

**CORROSION**

As the photograph clearly demonstrates, corrosion can be a major problem. In fact, it is reasonable to say that the single most important reason to paint a ship is to prevent corrosion.

For marine applications, mild steel remains the number one metal for constructional purposes by virtue of its relatively low cost, mechanical strength and ease of fabrication. Its main drawback is that it corrodes easily in seawater and unless adequately protected, rapidly loses strength which may result in structural failure.



Severe corrosion in a cargo hold

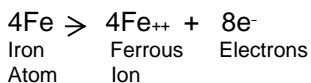
In general terms corrosion can be defined as the spontaneous reaction between a material and its environment which results in the degradation of that material. To be more specific, metallic corrosion is the oxidation of the metal at the metal/environment interface. This reaction subsequently results in a deterioration in the mechanical properties of the metal.

The majority of metals in nature are found in their mineral state, i.e. in their stable oxidised condition as oxides, chlorides, carbonates, sulphates, sulphides, etc. The extraction of a metal from the appropriate mineral involves a reduction process in which a great deal of energy is absorbed. As a consequence of this large energy input the metal is in a high energy condition and will endeavour to return to its former stable, oxidised, low energy state as quickly as environmental conditions will allow. It is the energy difference between the pure metal and its oxidised forms which is the driving force for corrosion.

**Corrosion mechanism**

Mild steel is an impure, heterogeneous material. This is a major factor contributing to its poor resistance to corrosion. The presence of what are referred to as anodic and cathodic sites on the steel surface and their reaction with oxygen and water results in the transformation of a metal atom to a metal ion by the loss of electrons i.e.

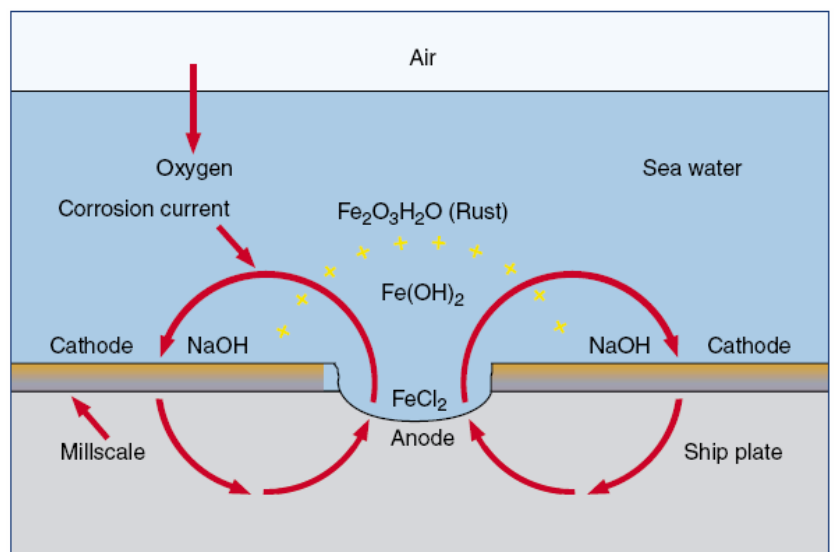
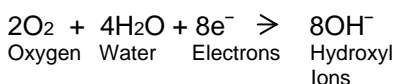
**Anodic Reaction:**



This process is referred to as electrochemical corrosion.

The reaction can only occur if there is a suitable electron acceptor to combine with the electrons released by the iron atom. Seawater contains dissolved atmospheric oxygen which readily serves this purpose. The oxygen is electrochemically reduced to hydroxyl ions in the cathodic reaction.

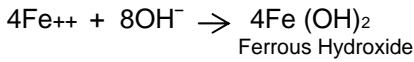
**Cathodic Reaction:**



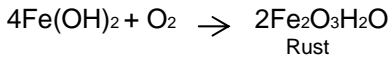
Corrosion mechanism

(The heterogeneous character of steel allows for some sites to favour the anodic reaction and for others to favour the cathodic reaction).

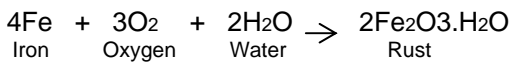
The ferrous ions and hydroxyl ions formed combine together to produce ferrous hydroxide:



The ferrous hydroxide formed reacts with more oxygen to form hydrated ferric oxide, the familiar reddish brown rust.



In theory, all of these reactions occur simultaneously and can be simply represented as:



In reality, the process is not so simple. Corrosion, and the rate at which corrosion occurs in seawater for example is dependant upon many factors, including oxygen concentration, pH (acidity/alkalinity), water temperature and the presence of dissolved salts such as chloride, sulphate, and sulphites.

Indeed, there are many different types of corrosion including pitting corrosion and bacterial corrosion, both of which are particularly relevant for the marine industry.

### Pitting corrosion

The main characteristic of this type of corrosive attack is that it is extremely localized and steel penetration can be deep in relation to the area under attack. This is one of the most dangerous forms of corrosion and can be most intense on millscaled or coated steel.



Pitting and corrosion in a ballast tank



Pitting and corrosion in a crude oil tank

### Bacterial corrosion

Also referred to as micro-biological corrosion or anaerobic (without oxygen) corrosion, this type of corrosion may occur if local operating conditions support bacterial activity. The following list summarises the principal requirements for bacterial corrosion to occur:

- stagnant (anaerobic) water
- a hydrocarbon food source e.g. oil or coatings
- the presence of sulphates
- an operating temperature between 20-40°C
- presence of bacteria



Pitting and corrosion in a crude oil tank after preparation by hydroblasting



Ballast tank after 5 years in service with an abrasion resistant aluminium pure epoxy system

Attack typically occurs in oil tanks, ballast tanks and cargo pipework

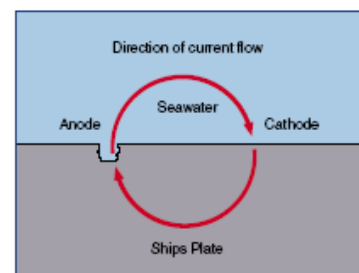
### Corrosion prevention

Preventing corrosion requires the elimination or suppression of the chemical reactions described earlier. There are two principal methods, usually used in conjunction, cathodic protection and coatings.

### Cathodic protection

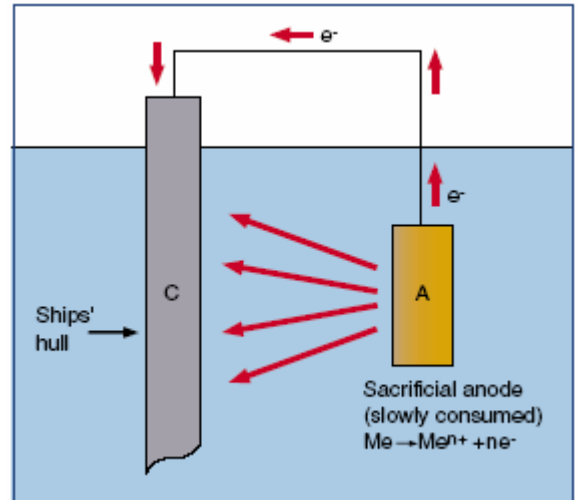
The objective with cathodic protection is to suppress the electrochemical reaction taking place at the anode. Under normal corrosive conditions, current flow from the anode results in a loss of metal at the anodic site with resultant protection of the metal at the cathodic site.

By making the structure you wish to protect cathodic, protection can therefore be provided. There are two methods commonly used to do this:



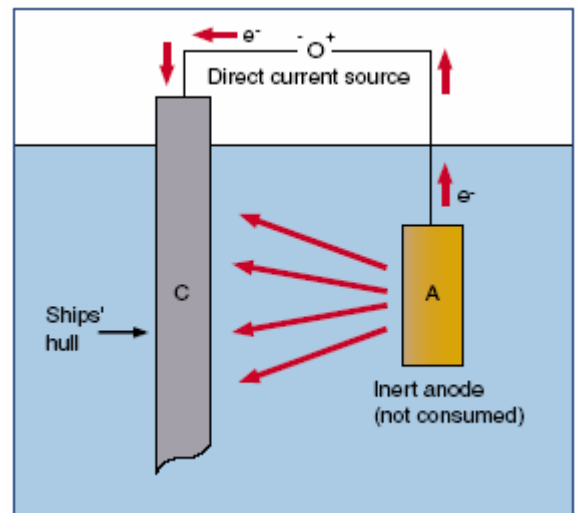
**Sacrificial anodes:**

When a metal corrodes it takes up its own electrical potential known as the corrosion potential with respect to a fixed reference. When two dissimilar metals are connected in seawater, the metal with the lowest potential will suffer the greatest corrosion (for more information, not included here, check information on the 'electrochemical series'). In simple terms, the affinity of a metal to return to its natural stable state (as described earlier) can be advantageously used in cathodic protection. Metals such as zinc and aluminium have a greater desire to return to their natural state than mild steel. The corrosion rate of mild steel can therefore be controlled by connecting it to for example, zinc, which will then become the anode and corrode in preference to the steel. In this example, the zinc anode is referred to as a sacrificial anode because it is slowly consumed (corrodes) during the protection process. It should be noted that if the mild steel has a lower potential than other connecting metals, e.g. stainless steel heating coils in a cargo tank, under the right conditions, the mild steel will corrode preferentially.



**Impressed current systems:**

In the same way that coupling mild steel to zinc results in a flow of electrons (and hence protection) to the mild steel, the structure can also be made cathodic by using a direct current source. An auxiliary anode made from a non consumable material replaces the anode of the sacrificial system. In this example, the anode is permanent and is not consumed during the protection process. Another example of the use of cathodic protection is the galvanising of steel using a thin layer of metallic zinc. Generally, cathodic protection systems are used in conjunction with coating systems.



**Coatings**

The effectiveness of coatings in preventing corrosion depends upon many factors, for example, coating type, end use and operating environment. Many theories exist to explain the mechanics of corrosion protection by coatings.

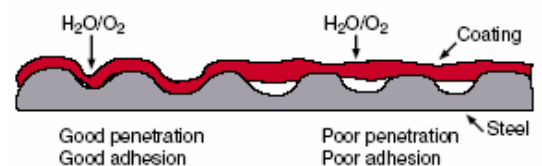
**Intact coatings**

Until about 30 years ago the predominant coatings protection theory was that coatings simply acted as a barrier to oxygen and water. Subsequent research has proven that oxygen and water, at a level sufficient to initiate the corrosion reaction, can indeed permeate through intact coatings.

Current theories propose that water permeating through a coating to the steel surface can cause displacement of the coating from the steel allowing corrosion to occur. Low permeability and good 'wet adhesion' i.e. adhesion under immersion, are widely believed to be the single most important aspects of corrosion control by coatings.

**Adhesion**

For maximum coatings adhesion steel surfaces must be clean, dry and free of oil, rust, salts and other contaminants. Whilst increasing surface roughness results in a greater surface area and potentially increased coatings adhesion, this is not always the case. If the coating does not 'wet out' and penetrate into all of the pores/crevices on the steel surface there will be areas of coating not in direct contact with the steel. In such cases more rapid oxygen and water passage through to steel will occur, resulting in corrosion and subsequent coating detachment.



Penetration of the coating into the surface or roughness profile can be improved by:

- reducing the relative surface tension of the coating
- reducing the coating viscosity
- modifying the coating solvent blend
- increasing coating curing time
- increasing coating application temperature

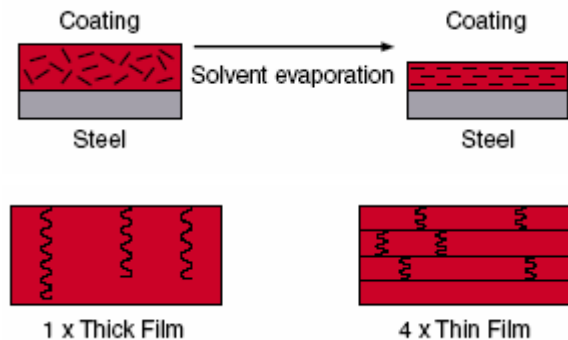
## Permeability

Highly cross linked, chemically curing systems are likely to have relatively low permeability characteristics. Pigmentation can also have a significant effect. Coating permeability decreases as a function of increasing pigment volume in the film up to a critical pigment volume concentration (CPVC). Pigment levels above the CPVC will result in voids in the coating and permeability will increase.

Pigment shape is also important with thin/flat (lamellar) pigment particles being preferred. The reason for this is that in solvent borne coatings, solvent evaporation causes the film to shrink and this results in the alignment of these lamellar pigments parallel to the surface, restricting the passage of oxygen and water. The most effective lamellar pigments are leafing aluminium flake and micaceous iron oxide.

Film thickness can also affect coatings permeability. In general, thicker films delay (but do not stop) the passage of oxygen and water to the steel surface. This is because in all coating films microscopic defects are present which can penetrate to the steel surface and act as conduits for oxygen and moisture. High film thickness (>400 um dft) can therefore offer a high degree of corrosion protection but this would best be achieved in multi-coat systems rather than in a single coat. High film thickness single coat (or some two coat specifications) also have disadvantages as, subject to coating type and formulation, solvent entrapment may occur which can lead to blistering.

Equally, high film thickness may also be a problem on complex structures e.g. ballast tanks and may result in cracking of the coating and subsequent corrosion.



## Non-intact (damaged) coatings

Coatings in service e.g. cargo hold coatings, deck coatings and hull coatings will be subjected to mechanical damage. Maintaining corrosion protection can therefore best be achieved by using coatings which offer both abrasion resistance and corrosion protection (see pages 14 and 15).

It is also recommended that coatings have good 'undercutting' resistance i.e. resistance to under film corrosion creep at damaged areas and have good resistance to the alkaline hydroxyl ions produced during the corrosion process.

Other mechanisms used to prevent corrosion in non-immersed, above water areas include:

- the use of anticorrosive pigments such as zinc phosphate. This pigment is slightly soluble and can form a corrosion inhibiting molecular layer at the steel surface.
- the use of metallic zinc as a sacrificial pigment, in essence the development of an "in situ" cathodic protection system.

With corrosion potentially costing the marine industry billions of dollars per year, effective corrosion control measures, including the correct choice of coating system, should be very carefully considered.