

9.5 Corrosion

The reactions that occur when metals corrode are redox reactions. The costs associated with corroding metals are substantial, especially because iron, which is particularly prone to corrosion in the presence of water and oxygen, is so widely used as a structural material for buildings, bridges, gas and water pipes and ships. The effect of corrosion in water pipes is evident in the pumping system shown in Figure 9.5.1.

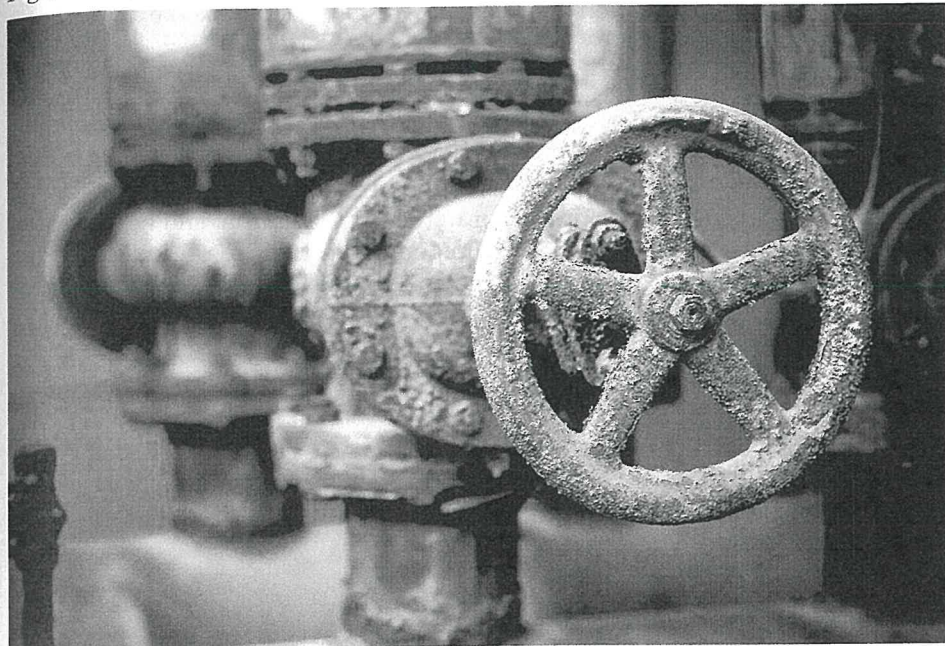


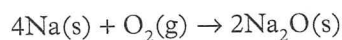
FIGURE 9.5.1 Corrosion is causing water to leak in these pipes in a pumping system.

In Australia, about \$50 billion (approximately 3% of gross domestic product) is spent each year in an effort to prevent metals from corroding and replacing metal that has corroded. In spite of such efforts, steel structures continue to corrode, eventually producing the familiar orange-brown flakes known as rust, although corrosion prevention methods can slow down the rate of corrosion considerably.

In this section, you will use your knowledge of redox chemistry and galvanic cells to consider the chemistry of corrosion. You will look at the redox reactions involved in corrosion both in the presence of water and in the absence of water.

DRY CORROSION

Direct reaction with oxygen in the air to form a metal oxide is known as **direct corrosion** or **dry corrosion**. Sodium is so reactive that it must be stored under oil to prevent contact with oxygen. The following equation represents the dry corrosion of sodium:



Dry corrosion of aluminium forms a tough, impervious coating of aluminium oxide (Al_2O_3), which protects the metal underneath from further contact with oxygen. The aluminium window frame in Figure 9.5.2 is lightweight and corrosion resistant. Therefore, it is an excellent material in situations where maintenance would be difficult.

Iron is much less reactive than sodium or aluminium; dry corrosion of iron is slow at room temperatures. When iron does corrode, it forms a coating that flakes off readily, leaving the metal underneath exposed to further corrosion.

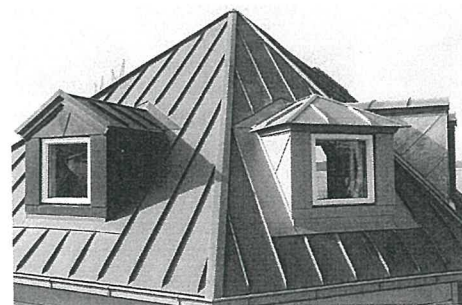


FIGURE 9.5.2 An aluminium window frame is resistant to corrosion and is a useful material in situations where maintenance would be difficult.

WET CORROSION

The presence of moisture accelerates the corrosion of iron. This process is known as **wet corrosion**. The best-known example of wet corrosion is the formation of rust as a flaky, brown-red coating on iron.

Wet corrosion can occur in moist air or by direct immersion in water. Several factors affect the rate at which wet corrosion occurs. Consider the observations represented in Figure 9.5.3.

Each of these observations gives you information about the factors that influence the rate of wet corrosion of iron. In general, corrosion is accelerated by:

- the presence of water
- impurities such as salt and acidic pollutants that dissolve in the water.

However, corrosion can be reduced when the iron is alloyed with certain other materials or when it has a protective coating. You will see this later when the methods of prevention of corrosion are discussed.

In order to understand the process of wet corrosion of iron, and how it can be prevented, it is useful to consider the reactions occurring as a form of galvanic cell, with an anode (oxidation) and a cathode (reduction). The conducting iron allows for electrons to travel between the anode (anodic site) and the cathode (cathodic site).

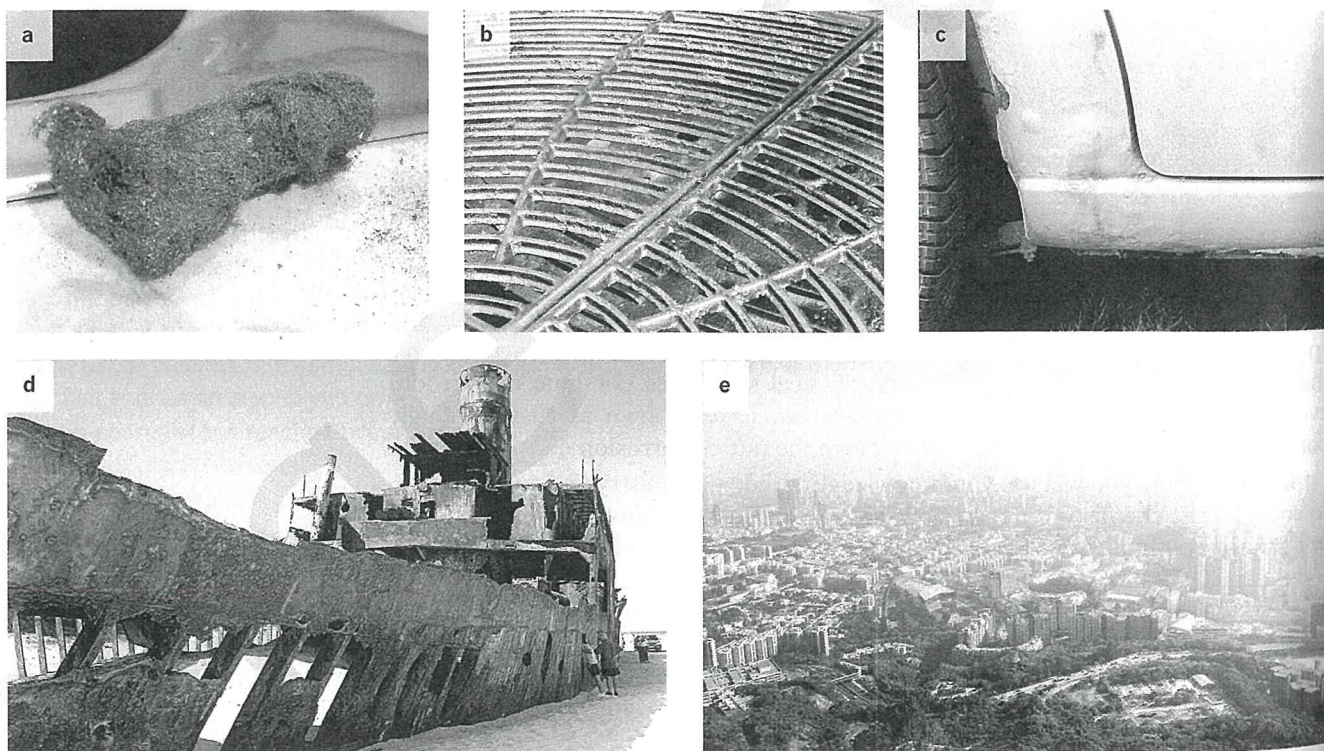
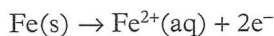


FIGURE 9.5.3 Wet corrosion. (a) A piece of steel wool (iron) does not corrode on supermarket shelves. However, once it becomes wet through use, it corrodes quickly. (b) An iron barbecue grill that has been coated with grease shows little sign of corrosion, even after being exposed to the rain for some time. (c) Rust in a car generally starts inside door frames, under mudguards, or in places where the paint has been chipped. (d) Shipwrecks corrode rapidly and will eventually disintegrate. (e) Corrosion occurs more rapidly in cities with a pollution problem, particularly where the pollutants include acidic oxides such as nitrogen dioxide and sulfur dioxide.

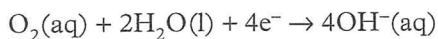
Wet corrosion process

Rust is a hydrated oxide of iron with the formula $\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$. There can be 1–3 water molecules associated with the iron oxide in its structure. An understanding of the steps involved in corrosion helps scientists to identify methods of corrosion prevention.

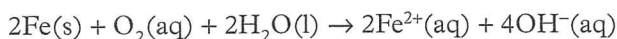
Step 1: Iron is oxidised to form Fe^{2+} ions at one region on the iron surface:



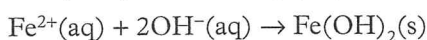
At the same time at another region on the surface, using the electrons produced by the oxidation process, oxygen is reduced in the presence of water to hydroxide ions:



The overall equation for step 1 is:



Step 2: The formation of a precipitate of iron(II) hydroxide:



Steps 1 and 2 of the wet corrosion process are summarised in Figure 9.5.4.

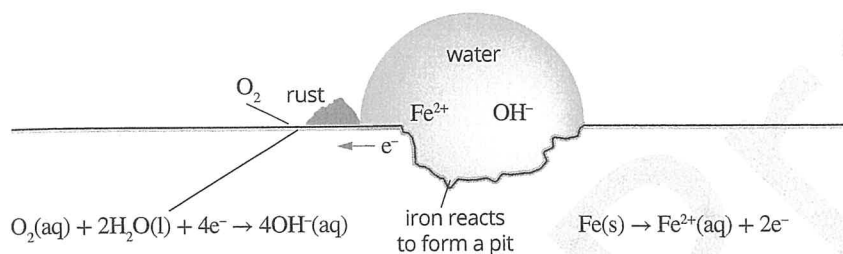
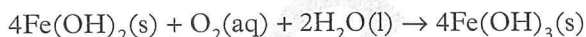


FIGURE 9.5.4 During wet corrosion, electrons are transferred through the iron from the area where oxidation occurs to the area where reduction occurs. Ions flow through the water droplets.

Step 3: Further oxidation of iron(II) hydroxide occurs in the presence of oxygen and water to produce iron(III) hydroxide, a red-brown precipitate:



Step 4: In air, the iron(III) hydroxide loses water to form hydrated iron(III) oxide ($\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$), which is known as rust.

The porous rust easily flakes off the surface of the iron, exposing the iron underneath to further oxidation.

The wet corrosion of iron is accelerated if the water contains dissolved ions. This is particularly evident in coastal areas where iron objects are exposed to seawater. The presence of dissolved ions in the water increases its conductivity, which results in an increase in the rate of iron corrosion.

Prevention of corrosion

There are several ways to protect iron and steel structures against corrosion. These depend on the environment in which the structure is located, the design and intended use of the structure, and the relative costs of various protection measures. All methods will prevent one of the processes described above from happening. If you stop one process, then you will stop the overall rusting process.

The simplest way relies on the creation of a barrier between the iron and oxygen and water to provide a surface protection. Other methods are based on an understanding of the electrochemical nature of corrosion.

Surface protection

Surface protection involves covering the surface of the iron to prevent contact with oxygen and moisture. Materials such as paint and plastic can be used for this purpose. Moving parts, such as a bicycle chain, can be coated with oil or grease to both reduce friction and prevent contact with oxygen and moisture.



FIGURE 9.5.5 These food cans are made from steel that has been plated with tin to prevent them corroding.

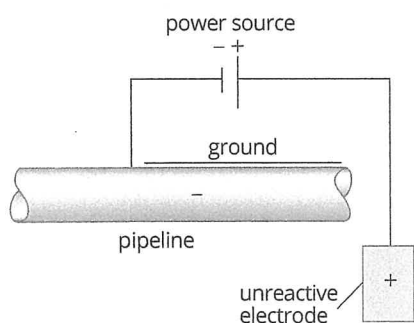


FIGURE 9.5.6 A pipeline carrying natural gas can be protected from corrosion if a direct current source is connected at intervals to give the pipe a negative charge.

Iron can also be protected by alloying with small quantities of metals such as chromium, nickel, manganese or molybdenum to produce stainless steel. The atoms of the metals used to make the **alloy** are all bonded into the metallic lattice. These metals oxidise slightly in air, but the oxide coating produced is continuous and unreactive. This oxide layer protects the metal from further oxidation.

Iron and steel can also be coated with thin layers of less reactive metals in a process known as **electroplating** (see Chapter 10). The ‘tin cans’ used to package food are made from steel plated with tin. Tin is a much less reactive metal than iron and does not corrode greatly in the atmosphere. In addition to the tin coating, cans used for food, such as the ones shown in Figure 9.5.5, have a plastic liner to prevent contact between the food and any metal oxides that may be present.

Electrochemical protection

Cathodic protection involves the use of a low-voltage, direct current (DC) power supply to give the iron being protected a negative charge. For corrosion to occur, the iron normally loses electrons (is oxidised). The act of making the iron negative pushes electrons towards the iron, thus reducing the chance of oxidation occurring. Instead, the iron becomes the site of the reduction reaction, and forms the cathode. This method, represented in Figure 9.5.6, is used to protect large-scale steel structures such as wharves and pipelines. A single DC source operating at 4.2 V and 2.5 A will protect many kilometres of pipeline.

Sacrificial protection also involves the iron acting as the cathode. A more easily oxidised metal, such as zinc, forms the anode and is ‘sacrificed’ in order to protect the iron from corrosion. The more reactive metal loses electrons and forms metal cations in preference to the iron.

Iron that has been coated in zinc is known as galvanised iron and is used widely for roofs and sheds, as shown in Figure 9.5.7a. Galvanised iron is an example of sacrificial protection. When the zinc coating is scratched, the iron is still protected because the zinc loses electrons more readily than the iron. The diagram in Figure 9.5.7b depicts this process. The zinc slowly corrodes but the iron is protected for years.

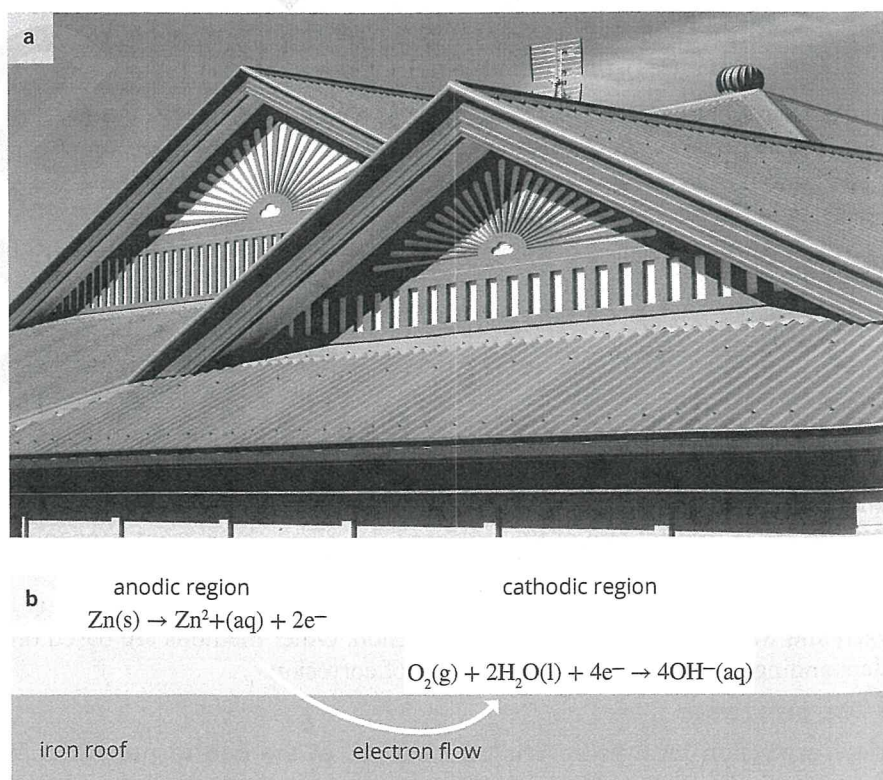


FIGURE 9.5.7 A galvanised iron roof is a common sight in Australia. The zinc coating is oxidised in preference to the iron, protecting the structural role of the iron.

Underground steel pipelines, bridge pillars and the steel hulls of ships can be protected by connecting them to blocks or plates of zinc, or other more reactive metals such as magnesium. Because these metals are more easily oxidised than iron, they lose electrons, which are transferred to the iron where reduction of oxygen and water occurs. The reactive metals, which are called **sacrificial anodes** are eventually consumed and must therefore be replaced, but this is less expensive than replacing the steel structures that are being protected (Figure 9.5.8).



FIGURE 9.5.8 These aluminium sacrificial anodes are attached to the underwater steel structures of offshore gas platforms to protect them against corrosion.

9.5 Review

SUMMARY

- Dry corrosion refers to the oxidation of a metal by oxygen gas.
- Wet corrosion involves both oxygen gas and water and can be considered as an electrochemical process.
- During the wet corrosion of iron, iron is oxidised to $\text{Fe}^{2+}(\text{aq})$ and oxygen gas is reduced to $\text{OH}^{-}(\text{aq})$. These form a precipitate of $\text{Fe}(\text{OH})_2(\text{s})$, which is converted to rust ($\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$).
- Protection measures against corrosion include surface coating, alloying, cathodic protection and the use of a more reactive metal as a sacrificial anode.

KEY QUESTIONS

- 1 Use equations to explain why the corrosion of iron is a redox process.
- 2 Explain why iron corrosion occurs more rapidly in coastal environments.
- 3
 - a Which one or more of the following metals could be used as a sacrificial anode to prevent the corrosion of iron: magnesium, zinc, lead, copper?
 - b Explain your answer to part a in terms of the reactivity series of metals.
- 4 Underwater steel pillars often corrode more rapidly just beneath the surface of the water than above. Suggest a reason for this.
- 5 Explain why it is common for steel nails to be coated with zinc rather than copper or tin.