The Corrosion Process

Revision 1

Cathodic Protection

All immersed & buried metals are susceptible to corrosion if they are not in a state of equilibrium with their environment. The corrosion is electrochemical in nature and occurs in natural, salt water & soils with all but noble metals.

Corrosion, can however, be suppressed if the metallic surfaces can be lowered to a state of electrochemical stability. This can be achieved either by enveloping the material beneath a stable passive protection film or by reducing the metal’s theremodynamic activity to a level at which the energy is insufficient for the corrosion reaction to proceed.

In the latter case protection can be achieved either by means of galvanic action or by the influence of impressed direct current (dc).

Suppression of corrosion by such means is termed as **Cathodic Protection.**

Electrochemical Theory of Corrosion

The corrosion of a metal may be summarised as the change from the metal to the metalion or the loss of one or more electrons from the metallic atom as follows.

$M \rightarrow Mn \quad + \quad ne-$ ..(a)

Metal → Positively charged metal ion +

- Negatively charged electrons

Substituting for Fe or steel we have

$Fe \rightarrow Fe{+}{+} \quad + \quad 2e-$ ...(b)

If a piece of iron is placed in water, the metallic iron goes into solution as ferrous ions and the metal assumes a negative charge from the excess electrons that remain. The passage of the metallic atom into the solution as an ion is thus equivalent to a flow of electric current from the metal into the solution.

$(Fe{+}{+} \; + \; 2e-)$ ...(c)

Solution	Metal
Fe++ ions	→ 2e – electrons current flow

The piece of metal or electrode at which current flows from the metal into the solution or electrolyte, is called the anode and the metal electrode where the current flows from the electrolyte onto the metal, is called the cathode.

Therefore, in the electrolyte, current flows from the anode to the cathode, whilst in the electrical circuit it flows (or is made to flow) from the cathode to the anode.

The two electrodes, anode and cathode, and the electrolyte form a cell in which the anode is the corroding electrode and the cathode the protecting electrode. In a cell which has iron (or carbon steel) electrodes and a dilute solution of common salt (or seawater) as the electrolyte the reactions would be –

(a) At the anode the iron would corrode thus

$\mathrm{Fe} \rightarrow \mathrm{Fe}{+}{+} + 2e-$

(b) At the cathode either hydrogen would be evolved thus

$2e + 2\mathrm{H} \rightarrow 2\mathrm{H} \rightarrow \mathrm{H2}$

or, the available oxygen would be converted thus

$\mathrm{H20} + 2e + 1/202 \rightarrow 2(\mathrm{OH})-$

Potential Series

If two pieces of different metals, say iron and copper, are immersed in a salt solution containing ions of both metals, then an electrical difference will exist between them and if they are connected electrically, current will flow between them. Each piece metal in the electrolyte will corrode on its surface and the metal will go into solution as positively charged ions and leave the remainder of the metal negatively charged. The negatively charged metal will attract the positively charged ions and so reduce the tendency for further corrosion of the metal. A balance will be reached when the metal has sufficient negative charge to attract as many positive ions back to its surface as are naturally formed by the metal corroding.

The two metals immersed in the salt solution will come to equilibrium most probably at different electrical potentials when they can be potentionmetrically measured. By this method an electrochemical series of metals and alloys can be established; those metals or alloys having a more negative potential are considered to be anodic whilst those having a more positive potential are considered to be cathodic. When any two metals are joined together in an electrolyte, the metal more negative will be the anode and hence corrode; also, the further the metals are from each other in the series, the greater will be the degree of corrosion of the anodic metal ignoring geometrical and size differences of anode and cathode; the other factor to be considered is the resistivity of the electrolyte, where low resistivity enhances the rate of corrosion whilst high resistivity retards it, as, for example, in high purity water. This helps to explain why corrosion occurs more readily in seawater and protective measures (such as cathodic protection) are necessary, whereas in fresh water, generally, the corrosion rates are not as aggressive.

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Corrosion takes many forms depending on the nature of the metal, the homogeneity of its structure, the nature of the corrosive medium, the galvanic effects between dissimilar metals, possible stray currents from external sources and many other factors. Where possible, the likelihood of corrosion attack and subsequent plant failure is avoided by the correct selection of materials for a particular service. However, in many instance, economics and strength dictate that steel be used for the construction material, especially in the case of large ships, offshore platforms and pipelines. Steel, of all the common construction materials is one of the most susceptible to corrosion attack under many conditions and, if adequate precautions are not taken, failures due to severe corrosion can result in interruptions or loss of plant operations and in extreme cases, loss of life.

Conditions Under Which Corrosion Occurs:

For a metal to suffer from galvanic corrosion, certain conditions must be met. These are:

1. There must be an anode and a cathode.

2. An electrical potential difference must exist between the anode and the cathode. (This potential can result from a variety of conditions such as non-uniform distribution of elements within structural steels, or through the proximity of dissimilar metals).

3. There must be an electrical continuity between the anode and the cathode (This can be the structural steel itself, or direct contact between dissimilar metals).

4. The anode and the cathode must be immersed in an electrically conductive electrolyte such as water, soil or concrete. For corrosion to occur, this immersion need not be continuous.
5.

Once the above conditions are met, an electric current will flow between anode and cathode and metal will be consumed at the anode.

The Nature of Corrosion Attack

The amount of metal consumed during the corrosion process is generally dependant on the amount of current flowing between the anode and cathode, and the type of metal suffering from corrosion attack.

Using steel as an example, one ampere of current discharging from an anodic area will result in consumption (corrosion) of approximately 9 kilograms of steel in one year. If the anodic area of the steel was very small in relation to the cathodic area, this would result in extremely severe localised corrosion and deep penetration of the steel within a very short period. Fortunately, corrosion currents of this magnitude are seldom encountered. However, even a very low corrosion current of say 1 milliamp, if restricted to a very small anodic area, could result in severe pitting and deep penetration of the steel over a number of years. Conversely, if the anodic area is very large in relation to the cathodic area, the current flow from the anode is very low in terms of current density per unit area, and any corrosion that occurs will be lower as consumption of the steel will be evenly distributed over the whole of the anodic area.

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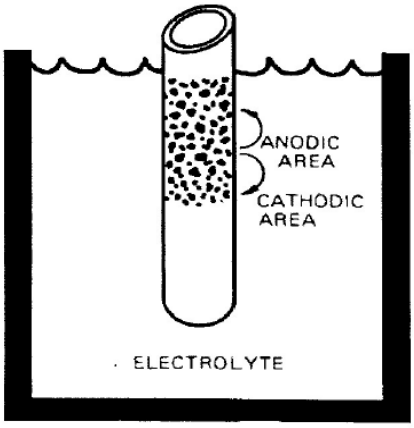


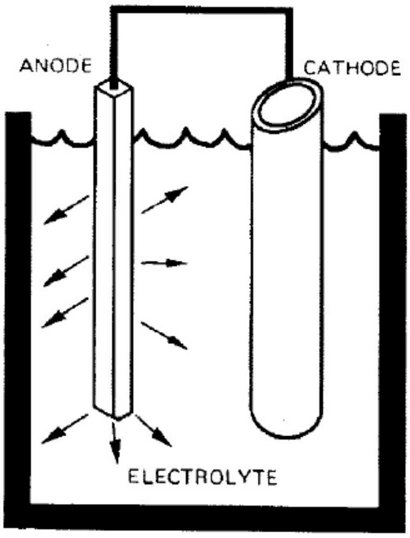
A Typical Corrosion Cell

Cathodic Protection

As corrosion occurs where current flows from the metal, and does not occur where the current is collected or flows into the metal, it follows that if current is caused to flow onto the entire metal surface then corrosion will cease. This is the basis of Cathodic Protection.

Cathodic Protection Methods

The necessary current required to prevent corrosion be provided by one of the two methods. The first method is to provide a metal of more negative value in the galvanic series than the metal to be protected. This additional metal will become the anode in the corrosion cell and will be consumed whilst flowing current into the cathode (this is the whole of the metal being protected). Metals used in this way are normally referred to as sacrificial anodes. Typical metals used as sacrificial anodes are alloys of zinc, aluminium and magnesium.

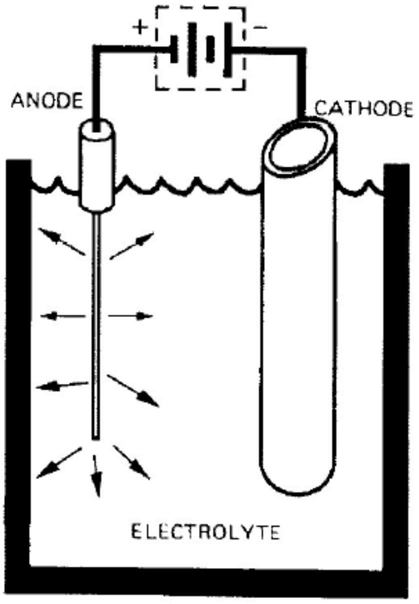


Neutralising a Corrosion Cell Using a Sacrificial Anode

The second means of providing cathodic protection is by the impressed current method where an external source of d.c. current is used to pass current through anodes manufactured from materials such as platinum, high silicon iron titanium MMO and others. The anode materials normally utilised for impressed current systems have a very low consumption rate for a given current output compared to sacrificial anode materials, and systems designed to provide very long service.

Cathodic Protection & Coatings

Cathodic Protection can be utilised as the sole means of preventing corrosion on a buried or submerged structure, or alternatively can be used in conjunction with a suitable protective coating to provide a combined anti-corrosion system. In a combined system, the main corrosion protection is provided by the applied coating and cathodic protection is used to prevent corrosion of the structure in areas of coating damage (defect), and to counteract the gradual deterioration of the coating system over a period of time.



Neutralising a Corrosion Cell by Using Impressed Current Systems

Choice of Cathodic Protection Systems

Generally, sacrificial anode cathodic protection systems are preferred where current and life requirements are low, or for larger systems where maintenance of the system during its operational life would be difficult or impractical. Impressed current cathodic protection systems tend to provide a more economic solution to corrosion problems where current and life requirements are high and where maintenance requirements for this type of system do not present problems. Additionally, because the current to the anodes is provided from an external power source, it is possible to achieve finer control of the system output to suit any changes in the operational environment over the life of a structure.