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Corrosion – Its Causes and Prevention in Heating & Cooling Systems

P. Munn Ph.D, C.Eng. MIM, MICorr, MWMSoc

Introduction

With the exception of inert metals like gold and platinum, in order to reduce ores to pure metal to use commercially or for making alloys, we have to expand a lot of energy. Corrosion is the natural process whereby metals in contact with the environment revert back to the thermodynamically more stable state of oxides, hydroxides, sulphates or other compounds. The rate of this process is determined by the kinetics of different anodic and cathodic reactions, which take place on the metal surface. This is influenced by many factors including temperature, water composition, pH and the presence and nature of surface films. Some of these factors may be out of our control but we may be able to reduce the rate of corrosion to an acceptable level by use of corrosion protection methods. These include paints and other coatings, cathodic protection and use of corrosion inhibitors.

Most people think of corrosion as rusty steel or iron. However, corrosion can occur on all common metals and can take many forms. Besides general corrosion, localised corrosion (which includes pitting, crevice and stress corrosion) can take place. Localised corrosion is usually much more serious as it can cause leakage and catastrophic failure in appliances and systems. The corrosion damage due to general corrosion may result in build up of corrosion products or sludge causing poor flow and blockages.

Corrosion Reactions

Aqueous corrosion processes involve both anodic (oxidation) and cathodic (reduction) reactions. There may be more than one of each but, in a freely corroding situation, the sum of the anodic currents are always equal to the sum of the cathodic currents.

Anodic processes are usually the metal dissolution reactions, which cause metal loss from the surface.

$$M \rightarrow M^{z+} + ze^- \qquad \text{I}$$

e.g. for iron $Fe \rightarrow Fe2+ + 2e-$ II

The electrons produced by the anodic reactions are consumed at the cathode. In acidic solutions, the predominant cathodic reaction is hydrogen ion reduction,

$$2H^+ + 2e^- \rightarrow H_2 \qquad \text{III}$$

but in waters of near neutral pH it is dissolved oxygen reduction.

$$2H_2O + O_2 + 4e^- \rightarrow 4OH^- \qquad \text{IV}$$

giving an overall reaction;

$$Fe + ½\ O_2 + H_2O \rightarrow Fe\ (OH)_2 \qquad \text{V}$$

Ferrous hydroxide reacts further building up the final corrosion product Fe_3O_4 (magnetite) in the following two ways:

With excess of oxygen:

$$3Fe(OH)_2 + ½\ O2 \rightarrow Fe_3O_4 + 3H_2O \qquad \text{VI}$$

or, in anaerobic conditions, according to the Schikorr reaction

$$3Fe(OH)_2 \rightarrow Fe_3O_4 + 2H_2O + H_2 \qquad \text{VII}$$

The corrosion product films formed on the metal surfaces offer varying degrees of protection from further corrosion. The best protection is formed by so-called passive films, which are microscopically thin, adherent layers on the surface. Classic examples of this are chromium rich passive layers on stainless steels and alumina (Al_2O_3) passive films on aluminium. Magnetite, on unalloyed steel, may form as passive layers or as loose corrosion debris depending on the circumstances. Copper pipes are protected in water systems by the build up of copper oxide/carbonate layers, although these are not true passive films.

In general corrosion, anodes and cathodes are dispersed over the whole surface of the metal and move around. In localised corrosion, however, small areas become anodic and are surrounded by much larger cathodic areas. This results in pitting attack, especially where passive films have become disrupted. Due to hydrolysis of metal cations, e.g. in the case of aluminium,

$$2Al^{3+} + 3H_2O \rightarrow Al_2O_3 + 6H^+ \qquad \text{VIII}$$

the pH within the pit becomes acidic and the anodic current draws in aggressive anions such as chlorides. Pit propagation then becomes autocatalytic leading to rapid attack. If the pits do not repassivate or are not stifled by corrosion products, then wall penetration will eventually occur.

Corrosion in Once-Through Water Systems

In once-through water systems, such as domestic drinking and hot water systems and in large cooling systems where river water is used for cooling, the water is usually saturated or nearly saturated with dissolved oxygen. This means that there is always sufficient reducable species, i.e. O_2, available to drive any anodic reactions if they are possible. Therefore, more care has to be made in the choice of metals and alloys used in construction. In general, unalloyed steels are usually avoided in favour of copper and copper alloys, aluminium, galvanised steel and stainless steels. However, even these materials are not immune for corrosion damage in adverse circumstances. Copper, for instance, can undergo various forms of pitting attack and erosion corrosion depending on water composition, temperature and flow conditions. At high chloride levels, both aluminium and stainless steels, suffer from pitting attack.

The direct coupling together of dissimilar metals, especially with widely varying electrochemical potentials should be avoided otherwise galvanic corrosion on the more active metal will occur. At the active end of the galvanic series is zinc, followed by aluminium and steel, whilst copper and brasses are at the more noble end. This means that galvanised steels and aluminium should never be connected to copper pipework in these systems.

Indirect galvanic action may also occur where there is no direct contact between the two metals. If copper ions enter solution, they will plate out on more noble metals downstream such as galvanised steel and aluminium forming efficient local cathodes on the surface of these metals and causing pitting attack. Therefore, if used, copper and copper alloys should always be downstream of more active metals.

Flow conditions may have a strong influence on the corrosion processes that take place. At high flow rates, turbulent flow may give rise to the phenomenon of erosion corrosion. However, low flow conditions may allow debris to settle in pipework and result in under deposit corrosion. In addition, periods of stagnation help stabilise local corrosion cells increasing the risk of pitting attack.

Corrosion in Recirculating Systems

In recirculating systems, conditions are different than in once-through systems in several respects with regards to the likelihood for corrosion damages. Firstly, oxygen levels in these systems are generally much lower, allowing more widespread use of unalloyed steels to be used. Secondly, the water composition, can vary substantially from the original filling or make-up water. However, corrosion debris is not removed from the system but continues to build-up or recirculate and this means that these systems are generally less tolerant of corrosion than once-through systems.

For recirculating heating and cooling systems, the primary corrosion protection method should be the avoidance of oxygen ingress. However, this is not easy to obtain, even in so-called sealed systems, especially in the case of large systems. Oxygen can enter systems in many ways, viz:

- as dissolved oxygen in the filling and make-up water
- by diffusion via an open expansion system
- through gaskets and 'O' rings on valves in the case of negative pressure
- by diffusion through non-barrier plastic pipes, rubber hoses or membranes of air-filled expansion vessels

Leakage due to wall perforation is unusual, except in case of gross aeration faults. However, secondary corrosion damages due to the effects of slow build up of corrosion products is not uncommon. This can manifest itself in blockages of pumps and valves, reduced circulation, reduced efficiency of heat exchangers and boiler noise.

Systems containing large amounts of steel or cast iron, may slowly build-up large amounts of magnetite sludge according to equations V and VI or VII. Alumina, because of its high volume compared to the mass of aluminium dissolved, may result in blockages in water channels on aluminium heat exchangers. Hydrogen produced due to reaction VII, on steel or cast iron surfaces, collects at the tops of radiators and can totally stop any flow in that radiator. Galvanic effects and erosion corrosion, although usually less severe or common than for once-through systems, may also occur in recirculating systems due to oxygen ingress.

For cooling systems containing glycol-based antifreeze, oxygen ingress causes the production of organic acids. Unless treated, this can increase significantly corrosion of ferrous metals, aluminium alloys and copper and copper alloys.

In recirculating systems, as opposed to once-through systems, it can often be economic to prevent corrosion damage due to the use of corrosion inhibitors. Their effectiveness is increased if systems are first cleaned out using a suitable chemical cleanser designed for the purpose. However, the use of inhibitors should not been seen as a substitute for good design and installation practices. The best inhibitors would be multi-component blends giving both anodic and cathodic inhibition for different metal types and which have been shown to not damage non-metallic parts of the system.

Summary

Corrosion is a natural electrochemical process with anodic and cathodic partial reactions. Corrosion can be general or localised, with localised corrosion usually being more damaging. In waters of near neutral pH, dissolved oxygen concentration determines primarily the type and rate of corrosion. Corrosion is also influenced by other factors such as temperature, water composition and flow.

In once-through heating and cooling systems, relatively high dissolved oxygen concentrations mean that material selection is more critical. In closed recirculating systems, care should be taken to minimise oxygen ingress. However, oxygen ingress may still occur leading to build up of corrosion products, which give rise to several problems. This can be prevented or minimised by use of properly designed corrosion inhibitors.