CHAPTER TWELVE Corrosion

SECTION 12.1 What is corrosion?



Figure 1.1 Why do cars rust?



Figure 1.2 A freshly cut piece of sodium with a shiny surface. A few minutes later the surface has corroded.

If you have an old bicycle then you will probably have seen how corrosion can destroy metals. For example, the steel in the cycle chain can slowly turn to rust, making it weaker and weaker until it eventually snaps.

During corrosion, the surface of a metal changes from being an element into a compound. Copper corrodes to form a green copper compound; this can be seen in the copper domes of old buildings which have turned green over the years.

Most metals corrode. However, *different metals corrode at different rates*. In general, the more reactive a metal is, the faster it corrodes. When a piece of sodium is cut open it has a bright, shiny surface, but this becomes dull after a few seconds as the metal corrodes (figure 1.2). Under normal conditions, lead corrodes very slowly and gold does not corrode at all.

The rusting of iron

Iron is the most widely used metal. Remember that steel is made mostly of iron. **Rusting** is the term used for the corrosion of iron (or steel). Only iron rusts; other metals are said to 'corrode'. **Rust** is the name of the compound which is formed when iron corrodes.

The rusting of iron and steel is a major problem. It costs millions of pounds each year to replace rusted cars, bridges, railings, etc. It is important, therefore, to know what causes rusting. The experiment in figure 1.3 gives some clues to this.

Four identical iron nails are placed in test tubes as shown. After one week they are examined to see if they have rusted. The results of the experiment are shown in figure 1.3. Note that in tube 1, calcium chloride is added to remove any moisture from the air. In tube 2 the water is boiled to drive out any dissolved air from the water. The layer of oil stops any air dissolving back into the water.



Figure 1.3 What causes iron nails to rust?

Ouestions

QI Look at the experiment in figure 1.4. Why do you think the second test tube with no iron filings was included?

From this experiment it can be concluded that both air and water are needed for rusting to occur. Also, salt speeds up rusting. In fact, the presence of most soluble ionic substances will make rusting occur faster.

Rusting, therefore, requires air, but which of the gases present in the air does it need? All of them, or just one? The experiment in figure 1.4 shows that oxygen is needed for rusting to take place. As the moist iron filings rust, the water level in the test tube rises. It rises by about one-fifth of the height of the tube – remember that oxygen makes up about one fifth of the air.

From these and other experiments, it can be concluded that for iron to rust, water and oxygen must be present.



Figure 1.5 In which solution has more rusting taken place?

Questions

Q2 Imagine that you have carried out the experiment shown in figure 1.5. What conclusion can you make concerning the results of the experiment?



Figure 1.4 What is required to make the moist iron filings rust?

What happens when iron rusts?

Rusting is a complicated process. However, the first step consists simply of iron atoms losing electrons and forming iron(II) ions:

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

Before the iron atoms can lose electrons, there has to be a substance present to accept them, such as oxygen. An electrolyte must also be present. In Chapter 7 you learnt that an electrolyte is an ionic compound which conducts electricity when dissolved in water. Electrolytes are often present in rain water, therefore an outdoor iron gate will rust quite quickly. Sodium chloride (common salt) is an electrolyte, and so rusting occurs faster when salt is present. For example, car bodies and bicycle frames rust more quickly if salt is spread on the roads in winter.

To find out if rusting is taking place, we can use ferroxyl indicator. This is a pale yellow-coloured solution which turns blue when it reacts with Fe²⁺ ions (the ions which are formed when iron metal starts to rust). In general, the more blue colour there is, the more rusting has taken place (figure 1.5).

Preventing corrosion SECTION 12.2

Physical protection

For a metal to corrode it needs to be exposed to air and water. One way to prevent corrosion is therefore to put a barrier around the metal to keep out air and water. This is why the Forth Railway Bridge girders are painted (figure 2.1). The paint forms a physical barrier which keeps air and water away from the steel underneath. Oil or grease also form a barrier which will cover metal surfaces.



Figure 2.1 The Forth Railway Bridge

Table 2.1 lists some physical barriers which are used to prevent corrosion of metals.

Small metal parts such as bolts and axles are often dipped in molten plastic before being packaged. The plastic solidifies to form a thin, protective layer over the metal. In the case of tin-plating, the metal to be protected is dipped into molten tin. Tin-plating can also be carried out using electrical methods, as described below.

A car body is made of steel. It can be protected against corrosion by dipping it into molten zinc (figure 2.2). This is called galvanising. This covers the steel with a tough layer of zinc. The zinc protects the steel from air and water. Steel objects which are protected in this way are called galvanised steel.



Figure 2.2 The dustbins and the cars are both protected from corrosion by zinc coating

Some motorway crash barriers are made from galvanised steel. The steel in the Forth Road Bridge was protected against corrosion by being sprayed with molten zinc (figure 2.3); 500 tonnes of zinc were used.

Galvanising also protects steel by a method called sacrificial protection – this is discussed later in this chapter.

Electroplating

You may have some gold-plated jewellery or perhaps some silver-plated spoons at home. Gold, silver, chromium and other metals can be deposited as shiny coatings on the surface of other metals. The name for this process is electroplating (figure 2.4).

Physical barriers to corrosion: paint oil or grease

oil or grease plastic coating tin-plating electroplating galvanising

 Table 2.1 Physical barriers preventing corrosion



Figure 2.3 The Forth Road Bridge



the reaction here is $Au^+(aq) + e^- \rightarrow Au(s)$

Figure 2.4 Gold plating a copper earring

The object to be plated (for example, a copper earring) is used as the negative electrode. It is in contact with a solution which contains ions of the metal with which it is to be plated. For example, the copper earring could be put in a solution containing gold ions. Metal ions are positively charged, therefore they are attracted to the negative electrode. When they reach the electrode they gain electrons and form a thin layer of metal. Some examples of reactions taking place at the negative electrode are:

silver-plating	${ m Ag^+}$ + ${ m e^-}$ $ ightarrow$	Ag
copper-plating	$Cu^{2+} + 2e^{-} \rightarrow$	Cu
chromium-plating	$Cr^{3+} + 3e^- \rightarrow$	Cr

Chromium-plating produces a very hard surface. Chromium-plated parts are used in the engines of military helicopters such as the Lynx.

Tin-plating is used to make the material for 'tin' cans. It is carried out by passing a steel strip through a solution containing tin ions. While it is in the solution, the steel is the negative electrode and a thin layer of tin is deposited on the steel.

Direct electrical protection

When a metal corrodes it loses electrons. Therefore, if electrons could be forced back to the metal, it would not corrode. Electrons can be supplied from the negative terminal of any direct current power supply such as a battery. This method of protection is most widely used in cars and trucks where the negative terminal of the battery is connected to the steel bodywork (see figure 2.5). Many piers and jetties and even some ocean liners when they are in port also use electrical protection to cut down on corrosion. While this method slows down corrosion considerably it unfortunately does not stop it completely.

Sacrificial protection

In Chapter 10 you read that all metals tend to lose electrons. When two metals are joined in a simple cell, electrons will flow from the metal which is higher in the electrochemical series to the one lower down in the series.

This fact is used in a method of preventing corrosion called sacrificial protection. For example, zinc is higher in the electrochemical series than iron. If iron is in contact with zinc then electrons will flow from the zinc to the iron and this will help prevent the iron from losing electrons and corroding. Because the zinc loses electrons, it corrodes. In other words the zinc is 'sacrificed' to protect the iron. Magnesium gives an even better protection. It is higher in the electrochemical series than zinc and so it loses electrons more readily.

Figure 2.6 shows how underground pipes such as gas pipes can be protected from corrosion by connecting them to scrap magnesium at regular intervals.



Figure 2.5 Direct electrical protection is being used to cut down the corrosion of this car's bodywork. Notice how the negative terminal of the battery is connected to the car body

Questions

Q1 If cars were to have their bodywork connected to the *positive* terminal of their batteries, what sort of problems would this be likely to cause?

Questions

- **Q2** In 1824 Sir Humphry Davy suggested to the Admiralty that the corrosion of copper parts on wooden ships could be prevented by attaching blocks of zinc to the ships' hulls. Explain why this method worked well.
- Q3 Galvanising gives iron two types of protection from corrosion. What are they?



Figure 2.6 The magnesium corrodes and supplies electrons to the iron in the steel pipe, protecting the pipe from corrosion

Some ships have zinc blocks attached to their hulls to protect against the corrosive action of sea water.

SECTION 12.3 More on corrosion

You have read in section 12.1 that corrosion occurs when metals *lose electrons* and form compounds. For example, magnesium metal atoms corrode as follows:

$$Mg \rightarrow Mg^{2+} + 2e^{-}$$

Reactions which involve a loss of electrons are oxidation reactions. When iron rusts, the initial oxidation reaction is:

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

Rusting is, however, a complicated process which involves more than one step. Further oxidation of the iron(II) ions can occur:

$$Fe^{2+} \rightarrow Fe^{3+} + e^{-}$$

The iron(III) ions which are produced can form iron(III) oxide. This is the substance which we call rust.

When an oxidation reaction occurs there must be a corresponding reduction reaction. In the case of rusting, this involves water and oxygen molecules reacting as follows:

$2H_2O + O_2 + 4e^- \rightarrow 4OH^-$

This reduction reaction helps to explain why water and oxygen are needed for the rusting of iron.

Water is also required because it usually contains electrolytes. As you remember, electrolytes are compounds that dissolve in water to produce ions. For example, carbon dioxide from the air will dissolve in water to form an electrolyte. During rusting, electrolytes assist with the movement of electrons from the iron to the water and oxygen molecules.

In most cases, the higher the concentration of electrolytes present the faster the iron or steel will rust. Common salt (sodium chloride) is an electrolyte and so the presence of salt speeds up rusting.



Figure 3.1 Why does sea water speed up rusting?

Questions

- QI Look at figure 3.3. In which direction would the electrons flow if the magnesium was replaced by copper?
- Q2 Which of the following would speed up the corrosion of iron by acting as electrolytes?
 - a) barium sulphate,
 - b) potassium nitrate,
 - c) calcium carbonate,

d) hydrochloric acid.

Q3 Imagine that a millionaire had a car in which the steel bumpers were gold-plated. What would happen if the gold was scratched and the steel was exposed?

Direction of electron flow during corrosion

A simple chemical cell set up as in figure 3.2 can be used to show that electrons flow away from iron as it corrodes.

In the iron/carbon cell, the blue colour around the iron shows that it is rusting. The milliammeter shows that the electrons are flowing away from the iron towards the carbon. These electrons are produced by the oxidation of the iron. The pink colour around the carbon is due to the formation of OH⁻ ions produced in the corresponding reduction reaction.

In figure 3.3 there is no blue colour around the iron. It has not rusted. This is because electrons have been flowing *towards* the iron from the magnesium. Magnesium is higher than iron in the electrochemical series. The pink colour surrounding the magnesium shows the formation of OH⁻ ions.

In figure 3.4 the rusting of iron is particularly rapid because iron is above tin in the electrochemical series. As a result, electrons flow from the iron to the tin.

This effect is seen with tin-plate, which is made from thin sheets of steel plated with tin. Tin-plate is used to make 'tin' cans for food. If a tin can is badly bashed or scratched the steel may become exposed. Rusting then occurs rapidly as electrons flow from the iron (the main metal in steel) to the tin. In such cases, the iron is 'sacrificed' and the tin is protected.



Figure 3.2 Iron in this cell rusts

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Figure 3.3 Iron in this cell does not rust

Figure 3.4 Iron in this cell rusts badly