. Materials, such as aluminium, titanium and stainless steels are known to be corrosion resistant in many conditions because their oxides (a chromium-rich, Fe-Cr oxide in the case of stainless steel) are protective and stable over a wide range of environments. This kind of behaviour, when a protective film forms on the surface, is known as “passivity”.

8.2 Importance of Cathodic Reaction:

8.2.1 When a component is corroding actively, i.e., not covered by a passive film, the actual rate of corrosion is often critically dependent upon the progress of the cathodic reaction. This is because, as mentioned in [4.2](#), in order to maintain charge neutrality upon the metal surface, the anodic and cathodic reactions have to balance over the entire component surface. Consequently, the anodic (metal wastage) reaction cannot occur any faster than the overall cathodic reaction rate.

As a general indicator, the hydrogen-production reaction:



is favoured in acidic conditions whereas the oxygen-reduction cathodic reaction:



occurs in neutral or alkaline environments.

8.2.2 Consequently, the supply of dissolved oxygen to the component surface very often controls the corrosion rate. Thin films of water, present on metal surfaces in damp atmospheric conditions, are likely to be highly oxygenated and hence corrosive. Likewise, corrosion rates in the splash/spray zone of a body of water are often higher than in totally submerged regions. Volumes of water of high oxygen content are more corrosive than de-oxygenated ones. Another important factor is that the diffusion of dissolved oxygen molecules in water is relatively slow and the rate of their supply to cathodic sites on a surface controls the rate of the reaction shown in Equation 3. This is manifested in severe polarisation of this reaction. Consequently, for any given oxygen content, flowing water will cause higher corrosion rates than stagnant conditions because the former situation depolarises the cathodic reaction by facilitating rapid supply of oxygen to the component surface.

8.2.3 In general, corrosion rates in acidic aqueous environments are faster than in neutral/alkaline ones. This is because the H_2 -evolution cathodic reaction (Equation 2) occurs much more readily than the oxygen-reduction reaction (partly because hydrogen ions diffuse more rapidly in water than do oxygen molecules).

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8.3 Summary of Effects of Various Water Characteristics on Corrosion:

8.3.1 Dissolved Gases

The influence of dissolved oxygen has been discussed in [8.2](#). The presence of certain other dissolved gases can also stimulate corrosion, e.g., carbon dioxide, CO_2 , does this by forming a weak acid, carbonic acid, H_2CO_3 , when dissolved in water. Some other gases, e.g., hydrogen sulphide, chlorine, bromine, ammonia, can impart extremely aggressive characteristics to a water in which they are present.

8.3.2 Velocity

As mentioned in [8.2](#), in neutral or alkaline water, higher velocities will cause increased general corrosion rates on account of an enhanced supply of the cathodic reactant, oxygen, to the component surface and also by removing corrosion products. Additionally, at high flow rates, local damage involving mechanical mechanisms such as erosion can be stimulated (see [9.8](#)).

8.3.2.1 However, in acidic conditions (where hydrogen evolution is the cathodic reaction) the velocity is not an important factor until it has reached a magnitude at which erosion damage is occurring.

8.3.3 Dissolved Salts

These substances, by virtue of their presence as charged ions (e.g., Na^+ , Cl^-) in solution in water, increase the electrical conductivity of the aqueous solution and hence reduce the possibility of the current flowing in corrosion cells being retarded by solution resistance. Additionally, certain ionic species are particularly aggressive, e.g., chlorides tend to break down the integrity of passive oxide films.

8.3.4 Temperature

The effect of this parameter is rather complex. On the one hand, there is a general tendency for the rates of anodic and cathodic reactions (and hence corrosion) to be accelerated by increases in temperature—as are most chemical reactions. On the other hand, the solubility of dissolved gases in water decreases with increasing temperature and there are some circumstances where this factor might counteract somewhat the above-mentioned accelerating effect at temperatures above about 60 – 70 °C where dissolved gases are involved in the corrosion process (e.g., the oxygen reduction cathodic reaction).

9: Localised Corrosion

9.1 As indicated initially in [Fig 6](#), there are a number of manifestations of the situation where the anodic and cathodic reactions are permanently separated spatially on a component surface. Three such types of localised corrosion are depicted in [Fig 8](#); these (and others) are described in [9.2–9.7](#).