General introduction

Modern technology has at its disposal a wide range of constructional materials - metals and alloys, plastics, rubber, ceramics, composites, wood, etc. and the selection of an appropriate material for a given application is the important responsibility of the design engineer. No general rules govern the choice of a particular material for a specific purpose, and a logical decision involves a consideration of the relevant properties, ease of fabrication, availability, relative costs, etc. of a variety of materials; frequently the ultimate decision is determined by economics rather than by properties, and ideally the material selected should be the cheapest possible that has adequate properties to fulfill the specific function.

Where metals are involved, mechanical, physical and chemical properties must be considered, and in this connection it should be observed that whereas mechanical and physical properties can be expressed in terms of constants, the chemical properties of a given metal are dependent entirely on the precise environmental conditions prevailing during service. The relative importance of mechanical, physical and chemical properties will depend in any given case on the application of the metal.

For example, for railway lines elasticity, tensile strength, hardness and abrasion resistance will be of major importance, whereas electrical conductivity will be of primary significance in electrical transmission.

In the case of heat-exchanger tubes, good thermal conductivity is necessary, but this may be outweighed in certain environments by chemical properties in relation to the aggressiveness of the two fluids involved - thus although the thermal conductivity of copper is superior to that of aluminium brass or the cupronickels, the alloys are preferred when high velocity sea water is used as the coolant, since copper has very poor chemical properties under these conditions.

While a metal or alloy may be selected largely on the basis of its mechanical or physical properties, the fact remains that there are very few applications where the effect of the interaction of a metal with its environment can be completely ignored, although the importance of this interaction will be of varying significance according to circumstances.
The effect of the metal/environment interaction on the environment itself is frequently more important than the actual deterioration of the metal. For instance, lead pipes cannot be used for conveying plumb solvent waters, since a level of lead > 0.1 p.p.m. is toxic; similarly, galvanized steel may not be used for certain foodstuffs owing to the toxicity of zinc salts.

In many chemical processes selection of a particular metal may be determined by the need to avoid contamination of the environment by traces of metallic impurities that would affect color or taste of products or catalyze undesirable reactions; thus copper and copper alloys cannot be used in soap manufacture, since traces of copper ions result in coloration and rancidification of the soap. In these circumstances it will be essential to use unreactive and relatively expensive metals, even though the environment would not result in the rapid deterioration of cheaper metals such as mild steel. A further possibility is that contamination of the environment by metals’ ions due to the corrosion of one metal can result in the enhanced corrosion of another when the two are in contact with the same environment.

Finally, it is necessary to point out that for a number of applications metals are selected in preference to other materials because of their visual appearance, and for this reason it is essential that brightness and reflectivity are retained during exposure to the atmosphere.

**Definitions of Corrosion**

In the case of non-metallic materials, the term corrosion invariably refers to their-deterioration from chemical causes, but a similar concept is not necessarily applicable to metals. Many authorities consider that the term metallic corrosion embraces all interactions of a metal or alloy (solid or liquid) with its environment, irrespective of whether this is deliberate and beneficial or adventitious and deleterious.

On the other hand, corrosion has been defined’ as ’the undesirable deterioration’ of a metal or alloy, i.e. an interaction of the metal with its environment that adversely affects those properties of the metal that are to be preserved. This definition-which will be referred to as the deterioration definition - is also applicable to non-metallic materials such as glass, concrete, etc. and embodies the concept that corrosion is always deleterious.
The scope of the term ‘corrosion’ is continually being extended, and Fontana and Staehle have stated that ‘corrosion will include the reaction of metals, glasses, ionic solids, polymeric solids and composites with environments that embrace liquid metals, gases, non-aqueous electrolytes and other non-aqueous solutions’. Vermilyea, who has defined corrosion as a process in which atoms or molecules are removed one at a time, considers that evaporation of a metal into vacuum should come within the scope of the term, since atomically it is similar to other corrosion processes.

Evans’ considers that corrosion may be regarded as a branch of chemical thermodynamics or kinetics, as the outcome of electron affinities of metals and non-metals, as short-circuited electrochemical cells, or as the demolition of the crystal structure of a metal.

These considerations lead to the conclusion that there is probably a need for two definitions of corrosion, which depend upon the approach adopted:

1. Definition of corrosion in the context of Corrosion Science: the reaction of a solid with its environment.
2. Definition of corrosion in the context of Corrosion Engineering: the reaction of an engineering constructional metal (material) with its environment with a consequent deterioration in properties of the metal (material).

As a first approach to the principles which govern the behaviour of metals in specific environments it is preferable for simplicity to disregard the detailed structure of the metal and to consider corrosion as a heterogeneous chemical reaction which occurs at a metal-on-metal interface and which involves the metal itself as one of the reactants. Corrosion can be expressed, therefore, by the simple chemical reaction:

\[ aA + bB = cC + dD \]

where \( A \) is the metal and \( B \) the non-metal reactant (or reactants) and \( C \) and \( D \) the products of the reaction. The nonmetallic reactants are frequently referred to as the environment although it should be observed that in a complex environment the major constituents may play a very subsidiary role in the reaction. Thus in the ‘atmospheric’ corrosion of steel, although nitrogen constitutes approximately 75% of the atmosphere, its effect, compared with that of moisture, oxygen, sulphur dioxide, solid particles, etc.
can be disregarded (in the high-temperature reaction of titanium with the atmosphere, on the other hand, nitrogen is a significant factor).

One of the reaction products (C) will be an oxidised form of the metal, and D will be a reduced form of the non-metal. C is usually referred to as the *corrosion product*, although the term could apply equally to D. In its simplest form, the reaction becomes

\[ aA + bB = cC \]

\[ \text{e.g.} \quad 4Fe + 3O_2 = 2Fe_2O_3 \]

where the reaction product can be regarded either as an oxidised form of the metal or as the reduced form of the non-metal. Reactions of this type which do not involve water or aqueous solutions are referred to as ‘dry’ corrosion reactions.

The corresponding reaction in aqueous solution is referred to as a ‘wet’ corrosion reaction, and the overall reaction (which actually occurs by a series of intermediate steps) can be expressed as

\[ 4Fe + 2H_2O + 3O_2 = 2Fe_2O_3 \cdot H_2O \]

Thus in all corrosion reactions one (or more) of the reaction products will be an oxidised form of the metal, aquo cations (e.g. Fe\(^{2+}\)\(_{\text{aq}}\), Fe\(^{3+}\)\(_{\text{aq}}\)), aquo anions (e.g. HFeO\(_2\)\(_{\text{aq}}\), FeO\(_4\)\(^2-\)\(_{\text{aq}}\)), or solid compounds (e.g. Fe(OH)\(_2\), Fe\(_3\)O\(_4\), Fe\(_5\)O\(_4\).H\(_2\)O, Fe\(_2\)O\(_3\).H\(_2\)O), while the other reaction product (or products) will be the reduced form of the non-metal. Corrosion may be regarded, therefore, as a heterogeneous redox reaction at a metal/nonmetal interface in which the metal is oxidized and the non-metal is reduced.

**Classification of Corrosion Processes**

A logical and scientific classification of corrosion processes, although desirable, is by no means simple, owing to the enormous variety of corrosive environments and the diversity of corrosion reactions, but the broad classification of corrosion reactions into ‘wet’ or ‘dry’ is now generally accepted, and the terms are in common use. The term ‘wet’ includes all reactions in which an aqueous solution is involved in the reaction mechanism; implicit in the term ‘dry’ is the absence of water or an aqueous solution. These terms are evidently ambiguous; for example, it is not always clear whether ‘wet’ is confined to aqueous solutions—the ‘wetting’ of solids by mercury indicates that liquid-metal corrosion should be classified as
‘wet’. Even if the term is restricted to aqueous solutions, the difficulty arises that the mechanism of growth of magnetite scale during the reaction of the interior of a boiler drum with dilute caustic soda at high temperatures and pressures is best interpreted in terms of a ‘dry’ corrosion process. Similar considerations apply to the reactions of aluminium and zirconium with high temperature water.

**Dry Corrosion**

These are generally metal/gas or metal/vapour reactions involving nonmetals such as oxygen, halogens, hydrogen sulphide, sulphur vapour, etc. and oxidation, scaling and tarnishing are the more important forms.

A characteristic of these reactions is that the initial oxidation of the metal, reduction of the non-metal, and formation of compound must occur at one and the same place at the metal/non-metal interface. Should the compound be volatile or discontinuous, further interaction at the interface (or through a thin film of constant thickness) is possible and in most cases the reaction rate will tend to remain constant with time (linear law).

**Wet Corrosion**

In ‘wet’ corrosion the oxidation of the metal and reduction of a species in solution (electron acceptor or oxidising agent) occur at different areas on the metal surface with consequent electron transfer through the metal from the anode (metal oxidised) to the cathode (electron acceptor reduced); the thermodynamically stable phases formed at the metal/solution interface may be solid compounds or hydrated ions (cations or anions) which may be transported away from the interface by processes such as migration, diffusion and convection (natural or forced). Under these circumstances the reactants will not be separated by a barrier and the rate law will tend to be linear.

Subsequent reaction with the solution may result in the formation of a stable solid phase, but as this will form away from the interface it will not be protective - the thermodynamically stable oxide can affect the kinetics of the reaction only if it forms a film or precipitates on the metal surface.
The corrosion can be classified to pure chemical and electrochemical corrosion according to mechanism (path) of corrosion:

**Pure chemical corrosion**

This is the reactions between the surface and environment such as effect of acids on the concrete:

$$CaCO_3 + 2HCl \rightarrow CaCl_2 + CO_2↑ + H_2O$$

The most pure chemical corrosion is the effect of CO gas on the metals especially nickel which represent one component of stainless steel:

$$Ni(s) + 4CO(g) \rightarrow Ni(CO)_4 \text{gas}↑$$

**Electrochemical corrosion**

The reaction between the metal and environment with electrons transfer on the surface between two position (anode and cathode), at anode the metal atoms transfer to metal ions as follow:

$$M \rightarrow M^{n} + ne \quad \text{(At Anode)}$$

While at cathode the reduction reactions can occur as follow:

$$2H^+ + 2e \rightarrow H_2 \quad \text{(in Acidic solution)}$$
$$O_2 + 4e + 4H^+ \rightarrow 2H_2O$$
$$O_2 + 4e + 2H_2O \rightarrow 4OH^- \quad \text{(in Basic and Neutral solution)}$$
$$M^{n} + e \rightarrow M^{(n-1)}$$
$$M^{n} + ne \rightarrow M \quad \text{(Coating)}$$

**Thermodynamic of corrosion**

Thermodynamics provides part of the scientific infrastructure needed to evaluate the course and rate of corrosion processes. Its principle value is in yielding information on intermediate products of the complementary anodic and cathodic partial reactions that together constitute a complete process. The structures and characteristics of these intermediate products can control the resistance of a metal surface to attack within such wide limits as
to make the difference between premature failure and sufficient life for its practical function.

An illustrative example concerns the behavior of iron in water containing dissolved oxygen. In neutral water, the anodic reaction produces a soluble ion, \( \text{Fe}^{2+} \) as an intermediate product and although the final product is a solid, it is precipitated from solution and does not protect the metal, whereas in alkaline water, the anodic reaction converts the iron surface directly into a thin protective solid layer. Such effects can be explained by thermodynamic assessments.

Corrosion science is frequently concerned with the exchange of electrons between half-reactions, i.e., anodic reactions that produce them and complementary cathodic reactions that consume them, and some means of accounting for the electrons is essential. Such an accounting system is based on the concept of oxidation that has wider implications in inorganic chemistry than the name suggests. It is approached through the idea of oxidation states.

The electrons lost by the metal are gained by the oxygen. This constitutes complementary reduction of the oxygen and by counting electrons it is found that its oxidation state is reduced from zero to –II. The idea of oxidation and reduction is so useful that the concept of oxidation states is extended to cover other compounds containing elements that differ significantly in electronegativity, whether or not they contain oxygen and whether the transfer of electrons is complete or partial.

In an isolated electrode process, the charge transferred accumulates until an equilibrium is established. As an example, consider the dissolution of a metal, \( M \), in an aqueous medium to produce ions, \( M^{n+} \):

\[
M \rightarrow M^{n+} + ne
\]

The accumulation of electrons in the metal establishes a negative charge on the metal relative to the solution, creating a potential difference opposing further egress of ions and promoting the reverse process, i.e., the discharge of ions and their return to the metal as deposited atoms.

A dynamic equilibrium is established when the metal has acquired a characteristic potential relative to the solution. Conditions for equilibrium at a given constant temperature are derived from a form of the Van’t Hoff reaction isotherm:
\[ \Delta G = \Delta G^\circ - RT \ln K \]

Where K is the activity quotient corresponding to a free energy change, \( \Delta G \):

\[
K = \frac{a_{product1}^x a_{product2}^x \ldots}{a_{reactant1}^x a_{reactant2}^x \ldots}
\]

And \( \Delta G^\circ \) is the free energy change for all reactants in their standard states.

In a normal chemical change without charge transfer, above equation does not specify an equilibrium condition but in an electrode process, \( \Delta G \) is balanced by the potential that the electrode acquires. This is expressed in electrical terms by replacing the Gibbs free energy terms, \( \Delta G \) and \( \Delta G^\circ \) in equation with the corresponding equilibrium electrical potential terms, \( E \) and \( E^\circ \), using the expressions:

\[
\Delta G = -nF \text{ and } \Delta G^\circ = -nF E^\circ
\]

where the potential, \( E^\circ \), corresponding to the standard Gibbs free energy change, \( \Delta G^\circ \), is called the standard electrode potential. This yields the Nernst Equation:

\[
E = E^\circ - \frac{RT}{nF} \ln K
\]

The equation is often applied at ambient temperature. Taking this as 298 K (25°C), inserting the values for \( R \) (8.314 J.mol\(^{-1}.K^{-1}\)) and \( F \) (96490 coulombs.mol \(^{-1}\)) and substituting 2.303 \( \log K \) for \( \ln K \), above equation becomes:

\[
E = E^\circ - \frac{0.0591}{n} \log K
\]

Since any particular electrode process proceeds by the gain or loss of electrons, i.e., by reduction or oxidation, it is often convenient to use the term, redox potential, to describe the potential of the system at equilibrium for the prevailing activities of participating species. It is simply an abbreviated form of the expression, reduction/oxidation potential.

The potential of the metal electrode (working electrode) is measured with respect to a standard Calomel electrode, which is non-polarizable. The reference electrode is kept in a separate container and it is connected
electrically with the working electrode placed in a container in contact with the electrolyte via a salt bridge. A high impedance voltmeter is connected between the working electrode and the reference electrode. The negative terminal of the voltmeter is connected to the working electrode and the positive to the reference electrode. The open circuit potential in the freely corroding state is shown by the voltmeter. The standard electrode potential for various metals show in the following table when the concentration of metal ions is 1g/L, but if not equal to 1g/L can be use Nernst equation.

**Examples:**

1: - Calculate the change in free energy to dissolution of iron in HCl.

\[ 2\text{H}^+ + 2\text{e} \rightarrow \text{H}_2 \quad \text{Cathode} \]

\[ \text{Fe} \rightarrow \text{Fe}^{2+} + 2\text{e} \quad \text{Anode} \]

\[ E = E_{\text{Cathode}} - E_{\text{Anode}} \]

\[ = E_{(\text{H}^+/\text{H}_2)} - E_{(\text{Fe}/\text{Fe}^{2+})} \]

\[ = 0 - (-0.44) = +0.44 \text{ Volt} \]

\[ \Delta G = -(2)(96500)(+0.44) = (-) \text{ Joul} \]

2: - Iron in neutral water.

\[ \text{O}_2 + 2\text{H}_2\text{O} + 4\text{e} \rightarrow 4\text{OH}^- \quad \text{Cathode} \]

\[ \text{Fe} \rightarrow \text{Fe}^{2+} + 2\text{e} \quad \text{Anode} \]

\[ E = E_{\text{Cathode}} - E_{\text{Anode}} \]

\[ = E_{(\text{O}_2/\text{OH}^-)} - E_{(\text{Fe}/\text{Fe}^{2+})} \]

\[ = +0.401 - (-0.44) = +0.841 \text{ Volt} \]

\[ \Delta G = (-) \]

3: - Gold in HCl.

\[ 2\text{H}^+ + 2\text{e} \rightarrow \text{H}_2 \quad \text{Cathode} \]

\[ \text{Au} \rightarrow \text{Au}^{+++} + 3\text{e} \quad \text{Anode} \]

\[ E = E_{\text{Cathode}} - E_{\text{Anode}} \]

\[ = 0 - (+1.498) = -1.498 \text{ Volt} \]

\[ \Delta G = + \]
### Table 1 Series of standard electrode potentials (electromotive forces)

Electrode reaction | Standard potential at 25 °C (77 °F), volts versus SHE
---|---
$\text{Au} \leftrightarrow \text{Au}^{+3} + 3e$ | +1.498
$\text{O}_2 + 4\text{H}^+ +4e \leftrightarrow 2\text{H}_2\text{O}$ | +1.229
$\text{Pt} \leftrightarrow \text{Pt}^{++} + 2e$ | +1.200
$\text{Pd} \leftrightarrow \text{Pd}^{++} + 2e$ | +0.987
$\text{Ag} \leftrightarrow \text{Ag}^+ + 1e$ | +0.799
$2\text{Hg} \leftrightarrow \text{Hg}_2^{++} + 2e$ | +0.788
$\text{Fe}^{3+} + 1e \leftrightarrow \text{Fe}^{2+}$ | +0.771
$\text{O}_2 + 2\text{H}_2\text{O} +4e \leftrightarrow 4\text{OH}^-$ | +0.401
$\text{Cu} \leftrightarrow \text{Cu}^{++} + 2e$ | +0.337
$\text{Sn}^{4+} +2e \leftrightarrow \text{Sn}^{++}$ | +0.150
$2\text{H}^+ + 2e \leftrightarrow \text{H}_2$ | 0.000
$\text{Pb} \leftrightarrow \text{Pb}^{2+} + 2e$ | -0.126
$\text{Sn} \leftrightarrow \text{Sn}^{2+} + 2e$ | -0.136
$\text{Ni} \leftrightarrow \text{Ni}^{2+} + 2e$ | -0.250
$\text{Co} \leftrightarrow \text{Co}^{2+} + 2e$ | -0.277
$\text{Cd} \leftrightarrow \text{Cd}^{2+} +2e$ | -0.403
$\text{Fe} \leftrightarrow \text{Fe}^{2+} + 2e$ | -0.440
$\text{Cr} \leftrightarrow \text{Cr}^{3+} +3e$ | -0.744
$\text{Zn} \leftrightarrow \text{Zn}^{2+} + 2e$ | -0.763
$\text{Al} \leftrightarrow \text{Al}^{3+} + 3e$ | -1.662
$\text{Mg} \leftrightarrow \text{Mg}^{2+} + 2e$ | -2.363
$\text{Na} \leftrightarrow \text{Na}^+ +1e$ | -2.714
$\text{K} \leftrightarrow \text{K}^+ + 1e$ | -2.925
Polarization and Overvoltage

Usually, the following electrode reactions are moved away from equilibrium.

\[
\begin{align*}
\text{Zn} & \rightarrow \text{Zn}^{2+} + 2e \\
2\text{H}^+ + 2e & \rightarrow \text{H}_2 
\end{align*}
\]

For each of the reactions the potential is moved away from the equilibrium potential as a result of the net electrode reaction occurring, i.e. a net electric current flowing through the interface between metal and liquid.

The deviation from equilibrium is called *polarization*, and we say that the electrode is polarized. A measure of polarization is the overvoltage, i.e. the difference between the real potential and the equilibrium potential. When a corrosion process takes place on a surface, the real potential adopts a value somewhere between the equilibrium potential of the cathodic and anodic reactions, respectively.

The reaction rate in each direction can also be expressed by the transport rate of electric charges, i.e. by current or current density, called, respectively, exchange current, \(I_o\), and (more frequently used) exchange current density, \(i_o\). The net reaction rate and net current density are zero.

The exchange current density \(i_o\) depends strongly on the electrode reaction, electrode material and electrolyte and significantly also on the temperature and concentrations.

When a reaction is moved away from its equilibrium, a net current is obtained in one of the directions. A larger or smaller resistance will always act against the current flow across the electrode interface, and as we have seen a certain overvoltage is required to cope with this resistance.

Depending on the type of resistance that limits the reaction rate, we are talking about three different kinds of polarization, namely activation polarization, concentration polarization and resistance (ohmic) polarization.

1- Activation polarization

Activation polarization is caused by the resistance against the reaction itself at the metal–electrolyte interface. There is an energy barrier that the actual atoms or ions have to overcome to be transferred to a new state. The rate-determining step may be ion or electron transfer across the interface, but it may also be some kind of conversion of a species involved in the reaction.
Activation polarization due to slow reaction at interface as shown in the following reaction (reduction of hydrogen):

\[ 2H^+ + 2e \rightarrow 2H \rightarrow H_2 \]

Ions \hspace{1cm} \text{atoms} \hspace{1cm} \text{molecules}

The step (1) represent transport the ions to atoms which was speed step, but step (2) represent combining hydrogen atoms to produce hydrogen molecules which was slow step.

2- Concentration Polarization

The electrode reactions involve both mass and charge transfer at the metal-electrolyte interface as well as transport of mass (ions and molecules) in the solution to and from the interface. Above we have introduced activation polarization, where the mass or charge transfer across the interface is rate determining. In other cases, the mass transport within the solution may be rate determining, and in this case we have concentration polarization. This implies either that there is a shortage of reactants at the electrode surface, or that an accumulation of reaction products occurs. We shall particularly consider the former case and use reduction of oxygen as an example primarily because the significance of this reaction is unique to corrosion in most natural environments:

\[ O_2 + 4H^+ + 4e \rightarrow 2H_2O \]

Oxygen concentration as a function of the distance from the electrode surface.
Maximum transport and reaction rate are attained when co approaches zero, and in this case the current density approaches the so-called (diffusion) limiting current density:

\[ i_L = D z F \frac{c_B}{\delta} \]

D is the diffusion coefficient (cm\(^2\)/s), and C is the concentration in mol/cm\(^3\), z (number of electrons per mole oxygen reacting) is 4 according to the reduction reaction of oxygen and \( \delta \) is thickness of diffusion layer.

The concentration polarization means that the current density cannot increase beyond \( i_L \) no matter how large the overvoltage is.

3- Resistance (Ohmic) Polarization

Surface layers on metals may have a considerable ohmic resistance. This is, for instance, the case for oxide films on stainless steels, aluminium, chromium etc., even if the film is very thin. When a current I (current density i) is flowing through the film, we will have an ohmic drop, i.e. a resistance polarization expressed by \( \eta = RI = ri \), where R (\( \Omega \)) and r (\( \Omega \) cm\(^2\)) are the resistances in the film on the total electrode surface and in 1 cm\(^2\) of it, respectively. Anodic resistance polarization affects the potential on surfaces passivated by oxides or other substances.

Passivity

If the metal is polarized to various potentials more positive than the corrosion potential \( E_{corr} \), and the respective current density values are recorded, an anodic polarization curve as shown in the following figure is determined. Other reactions than dissolution of metal are involved only at the bottom and top of the diagram. In these regions we also have reduction of hydrogen and development of oxygen, respectively, which cause the polarization curve to deviate from the overvoltage curve for dissolution of metal. In other regions these two curves are essentially identical.

When starting at the corrosion potential \( E_{corr} \) and increasing the potential, the corrosion current is increased, at first corresponding to activation polarization (with a straight overvoltage curve). As the potential is increased further the polarization curve will turn off to lower current than that corresponding to pure activation polarization. The reason for this
behaviour is primarily that the large corrosion rate causes a high concentration of metal ions in the electrolyte close to the metal surface. This in turn leads to:

i) Concentration polarization (increased equilibrium potential of the dissolution reaction).

ii) Deposition of corrosion products on the surface and consequently reduction of the effective area for the dissolution process.

By further increase of the potential a critical current density $i_{cr}$ (maximum corrosion current density) is reached at the potential $E_{pass}$, followed by a strong decrease in the current density, which is caused by passivation. The potential $E_{pass}$ is designated by different terms in the literature, namely primary passivation potential, primary passive potential or simply passivation potential. By further increase of the potential through a value $E_a$, a low and approximately constant anodic current density, the passive current density $i_p$, is recorded. With sufficient potential increase a current increase is measured again, indicating transpassivity and/or oxygen development.

As we have seen, there are four characteristic potential regions. Metals which - in certain pH ranges - change from an active to a passive state when the potential is increased are called active–passive metals.
The actual surface layers can be divided into three major groups:
a) Films that hinder the anodic dissolution effectively, but not the cathodic reaction. Examples of this type are typical passive films on Fe, Ni, Cr and their alloys. Cathodic reactions, e.g. oxygen reduction, can occur on the external side of the film because electron transfer across the film is allowed.
b) Films that hinder both the anodic and the cathodic reaction to a large extent. As a typical example we can mention passivating oxide films on aluminium, which, contrary to films on Fe, Ni and Cr, have high resistance against electron transfer. In natural oxides on aluminium there are, however, a large number of defects that allow some electron conductance and cathodic activity.
c) Deposits that reduce both anodic and cathodic reactions, but not sufficiently to give efficient passivity. This group comprises porous surface layers – e.g. rust and salts – deposited from the solution when the actual solubility product is exceeded. The oxygen reduction reaction is assumed to occur on the metal in the bottom of pores, and it is hindered more or less by the resistance of the deposit against oxygen diffusion. At the same time, the pores allow the anodic reaction, but this is also hindered more or less because of the deposit.

Passive films may be destroyed mechanically, chemically, electrochemically or by undermining the film.

Mechanical breakdown occurs by formation of cracks under deformation of the material, or by wear due to high flow velocity of the liquid, solid particles or components touching the surface. Under such conditions it is important whether the film has sufficient chemical or electrochemical self-repairing ability. In case of heavy continuous wear, activation cannot be avoided; this is indicated by a larger or smaller potential drop.

Chemical destruction occurs by direct dissolution of the film. The oxide has a certain solubility also in the passive state. By change of pH, or increase of temperature or concentration of aggressive species, the solubility may be so high that the passivity disappears completely or to some extent.

Electrochemical destruction occurs by potential changes from the passive region. This can happen by lowering the potential to the active
region, or by increasing it to the transpassive region as illustrated in Figure, or possibly only above a critical potential for localized corrosion.

In certain cases, e.g. for Fe in a moderately alkaline environment, a passive oxide can be reduced to other oxides or to the metallic state. For stainless steels and Cr the transpassivity phenomenon is indicated by a branch on the anodic polarization curve. The reason for this indication of transpassivity is that the oxide is generally dissolved and \( \text{Cr}_2\text{O}_7^{2-} \) and possibly \( \text{Fe}^{3+} \) are formed at potentials below the region where oxygen is developed. If the same steel is exposed to a neutral NaCl solution, a lower critical potential – the pitting potential – is found. Pitting potentials for various mixtures of NaCl and \( \text{Na}_2\text{SO}_4 \) solution are indicated. At potentials above the pitting potential, localized corrosion – pitting – occurs due to local attack and penetration of the oxide by \( \text{Cl}^- \) ions. However, it can be noticed already that salts like \( \text{NaNO}_3 \), \( \text{NaClO}_4 \) and \( \text{Na}_2\text{SO}_4 \) counteract NaCl, and thus lead to increased pitting potentials.

Depending on the availability of oxidizers, the passivity may be a) stable or b) conditional, practically unstable. A good demonstration of this is Faraday’s passivation experiment with iron in HNO\(_3\) solutions. In one case the piece of iron is immersed in 70% HNO\(_3\), and the iron is passive. The passivity can be confirmed by weighing the iron sample before and after a certain period of exposure.

If the oxide is scratched, heavy gas development occurs and stops again shortly after. It can be shown (again by weighing) that the sample does not corrode any more. This is an example of spontaneous passivation or self-passivation. If the acid is diluted with water, nothing happens as long as the sample is left undisturbed in the liquid. However, if the oxide film is injured mechanically, strong and permanent gas development occurs, indicating intensive and permanent corrosion. The same would have occurred if the iron piece originally was submerged directly in diluted acid.

**Pourbaix Diagram**

pH is an important variable of aqueous solutions, and it affects the equilibrium potentials of a majority of the possible reactions that can occur. On this basis, Marcel Pourbaix derived and presented his pH potential
diagrams, also called equilibrium diagrams and most frequently Pourbaix diagrams. These diagrams have become an import tool for the illustration of the possibilities of corrosion.

The Pourbaix diagram is a graphical representation of Nernst’s equation for the various reactions. From the potential equations of the reactions a) – f) we obtain the Pourbaix diagram for iron in water at 25°C.

\[
\begin{align*}
a) & \quad Fe^{2+} + 2e = Fe \\
b) & \quad Fe_3O_4 + 8H^+ + 8e = 3Fe + 4H_2O \\
c) & \quad Fe_3O_4 + 8H^+ + 2e = 3Fe^{2+} + 4H_2O \\
d) & \quad Fe_2O_3 + 6H^+ + 2e = 2Fe^{2+} + 3H_2O \\
e) & \quad O_2 + 4H^+ + 4e = 2H_2O \\
f) & \quad 2H^+ + 2e = H_2
\end{align*}
\]

Here, an activity of ferrous ions, \(a_{Fe^{2+}}=10^{-6}\) is presumed. This order of magnitude is assumed to be a realistic lower level of \(a_{Fe^{2+}}\), a for situations where corrosion is of practical significance.

In addition, for reaction a) the equilibrium potentials for \(a_{Fe^{2+}}=10^{-4}\) and \(10^{-2}\) have been given by dashed lines in the following figure.

For the reactions e) and f) gas pressures (\(P_{O_2}\) and \(P_{H_2}\)) of 1 atm have been presumed. The background and significance of the lines in the Pourbaix diagrams are now considered clear, but the regions between the lines are equally important. From the potential equation for the reaction \(Fe^{2+} + 2e = Fe\). We can see that the equilibrium potential increases with increasing activity of ferrous ions. If we start with an activity of \(10^{-6}\) and affect the potential to attain a level above the equilibrium potential at this activity, the system will (as any system that are moved away from equilibrium) try to re-establish equilibrium by itself. This can be done only by an increase of the \(Fe^{2+}\) activity, i.e. by the reaction going to the left. \(Fe^{2+}\) is therefore the dominating reaction product. In other words, we have a corrosion region above the equilibrium line of this reaction.

We see that the oxidized state of the material is the stable one when the potential is above the equilibrium potential. This is a general rule, and therefore we have \(Fe_3O_4\) and \(Fe_2O_3\) as stable products when we are above the lines b, c and d. Particularly, \(Fe_2O_3\) is known for its ability to form a
passivating film on the surface, i.e. an oxide film that prevents, to a great extent, Fe$^{2+}$ ions from being transported from the metal to the liquid.

Characteristic properties of such a film are low ionic conductivity, low porosity and good adherence to the substrate. When the potential is below the lines a and b, the metallic state (Fe) is the stable one. Therefore, the metal is immune to corrosion in this region.

As it is seen, the pH-potential plane is clearly divided into a corrosion region, a passivity region and an immunity region. There is also a small corrosion region at high pH, where the dissolved corrosion product is HFeO$_2$. Corresponding diagrams for other metals are shown in next figure.

Pourbaix diagram of iron in water at 25°C.

The main objectives of the Pourbaix diagrams are:

1. To show the directions of the various reactions at given pH and potential.
2. To make a basis for estimation of the corrosion product compositions at various pH and potential combinations.
3. To show which environmental pH and potential changes will reduce or prevent corrosion.
The validity of the diagrams is limited to reactions between pure metals, pure water and the species that can be formed from these. Small amounts of impurities and alloying elements in the metal and dissolved substances in the water do not necessarily influence strongly on the diagram, but in some cases they do. Typical examples of the latter are when iron base materials are alloyed with Cr and the water contains chloride. Chlorides destroy the passive films locally when the potential exceeds a certain level (pitting potential). It should also be noticed that the horizontal axis of the diagram refers to the pH close to the metal surface. This pH is affected by the local reaction and can therefore deviate, sometimes strongly, from the bulk pH.

**Kinetic of corrosion**

While the Pourbaix diagram shows a qualitative picture of what can happen at a given pH and potential, we also need knowledge about the electrode kinetics to predict:

a) which values the potential and the local pH can attain, and

b) the reaction rates for the actual pH-potential combinations.

In the long term, the degradation of engineering metals and alloys by corrosion is inevitable and so resistance to it is essentially concerned with the rates of corrosion.

The rate of any transformation is controlled by the magnitude of one or more energy barriers that every particulate entity, e.g., an atom or an ion must surmount to transform. These peaks are the energy maxima of intermediate transition states through which the entity must pass in transforming and the energy that must be acquired is the activation energy, $\Delta G^*$. The statistical distribution of energy among the particles ensures that at any instant a small but significant fraction of the particles has sufficient energy to surmount the peaks. This fraction and hence the fraction of particles transforming in a small time span, the reaction rate, $r$, depends on the value of the activation energy. An expression for reaction rate that applies to many reactions over moderate temperature ranges is Arrhenius’ equation:

$$r = A \exp\left(\frac{-\Delta G^*}{RT}\right)$$

[19]
To apply the equation to an electrode process, it must be restated in electrical terms. Ions transported across an electrode carry electric charge, so that the reaction rate, $r$, can be replaced by an electric current, $i$. The energy of the process is the product of the charge and the potential drop, $E$, through which it is carried. Thermodynamic quantities are expressed per mole of substance and because the charge on a mole of singly charged ions is the Faraday, $F = 96490$ coulombs, the free energy change, $\Delta G$ of an electrode process is:

$$\Delta G = -nFE$$

where $n$ is the charge number on the particular ion species transferred in the process, e.g., $z$ is 1 for $H^+$ or $Cl^-$, 2 for $Fe^{2+}$, 3 for $Fe^{3+}$ etc. Replacing $r$ in the Arrhenius equation, above equation with an appropriate change of constant:

$$i = kexp^{\frac{\Delta G^*}{RT}} = kexp^{\frac{nFE}{RT}}$$

**Rate of corrosion**

When exposed to corrosion medium, metals tend to enter into a chemical union with the elements of the corrosion medium, forming stable compounds similar to those found in nature. When metal loss occurs in this manner, the compound formed is referred to as the corrosion product and the surface is referred to as having been corroded.

Corrosion rates for materials are often expressed in terms of metal thickness loss per unit time. The rate of uniform attack is reported in various units. One common expression is mils per year (mpy); sometimes millimeters per year is used. In the United States, it is generally reported in inches penetration per year (ipy) and milligrams per square decimeter per day (mdd). To convert from ipy to mpy, multiply the ipy value by 1000 (i.e., 0.1 in. x 1000=100 mpy). Conversion of ipy to mdd or vice versa requires knowledge of the metal density.

For most chemical process equipment and structures, general corrosion rates of less than 3 mpy are considered acceptable. Rates between 3 and 20 mpy are routinely considered useful engineering materials for the given environment. In severe environments, materials exhibiting high general corrosion rates between 20 and 50 mpy might be considered economically justifiable. Materials that exhibit rates of general corrosion beyond this are usually unacceptable.
To determine the corrosion rate, a prepared specimen is exposed to the test environment for a period of time and then removed to determine how much metal has been lost. The exposure time, weight loss, surface area exposed, and density of the metal are used to calculate the corrosion rate of the metal using the formula:

$$C_R = \frac{\Delta W}{\text{area.time}} \text{ (mdd, gmd...)}$$

$$\text{mpy} = \frac{22.237 \Delta W}{\text{density.area.time}}$$

and

$$\text{Rate}_{(\text{mpy})} = \frac{1.44}{S.G.} \text{Rate}_{(\text{mdd})}$$

Where: $\Delta W$ in gram, density in g.cm$^{-3}$, area in inch$^2$ and time in days.

Most electrochemical work is achieved using what is called a potentiostat. A potentiostat is an electronic device that controls the voltage difference between a working electrode and a reference electrode. Both electrodes are contained in an electrochemical cell. The potentiostat implements this control by injecting current into the cell through an auxiliary electrode. In almost all applications, the potentiostat measures the current flow between the working and auxiliary electrodes as shown in the following figure. The controlled variable in a potentiostat is the cell potential, and the measured variable is the cell current.

A potentiostat typically functions with an electrochemical cell that contains three electrodes, and that is true for both field probes and lab cells. From polarization curve which obtained in potentiostat, can be measure the corrosion potential and corrosion current density, and the later uses to get the corrosion rate using the formula:

$$\text{Rate}_{(\text{mpy})} = 0.13i_{\text{corr}} \left( \frac{e}{p} \right)$$
The later equation derives from Faraday’s law:

\[ W = \frac{l e}{F} \]  

Or \[ W = \frac{lM}{zF} \]  

where \( e = M/z \)

\[ W = Sd\rho \]

From eq.(2) and (3), get:

\[ Sd\rho = \frac{lM}{zF} \]

\[ r = \frac{d}{t} = \frac{IM}{zFS\rho} \]

\[ r(mm/y) = \frac{Me}{zF\rho} \]

\[ r(mm/y) = 3.27i_{corr} \left( \frac{e}{\rho} \right) \]

\[ r(mpy) = 0.13i_{corr} \left( \frac{e}{\rho} \right) \]

**Electrochemical cells**

Corrosion in water and aqueous solution is an electrochemical “redox” reaction. If you keep in mind the electrochemical cell and the cell reaction involved, you may be able to stop or slow the corrosion.

Electrical current is commonly carried in two ways: by electron movement and by ion movement. In metallic conductors, some of the metal’s valence electrons are free to move between the atoms; these moving charged particles are the electric current. In solutions, electrically charged ions can move to produce a current. In an electric field (a voltage gradient) the positive ions are attracted to the negative side of the field while negatively charged ions move toward the positive side.

The amount of current carried by a conductor is directly proportional to the voltage gradient but inversely proportional to the resistance of the conductor itself. Ohm’s law states this relationship:

\[ I = V/R \]
where I is the current in amperes, V is the voltage gradient (volts), and R is the resistance of the conduction path (ohm).

The current is directly proportional to the corrosion rate. More current=more corrosion.

From Ohm’s law, then, it becomes obvious that to reduce corrosion you could:

- Reduce the voltage gradient. For example, do not electrically connect two metals that have very different corrosion potentials (voltages) if they could possibly form an electrochemical cell.

- Increase the resistance of the conduction path. A coat of paint on metal increases the electrical resistance of the path between the corrosive environment and the metal, and even though the resistance is not infinite, the paint provides some protection by reducing the current.

The electrical resistance of a conductor depends on the material of the conductor and the conduction path, thus:

\[ R = \rho \frac{l}{A} \]

where \( \rho \) is the electrical resistivity of the conduction path, \( l \) is the path length, and \( A \) is its cross sectional area.
Different Forms of Corrosion Classified on the Basis of Appearance

In the previous items we have mainly (more or less implicitly) assumed that:

1) electrochemical corrosion is the only deterioration mechanism;
2) anodic and cathodic reactions take place all over the electrode surface, but not simultaneously at the same place, i.e. the anodic and cathodic reactions exchange places, constantly or frequently. Closely related to this dynamic behaviour it is assumed that:
3) there are no significant macroscopic concentration differences in the electrolyte along the metal surface, and the metal is fairly homogeneous.

These three assumptions lead to uniform (general) corrosion. But this is only one of several corrosion forms that occur under different conditions. The other forms of corrosion depend on the deviations from the mentioned assumptions. Such deviations may be due to:
a) the design (the macro–geometry of the metal surfaces)
b) the combination of metal and environment
c) the state of the surface (particularly cleanliness and roughness)
d) other deterioration mechanisms

These conditions will cause various deviations in the geometry and appearance of the attack compared with uniform corrosion, and it is convenient to classify corrosion just after the appearance of the corroded surface. The advantage of such a classification is that a corrosion failure can be identified as a certain corrosion form by visual inspection, either by the naked eye or possibly by a magnifying glass or microscope. Since each form of corrosion has its characteristic causes, important steps to a complete diagnosis of failure can often be taken after a simple visual inspection.
On this basis, the following corrosion forms can be defined:

1. Uniform (general) corrosion
2. Galvanic (two–metal) corrosion
3. Thermogalvanic corrosion
4. Crevice corrosion (including deposit corrosion)
5. Pitting, pitting corrosion
6. Intergranular corrosion (including exfoliation)
7. Selective attack, selective leaching (de–alloying)
8. Erosion corrosion
9. Cavitation corrosion
10. Fretting corrosion
11. Stress corrosion cracking
12. Corrosion fatigue

A simple illustration of the various forms of corrosion is shown in following figure.

Main forms of corrosion grouped by their ease of recognition.
1- Uniform (General) Corrosion

By definition, attacks of this type are quite evenly distributed over the surface, and consequently it leads to a relatively uniform thickness reduction (following Figure). The necessary conditions for uniform corrosion have already been presented. Homogeneous materials without a significant passivation tendency in the actual environment are liable to this form of corrosion.

![Image of uniform corrosion](image)

Uniform (general) corrosion.

Uniform corrosion is assumed to be the most common form of corrosion and particularly responsible for most of the material loss.

Traditionally, however, it is not recognized as a dangerous form of corrosion, because:

1. Prediction of thickness reduction rate can be done by means of simple tests. Corresponding corrosion allowance can be added, taking into account strength requirements and lifetime.
2. Available protection methods are usually so efficient that the corrosion rate is reduced to an acceptable level. Actual methods are application of coatings, cathodic protection or possibly change of environment or material.

2- Galvanic Corrosion

- Conditions That Determine Corrosion Rates

When a metallic contact is made between a more noble metal and a less noble one, the corrosion rate will increase on the latter and decrease on the former. A necessary condition is that there is also an electrolytic connection between the metals.
The series of standard reversible potentials of the various metals are now and then used to explain and estimate the risk of galvanic corrosion. This can be very misleading, because 1) these potentials express thermodynamic properties, which do not tell us anything about the reaction rate (e.g. passivation tendencies are not taken into account), and 2) if the potential difference between the two metals in a galvanic couple is large, the more noble metal does not take part in the corrosion process with its own ions. Thus, under this condition, the reversible potential of the more noble metal does not play any role.

In addition to the standard reversible potential series we have practical galvanic series that show corrosion potentials of various metals in a given environment. In addition to the temperature, the flow velocity may have some effect upon the corrosion potential. To explain what conditions determine the rate of galvanic corrosion, and to predict the rate, we must study the overvoltage curves of the actual reactions that take place.

In order to take the area of each metal into account, it is recommended to draw these curves in the form of a potential–log current diagram. If current–density data are given, these data have to be multiplied by the actual area for each reaction.

**Example 1:** Copper accelerates corrosion considerably on unalloyed steel and even more on aluminium alloys in seawater because Cu is a more efficient cathode than steel and particularly aluminium.

**Example 2:** For copper alloys in contact with stainless steel in seawater, with an area ratio 1:1 between the materials, the galvanic coupling may give an increase in the corrosion rate on copper by a factor of 4–8. (In this case, stainless steel is the most efficient cathode).
Example 3: Titanium usually causes, in spite of its practical nobleness, little galvanic corrosion in contact with steel when the area ratio is about 1:1, because Ti is not an efficient cathode material (exceptions may occur in seawater with bacterial films). With a relatively large area of titanium, damaging corrosion may take place on steels, copper alloys etc.

- Prevention of Galvanic Corrosion

Galvanic corrosion can be prevented or made harmless in several ways:

1. Selecting adequate materials.
2. Using weld consumables that make the weld metal more noble than the base material.
3. Avoiding the combination of a large area of an old material (which has become more noble due to a surface film) with a small area of new, more active material.
4. Using favourable area ratios between more and less noble materials.
5. Insulating the parts of the couple from each other. Here, the use of “insulation materials” with insufficient resistivity should be warned against. A resistivity $\rho > 10^{10}$ ohm.cm and the use of chloroprene rubber have been recommended.

Design in order to prevent galvanic corrosion.
6. Applying non–metallic distance pieces (e.g. pipe extensions) so that galvanic corrosion becomes insignificant due to large a voltage drop in the water.

7. Using a metallic coating on one of the materials, e.g. thermally sprayed aluminium on steel in contact with aluminium parts.

8. Painting appropriately, i.e. primarily on the more noble material.


10. Adding inhibitors.

11. Designing to make less noble materials easy to replace or with sufficient corrosion allowance.

12. Avoiding access of humidity to the contact region between the materials. A sealer of a polysulphide-based, creep-resistant material may for instance be used.

13. Avoiding electrolytic deposition of a more noble material on a less noble one.

- **Application of Galvanic Elements in Corrosion Engineering**

  The most common example of beneficial application of galvanic elements in corrosion engineering is cathodic protection by use of sacrificial anodes. A coating of a material less noble than the substrate gives the same effect.

**3- Thermogalvanic Corrosion**

When a material in a corrosive environment is subject to a temperature gradient, a galvanic element may arise, causing what we call thermo–galvanic corrosion.
Usually, the hot surface forms the anode and the cold one the cathode. Partly, this is so because the anodic properties of the material depend on the temperature. In addition, the properties of the environment along the metal surface will also vary due to varying temperature and varying temperature gradient normal to the metal surface. Often this affects the cathodic reaction, which should also be taken into consideration when such a corrosion form is analyzed.

While ordinary galvanic corrosion (two-metal corrosion) can be identified by a visual inspection alone, for thermogalvanic corrosion we need also to know a little about the service conditions.

Thermogalvanic corrosion is prevented by appropriate design and measures to avoid uneven heating/cooling and forming of hot spots. For heat-insulated pipes and equipment is important that the insulation is continuous. The corrosion form may under certain conditions be prevented by cathodic protection or coatings.

### 4- Crevice Corrosion

**- Occurrence, Conditions**

This is localized corrosion concentrated in crevices in which the gap is sufficiently wide for liquid to penetrate into the crevice and sufficiently narrow for the liquid in the crevice to be stagnant.

Crevice corrosion (CC) occurs beneath flange gaskets, nail and screw heads and paint coating edges, in overlap joints, between tubes and tube
plates in heat exchangers etc. The same form of corrosion develops beneath deposits of, e.g. corrosion products, dirt, sand, leaves and marine organisms, hence it is called deposit corrosion in such cases.

The most typical crevice corrosion occurs on materials that are passive beforehand, or materials that can easily be passivated (stainless steels, aluminium, unalloyed or low alloy steels in more or less alkaline environments etc.), when these materials are exposed to aggressive species (e.g. chlorides) that can lead to local breakdown of the surface oxide layer.

Materials like conventional stainless steels can be heavily attacked by deposit corrosion in stagnant or slowly flowing seawater. A critical velocity of about 2 m/s has often been assumed, but more recent studies have indicated that crevice corrosion can occur at higher velocities too. The corrosion form is most frequently observed in environments containing chlorides, but can also occur in other salt solutions.

A special form of crevice corrosion that can develop on steel, aluminium and magnesium beneath a protecting film of lacquer, enamel, phosphate or metal is the so-called *filiform corrosion*, which leads to a characteristic stripe pattern. It has been observed most frequently in cans exposed to the atmosphere.

- **Mechanism**

A review of the mechanisms of crevice corrosion has recently been published by Combrade. The following figure shows two stages in the development of crevice corrosion. A flange joint of a metal M is exposed to neutral water containing oxygen and NaCl. For simplicity, we assume firstly that M is a univalent metal. The development can be divided into the following four stages:
I. In the beginning the metal corrodes at the same rate inside and outside the crevice (Figure a). The anodic reaction \((M \rightarrow M^+ + e)\) and the cathodic reaction \((O_2 + 2H_2O + 4e \rightarrow 4OH^-)\) occur on area elements distributed between each other all over the surface. If the metal is passive beforehand, the corrosion rate is low (corresponding to the passive current density) and the consumption of oxygen is correspondingly low.

The oxygen is gradually being consumed within the crevice. This is also the case when the metal surfaces are passive, provided that the crevice is so narrow and deep that oxygen is more slowly transported into the crevice than it is consumed inside it.

II. When the oxygen has been completely consumed inside the crevice, \(OH^-\) can no longer be produced there. Conversely, the dissolution of metal inside the crevice continues, supported by the oxygen reduction outside the crevice.

The concentration of metal ions within the crevice increases, and with missing \(OH^-\) production in the crevice, the charge equilibrium (electrical neutrality) is maintained by migration of \(Cl^-\) into the crevice (Figure b). In this way an increasing amount of dissociated metal chloride \((M^+Cl^-)\) is produced in the crevice. The metal chloride reacts with water (hydrolyzes):
\[
M^+Cl^- + H_2O \rightarrow MOH + H^+Cl^- 
\]

Metal hydroxide is deposited and hydrochloric acid is formed in the crevice, which causes a gradual reduction of the pH. This process leads to a critical corrosion state.

III. When the environment has become sufficiently aggressive, the surface oxide film is attacked. The crevice surfaces are transferred to an active state and the corrosion rate increases.

IV. The growth (or propagation) phase. Because of increased corrosion rate, the migration of \(Cl^-\) increases also, which contributes to a further
acceleration of the corrosion process. The process promotes itself, i.e. it is “auto–catalytic”. Since the pH has been strongly reduced, the hydrogen reaction (2H⁺ + 2e → H₂) can also possibly contribute as a second cathodic reaction. pH inside the crevice can reach values of 0–4 depending on the actual material–environment combination. At the same time, pH may increase to 9–10 on the metal surface outside the crevice, where the oxygen reduction takes place.

Various metals, e.g. Al, Fe, Cr and Ni, may suffer from crevice corrosion. The corresponding hydroxides deposited in the crevice are Al(OH)₃, Fe(OH)₂, Cr(OH)₃ or Ni(OH)₂. Cr(OH)₃ plays a vital role in crevice corrosion of stainless steel, in which also the content of Mo is important. The time until the crevice becomes active (stages I–III) is called the incubation (or initiation or induction) period. This may last, e.g. several months (under conditions giving a small passive current density). However, after the incubation period, penetration of plates with thickness of a few
millimetres may in extreme cases occur within some days. The length of the incubation time is difficult to predict.

Crevice corrosion is affected by several factors, of a metallurgical, environmental, electrochemical, surface physical, and last but not least, a geometrical nature. One of the most important factors is the crevice gap.

- **Galvanic Effects on Crevice Corrosion**

  If there is a crevice on a component made of a material liable to crevice corrosion, and this component is connected to a more noble material with free surfaces, crevice corrosion may be intensified strongly. Such a case is a couple of an aluminium component (with a crevice) and a steel plate in water containing some chloride. The corrosion form can be called galvanic crevice corrosion. The crevice corrosion rate will be particularly high if the more noble metal acts as an efficient cathode in the given environment. The explanation is the same as for ordinary galvanic corrosion. If, on the other hand, a less noble metal with free surface is connected to a nobler component with a crevice, the coupling will counteract crevice corrosion in the latter.

  Certainly, in many cases of stainless steel exposed to seawater, crevice corrosion is prevented by contact with unalloyed/low-alloy steel or cast iron. An example is stainless steel pumps or valves coupled to ordinary steel or iron pipes.

- **Prevention of Crevice Corrosion**

  Crevice corrosion can be prevented or reduced by appropriate:

  1. **Selection of material.** As dealt with in previous sections, conventional stainless steels, with martensitic, ferritic, austenitic or ferritic–austenitic (duplex) structure, are sensitive to crevice corrosion. Newer high-alloy steels
with high Mo content show by far better crevice corrosion properties in seawater and other Cl⁻-containing environments.

2. *Design and production*. Avoid as far as possible crevices and deposition.

3. *Cathodic protection*. The potential must be kept below the protection potential.

   An efficient method for internal protection of pipe joints is the “resistance controlled cathodic protection” (RCP).

4. *Measures for preventing deposition*.
   a) Inspection and cleaning during and between service periods.
   b) Separation of solid material from flowing media in process plants.
   c) Gravel filling around buried piping and structures.

5- *Pitting Corrosion*

   - *Conditions, Characteristic Features and Occurrence*

     Pitting corrosion (sometimes only called pitting) occurs on more or less passivated metals and alloys in environments containing chloride, bromide, iodide or perchlorate ions when the electrode potential exceeds a critical value, the pitting potential, which depends on various conditions.

     The pitting potential is not a thermodynamically defined potential and depends for one thing upon the rate of potential increase when the polarization curve is recorded. This form of corrosion is characterized by narrow pits with a radius of the same order of magnitude as, or less than, the depth. The pits may be of different shape, but a common feature is the sharp boundary (following figure). Pitting is a dangerous form of corrosion since the material in many cases may be penetrated without a clear warning (because the pits often are narrow and covered) and the pit growth is difficult to predict. This is connected to the fact that the extent and the
intensity of pitting corrosion is difficult to measure because the number and size of pits (diameter and depth) vary from region to region and within each region. Short-term testing in the laboratory for determination of pit growth is also problematic because, under realistic conditions, it may take long time, e.g. many months, before the pits become visible. Another problem is that the critical size, i.e. the maximum pit depth, increases with increasing surface area.

Aluminium is liable to pitting corrosion in media containing chloride, but the corrosion may not necessarily be of a serious nature. However, if aluminium is polarized by metallic contact with a more noble material, the former will be heavily attacked. Stainless steels are attacked in strongly oxidizing chloride solutions.

Copper and copper alloys may corrode by pitting in fresh water, particularly at temperatures > 60°C, pH < about 7.4, and where the ratio between sulphate and carbonate contents in the water is relatively high.

Growth of organisms also increases the risk of corrosion, and a transition to deposit corrosion may then occur.

Different shapes of corrosion pits.
- **Mechanisms**

  We distinguish roughly between the mechanism of pitting initiation and that of pit growth. For more detailed discussions, however, the pitting process is often considered to consist of the following stages: 1) Local breakdown of passivity (pit nucleation), 2) early pit growth, 3) late (stable) pit growth, and (possibly) 4) repassivation. The initial stage is not fully understood, but various theories exist.

  On materials that often operate in a less pronounced passive state, such as copper, zinc and tin, pitting corrosion may start in pores in surface layers of corrosion products. For materials that are typically passive initially, e.g. aluminium and stainless steels, it is assumed that pitting is initiated by adsorption of halide ions that penetrate the passive film at certain positions.

  This happens at weak points of the oxide film, e.g. at irregularities in the oxide structure due to grain boundaries or inclusions in the metal. Absorption of halide ions causes strong increase of the ion conductivity in the oxide film so that metal ions can migrate through the film.

  In this way localized dissolution occurs, and intrusions are subsequently formed in the metal surface. Another theory is that the initial adsorption of aggressive anions at the oxide surface enhances catalytically the transfer of metal cations from the oxide to the electrolyte and thus causes successive local thinning of the oxide film. A third possibility is that the attacks start at fissures in the passive layer. Which of the mechanisms is the most effective depends on both material and environment.

  The next stage, i.e. the stable growth of the pit, proceeds essentially by the same mechanism as that of crevice corrosion. Generally, the anodic dissolution occurs inside the pit, often mainly at the bottom, while the cathodic reaction is localized outside the pit, on inclusions or other parts of
the surface which are sufficiently efficient cathodes. Hydrolysis in the pit leads to an acidic, aggressive pit solution, which also may allow an additional cathodic reaction here, namely reduction of hydrogen ions. Metal cations from the dissolution reaction migrate and diffuse towards the mouth of the pit where they react with OH\(^-\) ions from the cathodic reaction, forming metal hydroxide deposits that may cover the pit more or less.

- **Influencing Factors**

Factors of general significance for pitting are:

**a) pH and chloride concentration:** The pitting potential and pitting resistance normally increase with increasing pH and decreasing chloride concentration.

The negative effect of increased Cl\(^-\) concentration on the pitting potential \(E_p\) is of great significance. For an 18-8 CrNi steel, \(E_p\) can be expressed by:

\[
E_p = 0.168 - 0.088 \log a_{Cl^-}, (V, SHE)
\]

where \(a_{Cl^-}\) = activity \(\approx\) concentration of Cl\(^-\).

While for aluminium:

\[
E_p = -0.504 - 0.124 \log a_{Cl^-}, (V, SHE)
\]

**b) Flow velocity:** When pitting is initiated, an aggressive environment is established within the pit, and this is combined with an increased pH at the adjacent free surface. The increased pH gives an increased resistance to initiation of new pits around the first one formed. If there is no movement of the liquid, these conditions will be conserved, and the result is large and few pits. Liquid flow gives a higher probability for washing away the aggressive environment in the pit, and at the same time it increases the transport of
oxygen to the active area, so that the pit may be passivated before it gets the chance to grow to a considerable size. The alkaline layer around an active pit is also washed away to a higher extent, and pit initiation in the neighbourhood of an active pit occurs more easily.

This means that increased flow velocity results in smaller but more numerous pits, which makes pitting corrosion less serious.

c) **The gravity force:** Horizontal top surfaces are often heavily pitted, while underside surfaces are hardly, or not at all, attacked. Vertical surfaces are intermediate as to the extent of pitting. The reason is that the aggressive environment in the pits has a higher density than pure water.

d) **Cu$^{2+}$ and Fe$^{3+}$ ions** favour pit initiation and accelerate pit growth because they lead to increased potential. The Cu ions have a double effect because Cu is precipitated on the material surface and forms efficient cathodes.

e) **Metallurgical properties:** Impurities and inclusions are important, e.g. AlFe secondary phase, which contributes to the localization of pits on aluminium because 1) the oxide film on top of and around the inclusion is weak, thin and stressed, 2) such inclusions are efficient cathodes. Pitting of this type will usually last only until the pits are so large that the inclusions are falling out.

f) **The insulating ability of the oxide:** If the oxide insulates efficiently, the surface is inactive as a cathode. This is to a certain extent the case for aluminium in seawater; which is the direct reason for the relative slow growth of pits in this case.

g) **Surface roughness:** The main trend is that smooth surfaces get few, large pits while rough surfaces get numerous smaller pits.

h) **Temperature:** Increasing temperature gives usually decreasing pitting potential and increasing liability to pitting corrosion.
i) **Galvanic contact** with a more noble material increases the tendency to and the rate of pitting corrosion (the corrosion potential is lifted).

- **Prevention of Pitting Corrosion**

  The best way to prevent pitting is *appropriate materials selection*. Among aluminium alloys, those alloyed with magnesium and/or manganese and the commercially pure grades are the best ones. These perform quite well in seawater. Aluminium with magnesium (e.g. AlMg 4.5 Mn) is used in hulls of high-speed vessels and small boats, in deck structures on ships and boats and in helicopter decks on oil and gas platforms. AlMgSi alloys will normally acquire somewhat larger pits, but they are used in profiles, e.g. in marine atmospheres. Aluminium alloys with Cu and Zn are generally less corrosion resistant.

  In stainless steels, increased content of Cr as well as Ni and Mo gives higher resistance against pitting, while Si, S and C have the opposite effect. Modern highalloy steels with higher content of Mo (6–7%) have very good pitting resistance. Some Ni alloys and particularly titanium are even better.

  **Cathodic protection** can also be applied to prevent pitting. Regarding aluminium, strong cathodic polarization should be avoided because this can lead to a large increase of pH close to the metal surface, which can cause so-called alkaline corrosion. Use of sacrificial anodes of Zn or Al alloys is therefore safer than impressed current.

  Pitting can also be counteracted by *change of environment*. For instance, pitting of copper and copper alloys in hot water can be prevented by water treatment, implying pH > 8.0 and $[\text{HCO}_3^-]/[\text{SO}_4^{2-}] > 1$. 

[40]
Examples:

**Pitting of Carbon Steels**

The reactions of significance are given in the diagram, but certain features of the mechanism are of interest since they illustrate the complexity of the process.

**Pit interior:** Within the pit the primary anodic reaction is

\[ Fe \rightarrow Fe^{2+} + 2e^{-} \]

which is followed by hydrolysis and the generation of \( H^+ \)

\[ Fe^{2+} + H_2O \rightarrow FeOH^+ + H^+ \]

The decrease in pH results in dissolution of some of the MnS

\[ MnS + 2H^+ \rightarrow H_2S + Mn^{2+} \]

thus providing \( S^{2-} \) and \( HS^- \) that stimulate attack by decreasing the activation overpotential for the dissolution of Fe (and Ni).

The electrons released are partly accepted by dissolved oxygen at the surface millscale and partly by the \( H^+ \), with the consequent formation of \( H_2 \) gas. The concentration of chloride ions within the pit will increase owing to migration, and this too will stimulate dissolution.

**Pit mouth:** A membrane of magnetite (\( Fe_3O_4 \)) and rust (\( FeOOH \)) is formed, which prevents the intermingling of the acid anolyte and alkaline catholyte, by the following steps:

Oxidation of \( FeOH^+ \) and \( Fe^{2+} \) by dissolved oxygen occurs

\[ 2FeOH^+ + \frac{1}{2} O_2 + 2H^+ \rightarrow 2FeOH^{2+} + H_2O \]

\[ 2Fe^{2+} + \frac{1}{2} O_2 + 2H^+ \rightarrow 2Fe^{3+} + H_2O \]

followed by hydrolysis of the reaction products

\[ FeOH^{2+} + H_2O \rightarrow Fe(OH)_2^{+} + H^+ \]

\[ Fe^{3+} + H_2O \rightarrow FeOH^{2+} + H^+ \]

and the precipitation of magnetite and rust
2FeOH\(^{2+}\) + Fe\(^{2+}\) + 2H\(_2\)O → Fe\(_3\)O\(_4\) + 6H\(^{+}\)

Fe(OH)\(_2\)\(^{+}\) + OH\(^{-}\) → FeOOH + H\(_2\)O

**Outside the pit:** Reduction of dissolved oxygen

O\(_2\) + 2H\(_2\)O + 4e → 4OH\(^{-}\)

and reduction of rust to magnetite

3FeOOH + e → Fe\(_3\)O\(_4\) + H\(_2\)O + OH\(^{-}\)

This area will be passivated by the increase in pH due to the cathodically produced OH\(^{-}\) ions, and partially cathodically protected by the electrons liberated by the anodic processes within the pit. The tubercle thus results in an occluded cell with the consequent acidification of the anodic sites.

**Pitting of Aluminium**

The pitting of aluminium in chloride-containing waters follows a similar mechanism to that of steels, and again the characteristic feature of the process is the formation of acid within the occluded. The passivating film of Al\(_2\)O\(_3\), surrounding the pit acts as the cathode, but its effectiveness in reducing dissolved oxygen is significantly enhanced if copper is either
deposited on the surface or enters the lattice of the $\text{Al}_2\text{O}_3$, and it is well known that the pitting of aluminium occurs rapidly when the water contains a trace of copper ions. Similar considerations apply to intermetallic phases such as $\text{FeAl}_3$, and $\text{CuAl}_2$, which can increase the kinetics of oxygen reduction.

Pit on aluminum showing how the rate of pitting may be facilitated by an intermetallic phase $\text{Al}_3\text{Fe}$ or by a deposit of copper.

**Pitting of Copper**

Copper and its alloys in certain fresh waters give rise to a form of localized attack that is referred to as nodular pitting in which the attacked areas are covered by small mounds or nodules composed of corrosion products and of $\text{CaCO}_3$ precipitated from the water. This is a serious problem in view of the extensive use of copper pipes and tanks for water supplies, and in aggressive water these may perforate in a relatively short time. The following figure shows the type of pit and corrosion products that form on copper pipes used for hard (or moderately hard) well waters, and this type of attack is most prevalent when the pipe is used for conveying cold water. The pit interior is almost invariably covered with solid $\text{Cu}_2\text{Cl}_2$, and across the mouth of the pit there is a thin membrane of $\text{Cu}_2\text{O}$ containing one or more holes; this membrane is supported on the underside by a more
substantial layer of coarsely crystalline Cu₂O formed by hydrolysis of Cu₂Cl₂. Above the Cu₂O membrane there is a roughly hemispherical mound of CaCO₃ containing insoluble copper salts, mainly basic carbonate and chloride.

Pit formed on a copper surface.

6- Intergranular Corrosion

- General Characteristics, Causes and Occurrence

Intergranular corrosion is localized attack on or at grain boundaries with insignificant corrosion on other parts of the surface. The attacks propagate into the material. This is a dangerous form of corrosion because the cohesive forces between the grains may be too small to withstand tensile stresses; the toughness of the material is seriously reduced at a relatively early stage, and fracture can occur without warning. Grains may fall out, leaving pits or grooves, but this may not be particularly important.

The general cause of intergranular corrosion is the presence of galvanic elements due to differences in concentration of impurities or alloying elements between the material in or at the grain boundaries and the interior of the grains:

a) Impurities segregated to the grain boundaries (causing, e.g. the AlFe secondary phase in aluminium).
b) Larger amount of a dissolved alloying element at the grain boundaries (e.g. Zn in brass).

c) Smaller amount of a dissolved alloying element at the grain boundaries (e.g. Cr in stainless steel).

In most cases there is a zone of less noble material in/at the grain boundaries, which acts as an anode, while the other parts of the surface form the cathode. The area ratio between the cathode and the anode is very large, and the corrosion intensity can therefore be high.

In some cases, precipitates at the grain boundaries may be more noble than the bulk material; these precipitates will stimulate grain boundary attacks by acting as efficient local cathodes (e.g. CuAl₂ in aluminium alloys).

Intergranular corrosion occurs in stainless steels and alloys based on nickel, aluminium, magnesium, copper and cast zinc.

7- Selective Corrosion (Selective Leaching)

This form of corrosion is observed in alloys in which one element is clearly less noble than the other. The corrosion mechanism implies that the less noble element is removed from the material. A porous material with very low strength and ductility is the result. Regions that are selectively corroded are sometimes covered with corrosion products or other deposits, and since the component keeps exactly the original shape, the attacks may be difficult to discover. Serious material failure may therefore occur without warning. The most common example of selective corrosion is dezincification of brass, in which zinc is removed from the alloy and copper remains. After cleaning the surface, dezincification is easy to demonstrate.
because the Zn–depleted regions have a characteristically red copper colour in contrast to the original yellow brass. Dezincification occurs in two forms: a) Uniform (layer) dezincification, where the front of the selective attack moves more or less uniformly through the material. This form is favoured by high Zn content and acidic solutions. b) Localized (plug-type) dezincification, where the localization and form of attack are determined more or less arbitrarily. This type occurs more often in alloys with somewhat lower Zn content and in neutral, alkaline and slightly acidic solutions.

The liability to dezincification increases with increasing Zn content and temperature and is promoted by a stagnant solution, porous surface layers and oxygen in the corrosive medium (but oxygen is not strictly necessary).

There has been some doubt about the mechanism, but the following is commonly accepted: brass dissolves, subsequently zinc ions stay in solution while copper is deposited electrolytically and forms a porous material with poor strength and ductility.

Dezincification can be reduced or prevented by:

a) Removing oxygen from the solution.

b) Cathodic protection.

(For economical reasons the use of a) and b) has been limited.)

c) Appropriate selection of alloy.
8- Erosion and Abrasion Corrosion

- Characteristic Features and Occurrence

When there is a relative movement between a corrosive fluid and a metallic material immersed in it, the material surface is in many cases exposed to mechanical wear effects leading to increased corrosion, which we usually call erosion corrosion. The mechanism is that deposits of corrosion products, or salts precipitated because of the corrosion process, are worn off, dissolved or prevented from being formed, so that the material surface becomes metallically clean and therefore more active. In extreme cases, erosion corrosion may be accompanied by pure mechanical erosion, by which solid particles in the fluid may tear out particles from the material itself and cause plastic deformation, which may make the metal even more active. The results of erosion corrosion are grooves or pits with a pattern determined by the flow direction and the local flow conditions.

Reasonably, the corrosion form is typical at relatively high velocities between the material surface and the fluid, and it is particularly intensive in cases of two-phase or multiphase flow, i.e. liquid–gas and liquid–solid particle flow. Components often liable to erosion corrosion are propellers, pumps, turbine parts, valves, heat exchanger tubes, nozzles, bends, and equipment exposed to liquid sputter or jets.

Most sensitive materials are those normally protected by corrosion products with inferior strength and adhesion to the substrate, e.g. lead, copper and its alloys, steel, and under some conditions aluminium/aluminium alloys. Stainless steel, titanium and nickel alloys are much more resistant because of a passive surface film with high strength and adhesion. In some cases, the wear effects are more abrasive than erosive.
- Types and Mechanisms

Leaving cavitation corrosion and fretting aside as separate corrosion forms, erosion and abrasion corrosion can be divided into three types, a), b) and c), as described below. The first two types are erosion corrosion, while type c) is to be considered as abrasion corrosion. The three types may overlap each other and partly occur simultaneously in the same system.

a) Impingement corrosion, often occurring in systems with two-phase or multiphase flow, particularly where the flow is forced to change direction.

Numerous impacts from liquid drops in a gas stream, or particles or gas bubbles in a liquid flow lead to pits with a direction pattern as shown in following figure (a). In cases with solid particles, the situation can be illustrated as in next figure, where corrosion products are removed and the surface locally activated.

b) Turbulence corrosion, which occurs in areas with particularly strong turbulence such as the inlet end of heat exchanger tubes following figure (b).

c) Increased corrosion due to removal of corrosion products by wear due to particles moving along and in contact with the corroding surface, or by wear between components in moving contacts with each other.

![Diagram](image.png)

a) Impingement, and b) turbulence corrosion.
In addition to the general mechanisms of erosion corrosion described in this section, there are also some special mechanisms occurring under certain conditions of materials and environments.

In some cases deposits may also be removed by high shear stresses (force components parallel to the surface).

The shear stresses may vary considerably as a consequence of flow fluctuations or repeated impacts. Therefore, it is possible that deposits of corrosion products are destroyed either by extreme values of shear stress or by fatigue. The pure erosion rate can be expressed by the following formula:

\[ W (mm/yr) = K_{mat} \times K_{env} \times c \times v^n \times f(\beta) \]

where \( K_{mat} \) is a material factor depending in a complex manner on (among other properties) hardness and ductility of the substrate; \( K_{env} \) is an environmental factor that includes the effects of size, shape (sharpness), density and hardness of the particles; \( c \) is the concentration of particles, \( n \) is the so-called velocity exponent, \( v \) is the particle velocity, and \( \beta \) the impact angle. This equation is very useful in connection with erosion testing in the laboratory.

9- Cavitation Corrosion

This corrosion form is closely related to erosion corrosion, but the appearance of the attack differs from the erosion corrosion attacks described in the last section. While the latter has a pattern reflecting the flow direction, cavitation attacks are deep pits grown perpendicularly to the surface. The pits are often localized close to each other or grown together over smaller or larger areas, making a rough, spongy surface.

Cavitation corrosion has a special mechanism, which is also one of the reasons that it is considered as a separate corrosion form here. In other hand
there are many authors considered this corrosion as a subgroup of erosion corrosion.

Cavitation corrosion occurs at high flow velocities and fluid dynamic conditions causing large pressure variations, as often is the case for water turbines, propellers, pump rotors and the external surface of wet cylinder linings in diesel engines.

Vapour bubbles formed in low-pressure zones, or at moments of low pressure at the actual positions, collapse very rapidly when they suddenly enter a high-pressure zone or high-pressure moment. When this happens close to the metal surface, the bubble collapse causes a concentrated and intense impact against the metal, with the induction of high local stress and possibly local plastic deformation of the material.

Parts of any protecting film are removed. Repeated impacts may lead to microscopic fatigue and crack formation, and subsequent removal of particles from the material itself. During this process the material is strongly activated at the attacked points, and high local corrosion rates are possible.

In some cases, however, the corrosion contribution is small and the deterioration form is more correctly called cavitation erosion.
10- Fretting Corrosion (Fretting Oxidation)

Fretting wear occurs at the interface between two closely fitting components when they are subject to repeated slight relative motion (slip). The relative motion may vary from less than a nanometre to several micrometres in amplitude. Vulnerable objects are shrink fits, press fits, bolted joints, and other assemblies where the interface is under load.

Sometimes the attack is serious, particularly because it may lead to macroscopic motion between the parts, or fatigue cracks may develop in the shaft. The mechanical contribution to fretting damage may include elements of adhesive wear, microscopic fatigue crack development and delamination that result in removal of small particles from the metal lattice. The particles form debris, which may partly adhere to the fretting surfaces and be trapped between these, and may partly escape from the fretting area.

The exact mechanism of combined fretting and oxidation is not fully understood. The following successive steps in the process have been proposed: the relative motion between the parts may promote oxidation of the surface, the oxide film is partly worn off, the fresh metal surface is highly active and oxidizes again, and this circular process is repeated.

Another explanation is that, firstly, metal particles are released from the crystal structure by adhesive wear, microfatigue and delamination, then the particles oxidize, forming a debris consisting of brittle and friable oxide particles. This debris will to a considerable extent move out from the interfacial area between the components, and thus allow the deterioration process to continue at a high rate.

Fretting oxidation is reduced or prevented by use of lubricants (e.g. low-viscosity oil, molybdenum sulphide), which hinder the access of oxygen and at the same time suppress adhesive wear. Other protection methods are
to prevent oxygen access by use of gaskets or sealing materials, to change some mechanical parameters, and to use suitable materials in the components. One can use hard materials in both parts, alternatively a hard material in one part and a soft one in the other. The soft material may be a coating (e.g. of Sn, Pb, Ag) when both components are made of steel.

11- Stress Corrosion Cracking (SCC)

- Characteristic Features and Occurrence

Stress corrosion cracking can be defined as crack formation due to simultaneous effects of static tensile stresses and corrosion. The tensile stresses may originate from external load, centrifugal forces or temperature changes, or they may be internal stresses induced by cold working, welding or heat treatment. The cracks are mainly formed in planes normal to the tensile stresses, and propagate intergranularly or transgranularly, more or less branched. If they are not detected in time, they will cause fast, unstable fracture.

Macroskopically, the crack surfaces may look brittle and discoloured, dull or darkened by oxide layers. The initiation site may be discovered as a pit (formed by pitting or deposit corrosion) or, e.g. as a defect caused by forming or machining. On parts in service it may, however, be difficult to discover cracks, because they are narrow and filled or covered by corrosion products.

Earlier, SCC was always associated with alloys, but during the last few decades it has also been detected in pure metals, e.g. copper. It should be noticed that SCC has occurred in low-alloy steel with medium or low strength, for instance in clean, saturated water vapour.
The factors determining the mechanisms and the course of development can be sorted into three main groups:

1. Environmental and electrochemical factors.
3. Mechanical stress and strain.

- **Prevention of SCC**

  Stress corrosion cracking can be prevented by affecting one or more of the determining metallurgical, mechanical, environmental or electrochemical factors dealt with in the previous sections:

  a) Selecting the right material.

  b) Reducing the stress and stress intensity to below the threshold values. Annealing to remove residual stresses due to welding or cold working.

  c) Making the environment less aggressive by removal of oxygen, distillation or ion exchange.

  d) Using cathodic protection by sacrificial anodes (in cases where the material is not liable to hydrogen embrittlement).

  e) Supplying inhibitors, particularly in less aggressive corrosion media.

12- **Corrosion Fatigue**

- **Definition, Characteristic Features and Occurrence**

  Corrosion fatigue (CF) is crack formation due to varying stresses combined with corrosion. Alternatively, it may be defined as fatigue stimulated and accelerated by corrosion. The external difference between these two forms of deterioration is only that CF develops under varying stresses and SCC under static stresses.
The crack development can be divided into four stages: 1. Initiation 2. Crack growth stage I, with crack growth direction about 45° relative to the tensile stress direction. 3. Crack growth stage II. 4. Fast fracture.

The stages of development of a fatigue fracture.

The observations dealt with above have been explained by various theories. The effect of corrosion is mainly ascribed to three different mechanisms:

i) Formation of corrosion pits and grooves leading to stress concentrations.

ii) Mutual acceleration of corrosion and mechanical deterioration.

iii) Absorption and adsorption of species from the environment, including absorption of hydrogen and resulting embrittlement.

- Prevention of Corrosion Fatigue

a) Moderate cathodic polarization provides adequate protection against the environmental contribution to CF of ordinary structural steels, provided that the initial defects are reasonably small.

b) Reduction of the tensile stress level, e.g. by stress annealing and good design, is efficient.
c) Reliable coatings on the areas where the fatigue stresses are highest can be utilized more than has been done (anodic coatings, e.g. Zn on steel, and organic coatings).

d) By reasonable materials selection combined with adequate design, CF damage can be avoided or reduced.

e) Change of environment, e.g. de-aeration or use of inhibitors, is sometimes applicable. De–aeration will not always hinder CF, but can at least in neutral waters prevent initiation of CF on steel surfaces without surface defects.

f) Anodic protection has been shown to increase the fatigue strength of carbon steel and stainless steel in oxidizing environments (it improves passivation).