Topic 12 : Corrosion

Revised March 2002

Corrosion involves oxidation of the metal at its surface. The metal reacts with the oxidising agent(s) and becomes a compound.

Examples :

1. Magnesium corrodes rapidly in dilute acid :

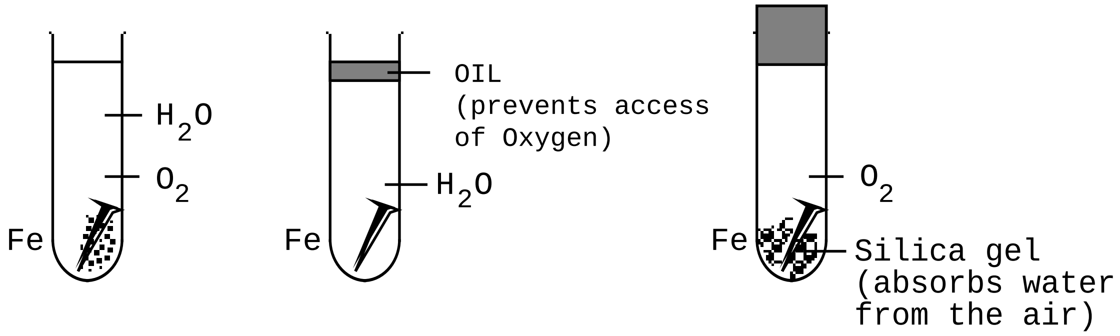
$$Mg + 2\,H^{+}Cl^{-} \rightarrow Mg^{2+}(Cl^{-})_2 + H_2$$

2. Aluminium corrodes slowly in air :

$$4\,Al + 3\,O_2 \rightarrow 2\,(Al^{3+})_2(O^{2-})_3$$

3. Iron corrodes slowly in moist air (Rusting).

Both Oxygen AND Water are required as the following experiment shows :



RUSTING **NO RUSTING** **NO RUSTING**

This is what happens to the Iron :

1. Iron is oxidised in two stages :

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

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

2. The electrons lost by the Iron are picked up by the Oxygen and Water which are therefore reduced in the process :

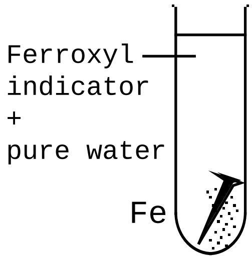
$$O_2 + 2\,H_2O + 4e \rightarrow 4\,OH^{-}$$

3. Hydroxide ions react with Iron(III) ions to form the brown precipitate, Iron(III) hydroxide (rust ?) :

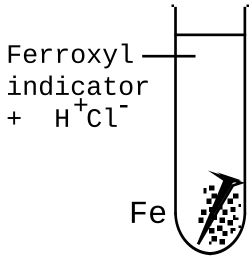
$$Fe^{3+} + 3\,OH^{-} \rightarrow Fe^{3+}(OH^{-})_3$$

Experiment

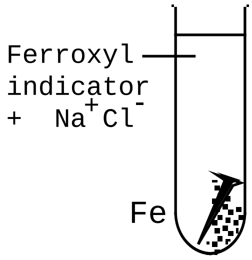
To investigate the effect of (a) acid (b) Sodium chloride on the corrosion of Iron.



SLOW RUSTING



RAPID RUSTING

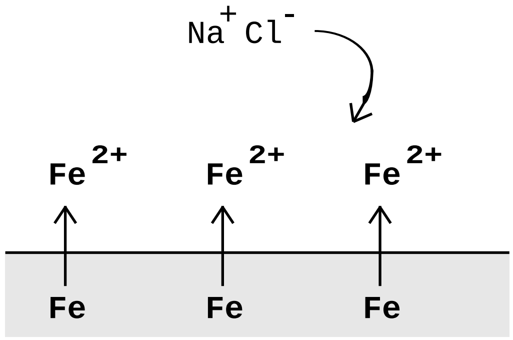


RAPID RUSTING

When the Iron starts to rust, Fe^{2+} ions are formed. These turn Ferroxyl indicator blue. The blue colour appears very quickly when salt and acid are present.

As Iron corrodes an area of positive charge builds up around its surface due to the Iron(II) ions. This repels any additional Iron(II) ions which try to form and thus slows down corrosion.

Both Sodium chloride and Hydrochloric acid are electrolytes. The chloride ions diffuse into the area of positive charge around the Iron, cancelling out the charge and allowing more Iron(II) ions to form e.g.



Salt, spread on roads, increases the corrosion rate of car bodywork.

Acid solutions can speed up corrosion in another way : since Fe is more reactive than H, the Hydrogen ions in the acid can pull electrons off Fe and thus speed up the first step in corrosion :

$2\,H^+ + 2e \rightarrow H_2$

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

Corrosion of Iron is rapid in areas where the rain water is acidic.

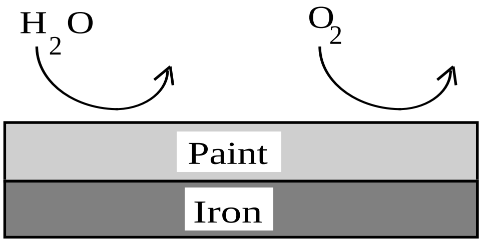
Carbon dioxide speeds up corrosion because it reacts with Water to produce Carbonic acid :

$CO_2 + H_2O \rightarrow (H^+)_2CO_3^{2-}$

Preventing Corrosion

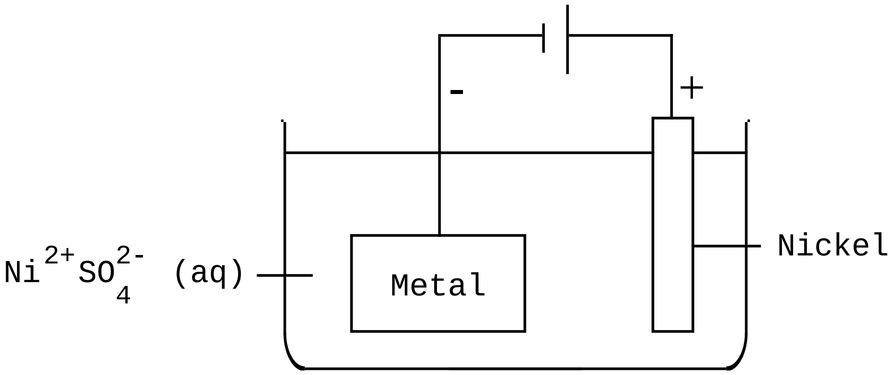
Method 1

Stop the oxidising agents getting to the metal using a barrier e.g. oil, grease, paint, plastic, metal :



Coating with metals is achieved by two methods :

1. If the metal has a low melting point the Iron is simply dipped in the molten metal e.g. tin plating, galvanising (coating with Zinc)
2. By electroplating (using electrolysis) e.g. Nickel plating



At the cathode (-ve) reduction of Nickel(II) ions occurs and the Nickel is deposited on the metal :

$$Ni^{2+} + 2e \rightarrow Ni$$

At the anode (+ve) electrons are pulled off Nickel by the positive charge. Nickel is oxidised and passes into solution as Nickel(II) ions.

$$Ni \rightarrow Ni^{2+} + 2e$$

This replaces Nickel(II) ions reduced at the cathode.

Method 2 (Cathodic Protection)

Electrons are lost during the first step in the corrosion of Iron :

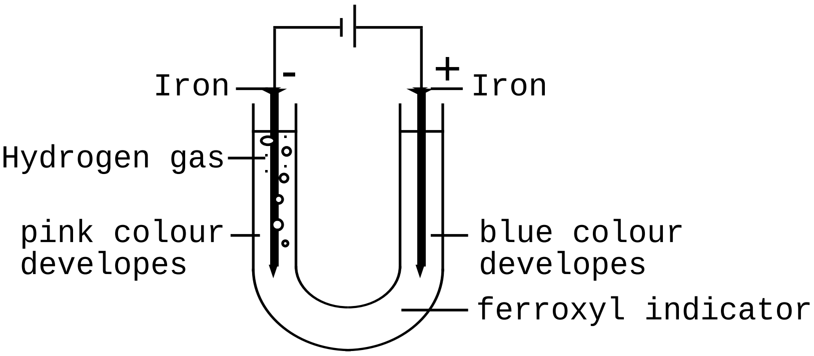
$Fe \rightarrow Fe^{2+} + 2e$

Cathodic protection involves forcing these electrons back on to the Iron i.e. attempting to reverse the first step.

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

This can be done in two ways :

1. By connecting the Iron to the negative terminal of a battery :



At the anode (+ve) electrons are pumped away from the Iron, speeding up the corrosion rate :

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

and leading to the production of Fe^{2+} ions which turn the indicator blue.
At the cathode (-ve) electrons are pumped on to the Iron, slowing down the corrosion rate. NO Iron(II) ions are produced so NO blue colour appears. Instead a pink colour appears !

Remember that Water, due to its ionisation, contains H^+ ions.

$H_2O \rightleftharpoons H^+ + OH^-$

As the electrons are pumped on to the Iron the excess electrons 'spill over' into the solution where they are picked up by H^+ ions in the Water :

$2H^+ + 2e \rightarrow H_2$

Removal of the Hydrogen ions from Water leaves excess hydroxide ions. Hydroxide ions turn Ferroxyl indicator pink.

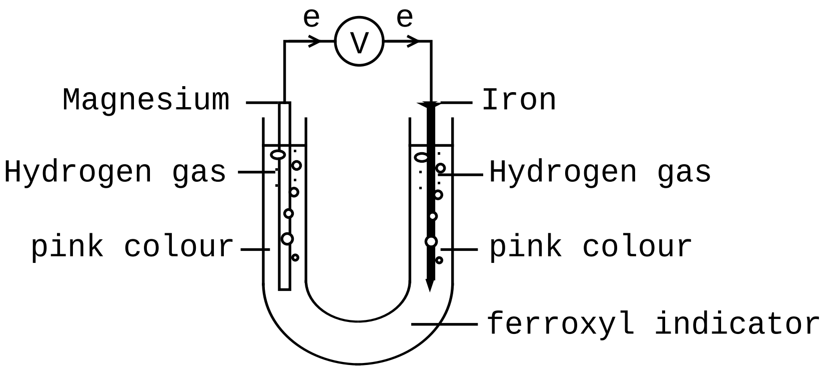
2. By connecting the Iron to a more reactive metal (e.g. Magnesium)

Electrons flow from the more reactive metal (Magnesium) to the less reactive metal's ions (Iron(II)) thus preventing loss of electrons by Iron :

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

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

The direction of electron flow can be shown with a cell :



NO blue colour appears round the Iron so no Iron(II) ions are being produced.

Excess electrons are captured by hydrogen ions in the Water forming Hydrogen gas :

$2\,H^+ + 2e \rightarrow H_2$

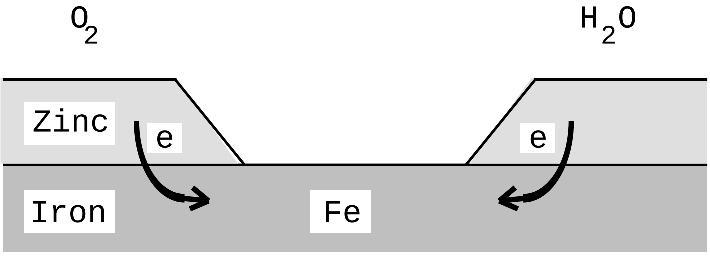
This leaves excess OH^- ions which turn the indicator pink.

Magnesium scrap is connected to oil pipelines made of Iron to prevent corrosion.

Notice that, as a result of protecting the Iron, the Magnesium loses electrons, forms ions and corrodes itself.

The Magnesium therefore sacrifices itself to save the Iron (Sacrificial Protection).

Galvanising (coating with Zinc) is the most common use of sacrificial protection. If the Zinc layer cracks:



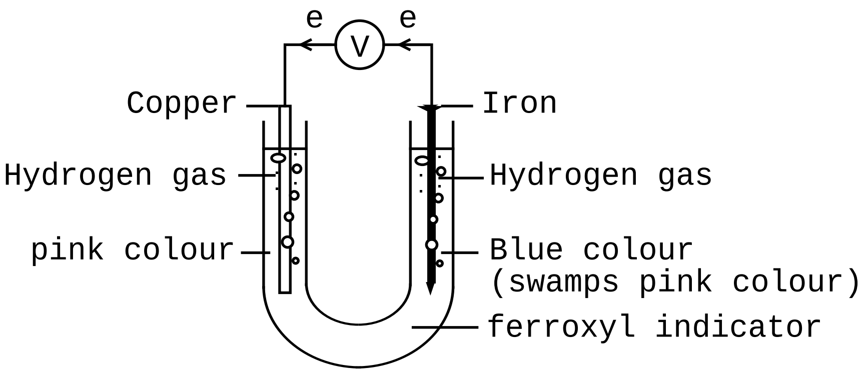
the Oxygen and Water can get to the Iron but corrosion still does not occur because electrons flow from Zinc to Iron preventing loss of

electrons by Iron. Bridge girders are galvanised.
Notice that if Iron is connected to a less reactive metal (e.g. Copper) the Iron will corrode more rapidly than usual. Electrons flow from the more reactive metal (Iron) to the less reactive metal's ions (Copper(II)) :

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

$Cu^{2+} + 2e \rightarrow Cu$

The direction of electron flow can be shown with a cell :



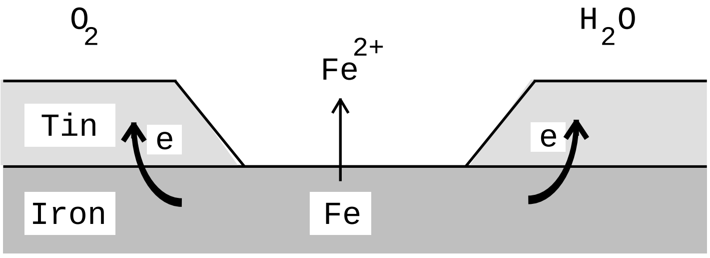
A blue colour appears round the Iron showing that Iron(II) ions are being produced.
Excess electrons are captured by hydrogen ions in the Water forming Hydrogen gas :

$2 H^+ + 2e \rightarrow H_2$

This leaves excess OH^- ions which turn the indicator pink.

Replacing Copper, in the above cell, with Carbon has a similar effect. Carbon, in the form of Graphite, is a unique non-metal : it conducts electricity ! Since it is a non-metal it has a high E.A.P. (much higher than Iron). Thus, when Iron is in contact with Carbon, electrons flow towards the Carbon **and are conducted away from Iron by the Carbon**. This speeds up the corrosion of Iron.

Like Copper, Tin is also less reactive than Iron. In Tin - plated Iron, if the Tin layer cracks :



the Oxygen and Water can get to the Iron. Electrons flow from Iron to Tin allowing the Iron to form ions and corrode. Corrosion is more rapid than in an uncoated piece of Iron : the Tin(II) ions pull electrons off the Iron :

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

$Sn^{2+} + 2e \rightarrow Sn$