A SHORT INTRODUCTION TO CORROSION AND ITS CONTROL

CORROSION OF METALS AND ITS PREVENTION

WHAT IS CORROSION

Corrosion is the deterioration of materials by chemical interaction with their environment. The term corrosion is sometimes also applied to the degradation of plastics, concrete and wood, but generally refers to metals. The most widely used metal is iron (usually as steel) and the following discussion is mainly related to its corrosion.

THE CONSEQUENCES OF CORROSION

The consequences of corrosion are many and varied and the effects of these on the safe, reliable and efficient operation of equipment or structures are often more serious than the simple loss of a mass of metal. Failures of various kinds and the need for expensive replacements may occur even though the amount of metal destroyed is quite small. Some of the major harmful effects of corrosion can be summarised as follows:

1. Reduction of metal thickness leading to loss of mechanical strength and structural failure or breakdown. When the metal is lost in localised zones so as to give a crack-like structure, very considerable weakening may result from quite a small amount of metal loss.

2. Hazards or injuries to people arising from structural failure or breakdown (e.g. bridges, cars, aircraft).

3. Loss of time in availability of profile-making industrial equipment.

4. Reduced value of goods due to deterioration of appearance.

5. Contamination of fluids in vessels and pipes (e.g. beer goes cloudy when small quantities of heavy metals are released by corrosion).

6. Perforation of vessels and pipes allowing escape of their contents and possible harm to the surroundings. For example a leaky domestic radiator can cause expensive damage to carpets and decorations, while corrosive sea water may enter the boilers of a power station if the condenser tubes perforate.

7. Loss of technically important surface properties of a metallic component. These could include frictional and bearing properties, ease of fluid flow over a pipe surface, electrical conductivity of contacts, surface reflectivity or heat transfer across a surface.
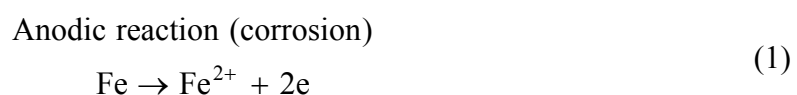
8.   Mechanical damage to valves, pumps, etc, or blockage of pipes by solid corrosion products.

9.   Added complexity and expense of equipment which needs to be designed to withstand a certain amount of corrosion, and to allow corroded components to be conveniently replaced.
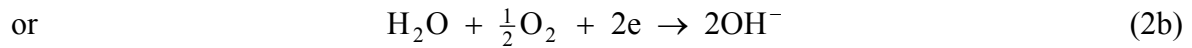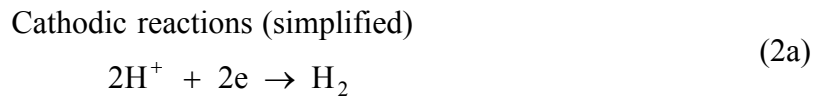
CHEMISTRY OF CORROSION

Common structural metals are obtained from their ores or naturally-occurring compounds by the expenditure of large amounts of energy. These metals can therefore be regarded as being in a metastable state and will tend to lose their energy by reverting to compounds more or less similar to their original states. Since most metallic compounds, and especially corrosion products, have little mechanical strength a severely corroded piece of metal is quite useless for its original purpose.

Virtually all corrosion reactions are electrochemical in nature, at anodic sites on the surface the iron goes into solution as ferrous ions, this constituting the anodic reaction. As iron atoms undergo oxidation to ions they release electrons whose negative charge would quickly build up in the metal and prevent further anodic reaction, or corrosion. Thus this dissolution will only continue if the electrons released can pass to a site on the metal surface where a cathodic reaction is possible. At a cathodic site the electrons react with some reducible component of the electrolyte and are themselves removed from the metal. The rates of the anodic and cathodic reactions must be equivalent according to Faraday's Laws, being determined by the total flow of electrons from anodes to cathodes which is called the "corrosion current", I_{cor}. Since the corrosion current must also flow through the electrolyte by ionic conduction the conductivity of the electrolyte will influence the way in which corrosion cells operate. The corroding piece of metal is described as a "mixed electrode" since simultaneous anodic and cathodic reactions are proceeding on its surface. The mixed electrode is a complete electrochemical cell on one metal surface.

The most common and important electrochemical reactions in the corrosion of iron are thus

$$\text{Anodic reaction (corrosion)}$$
$$\text{Fe} \rightarrow \text{Fe}^{2+} + 2e \qquad (1)$$

[CORROSION&PROTECTION/BM]

$$\text{Cathodic reactions (simplified)}$$
$$2H^+ + 2e \rightarrow H_2 \qquad\qquad \text{(2a)}$$

or
$$H_2O + \tfrac{1}{2}O_2 + 2e \rightarrow 2OH^- \qquad\qquad \text{(2b)}$$

Reaction 2a is most common in acids and in the pH range 6.5 – 8.5 the most important reaction is oxygen reduction 2b. In this latter case corrosion is usually accompanied by the formation of solid corrosion debris from the reaction between the anodic and cathodic products.

$$Fe^{2+} + 2OH^- \rightarrow Fe(OH)_2, \quad \text{iron (II) hydroxide}$$

Pure iron (II) hydroxide is white but the material initially produced by corrosion is normally a greenish colour due to partial oxidation in air.

$$2Fe(OH)_2 + H_2O + \tfrac{1}{2}O_2 \rightarrow 2Fe(OH)_3, \quad \text{hydrated iron (III) oxide}$$
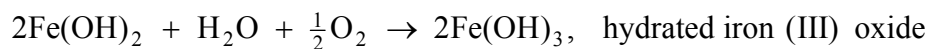
Further hydration and oxidation reactions can occur and the reddish rust that eventually forms is a complex mixture whose exact constitution will depend on other trace elements which are present. Because the rust is precipitated as a result of secondary reactions it is porous and absorbent and tends to act as a sort of harmful poultice which encourages further corrosion. For other metals or different environments different types of anodic and cathodic reactions may occur. If solid corrosion products are produced directly on the surface as the first result of anodic oxidation these may provide a highly protective surface film which retards further corrosion, the surface is then said to be "passive". An example of such a process would be the production of an oxide film on iron in water, a reaction which is encouraged by oxidising conditions or elevated temperatures.

$$2Fe + 3H_2O \rightarrow Fe_2O_3 + 6H^+ + 6e$$

FACTORS THAT CONTROL THE CORROSION RATE

Certain factors can tend to accelerate the action of a corrosion cell.

These include:

(a)   Establishment of well-defined locations on the surface for the anodic and cathodic reactions. This concentrates the damage on small areas where it may have more serious effects, this being described as "local cell action". Such effects can occur when metals of differing electrochemical properties are placed in contact, giving a "galvanic couple". Galvanic effects may be predicted by means of a study of the Galvanic Series which is a list of metals and alloys placed in order of their potentials in the corrosive environment, such as sea water. Metals having a more positive (noble) potential will tend to extract electrons from a metal which is in a more negative (base) position in the series and hence accelerate its corrosion when in contact with it. The Galvanic Series should not be confused with the Electrochemical Series, which lists the potentials only of pure metals in equilibrium with standard solutions of their ions.

Galvanic effects can occur on metallic surfaces which contain more than one phase, so that "local cells" are set up on the heterogeneous surface. Localised corrosion cells can also be set up on surfaces where the metal is in a varying condition of stress, where rust, dirt or crevices cause differential access of air, where temperature variations occur, or where fluid flow is not uniform.

(b)   Stimulation of the anodic or cathodic reaction. Aggressive ions such as chloride tend to prevent the formation of protective oxide films on the metal surface and thus increase corrosion. Sodium chloride is encountered in marine conditions and is spread on roads in winter for de-icing.

Quite small concentrations of sulphur dioxide released into the atmosphere by the combustion of fuels can dissolve in the invisibly thin surface film of moisture which is usually present on metallic surfaces when the relative humidity is over 60-70%. The acidic electrolyte that is formed under these conditions seems to be capable of stimulating both the anodic and the cathodic reactions.

In practical terms it is not usually possible to eliminate completely all corrosion damage to metals used for the construction of industrial plant. The rate at which attack is of prime importance is usually expressed in one of two ways:

(1)   Weight loss per unit area per unit time, usually mdd (milligrams per square decimetre per day)

(2)   A rate of penetration, i.e. the thickness of metal lost. This may be expressed in American units, mpy (mils per year, a mil being a thousandth of an inch) or in metric units, mmpy (millimetres per year).

Taking as an example the corrosion of heat exchanger tubes in industrial cooling water a typical corrosion rate in untreated water would be 40-50 mpy (210-260 mdd); the use of a corrosion inhibitor could reduce this to less than 5 mpy (26 mdd). The mild steel tubing used in heat exchangers is a maximum of 200 thousandths of an inch thick, thus with corrosion rates of 40-50 mpy in untreated water, severe problems might be expected within four or five years. If suitable water treatment with corrosion inhibitors is used a life of at least twenty years might be expected. This, of course, is ignoring the fact that at some time before the metal corrodes away the tubing may have thinned to a point where its required mechanical strength is not attained. When designing equipment for a certain service life engineers often add a "corrosion allowance" to the metal thickness, permitting a certain amount of thinning before serious weakening occurs. In a cooling water system the factors influencing the rate of attack are:

(a)   the condition of the metal surface

Corrosion debris and other deposits - corrosion under the deposits, with a possibility of pitting (severe attack in small spots)

(b)   the nature of the environment

pH   - in the range of 4-10 corrosion rate is fairly independent of pH, but it increases rapidly when the pH falls below 4.

Oxygen content   - increase in oxygen concentration usually gives an increase in corrosion rate.

Flow rate   - increased water flow increased oxygen access to the surface and removes protective surface films, so usually increases corrosion, but can sometimes improve access for corrosion-inhibiting reactants.

Water type   - very important, in general low corrosion rates are found with scale-forming (hard) waters. Aggressive ions which accelerate corrosion are Cl^-, SO_4^{2-} but quite complex interactions may occur between the various dissolved species in natural waters.

CORROSION PREVENTION

By retarding either the anodic or cathodic reactions the rate of corrosion can be reduced. This can be achieved in several ways:

1.   Conditioning the Metal

This can be sub-divided into two main groups:

(a)   *Coating the metal*, in order to interpose a corrosion resistant coating between metal and environment. The coating may consist of:

(i)   another metal, e.g. zinc or tin coatings on steel,
(ii)   a protective coating derived from the metal itself, e.g. aluminium oxide on "anodised" aluminium,
(iii)   organic coatings, such as resins, plastics, paints, enamel, oils and greases.

The action of protective coatings is often more complex than simply providing a barrier between metal and environment. Paints may contain a corrosion inhibitor (see Section 2): zinc coating in iron or steel confers cathodic protection (see Section 3).

(b) *Alloying the metal* to produce a more corrosion resistant alloy, e.g. stainless steel, in which ordinary steel is alloyed with chromium and nickel. Stainless steel is protected by an invisibly thin, naturally formed film of chromium sesquioxide Cr_2O_3.

2. Conditioning the Corrosive Environment

(a) *Removal of Oxygen*

By the removal of oxygen from water systems in the pH range 6.5-8.5 one of the components required for corrosion would be absent. The removal of oxygen could be achieved by the use of strong reducing agents e.g. sulphite.

However, for open evaporative cooling systems this approach to corrosion prevention is not practical since fresh oxygen from the atmosphere will have continual access.

(b) *Corrosion Inhibitors*

A corrosion inhibitor is a chemical additive, which, when added to a corrosive aqueous environment, reduces the rate of metal wastage. It can function in one of the following ways:

   (i) anodic inhibitors – as the name implies an anodic inhibitor interferes with the anodic process.

$$Fe \rightarrow Fe^{++} + 2e^{-} \qquad (1)$$

   If an anodic inhibitor is not present at a concentration level sufficient to block off all the anodic sites, localised attack such as pitting corrosion can become a serious problem due to the oxidising nature of the inhibitor which raises the metal potential and encourages the anodic reaction (equation 1). Anodic inhibitors are thus classified as "dangerous inhibitors". Other examples of anodic inhibitors include orthophosphate, nitrite, ferricyanide and silicates.

   (ii) cathodic inhibitors – the major cathodic reaction in cooling systems is the reduction of oxygen.

$$\tfrac{1}{2}O_2 + H_2O + 2e \rightarrow 2OH^{-} \qquad (2)b$$

7

There are other cathodic reactions and additives that suppress these reactions called cathodic inhibitors. They function by reducing the available area for the cathodic reaction. This is often achieved by precipitating an insoluble species onto the cathodic sites. Zinc ions are used as cathodic inhibitors because of the precipitation of $Zn(OH)_2$ at cathodic sites as a consequence of the localised high pH. (See reaction 2(b)). Cathodic inhibitors are classed as safe because they do not cause localised corrosion.

(iii) adsorption type corrosion inhibitors– many organic inhibitors work by an adsorption mechanism. The resultant film of chemisorbed inhibitor is then responsible for protection either by physically blocking the surface from the corrosion environment or by retarding the electrochemical processes. The main functional groups capable of forming chemisorbed bonds with metal surfaces are amino ($-NH_2$), carboxyl ($-COOH$), and phosphonate ($-PO_3H_2$) although other functional groups or atoms can form co-ordinate bonds with metal surfaces.

(iv) mixed inhibitors – because of the danger of pitting when using anodic inhibitors alone, it became common practice to incorporate a cathodic inhibitor into formulated performance was obtained by a combination of inhibitors than from the sum of the individual performances. This observation is generally referred to a 'synergism' and demonstrates the synergistic action which exists between zinc and chromate ions.

3. Electrochemical Control

Since corrosion is an electrochemical process its progress may be studied by measuring the changes which occur in metal potential with time or with applied electrical currents. Conversely, the rate of corrosion reactions may be controlled by passing anodic or cathodic currents into the metal. If, for example, electrons are passed into the metal and reach the metal/electrolyte interface (a cathodic current) the anodic reaction will be stifled while the cathodic reaction rate increases. This process is called cathodic protection and can only be applied if there is a suitable conducting medium such as earth or water through which a

current can flow to the metal to be protected In most soils or natural waters corrosion of steel is prevented if the potential of the metal surface is lowered by 300 or 400 mV. Cathodic protection may be achieved by using a DC power supply (impressed current) or by obtaining electrons from the anodic dissolution of a metal low in the galvanic series such as aluminium, zinc or magnesium (sacrificial anodes). Similar protection is obtained when steel is coated with a layer of zinc. Even at scratches or cut edges where some bare metal is exposed the zinc is able to pass protective current through the thin layer of surface moisture.

In certain chemical environments it is sometimes possible to achieve anodic protection, passing a current which takes electrons out of the metal and raises its potential. Initially this stimulates anodic corrosion, but in favourable circumstances this will be followed by the formation of a protective oxidised passive surface film.