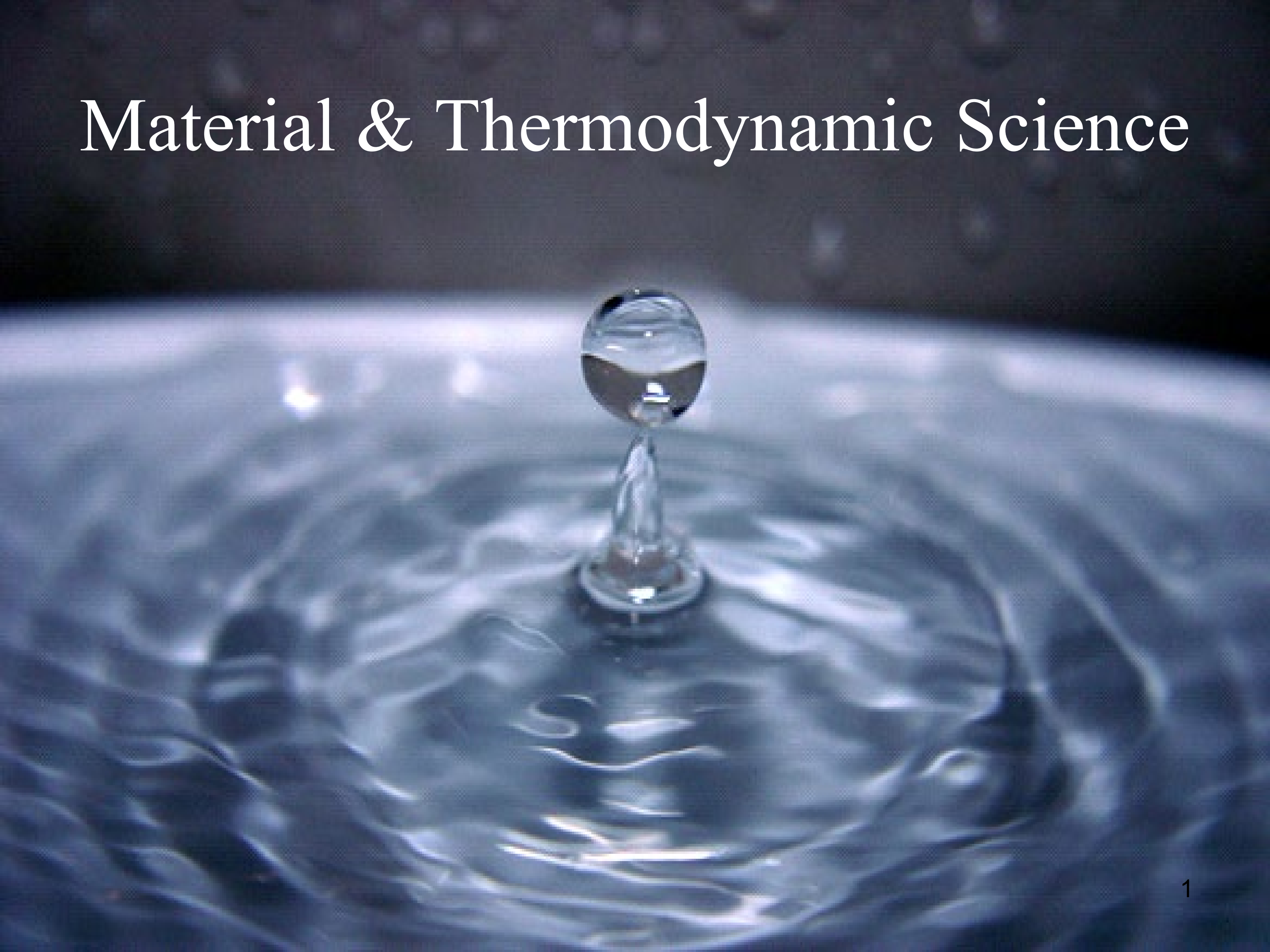
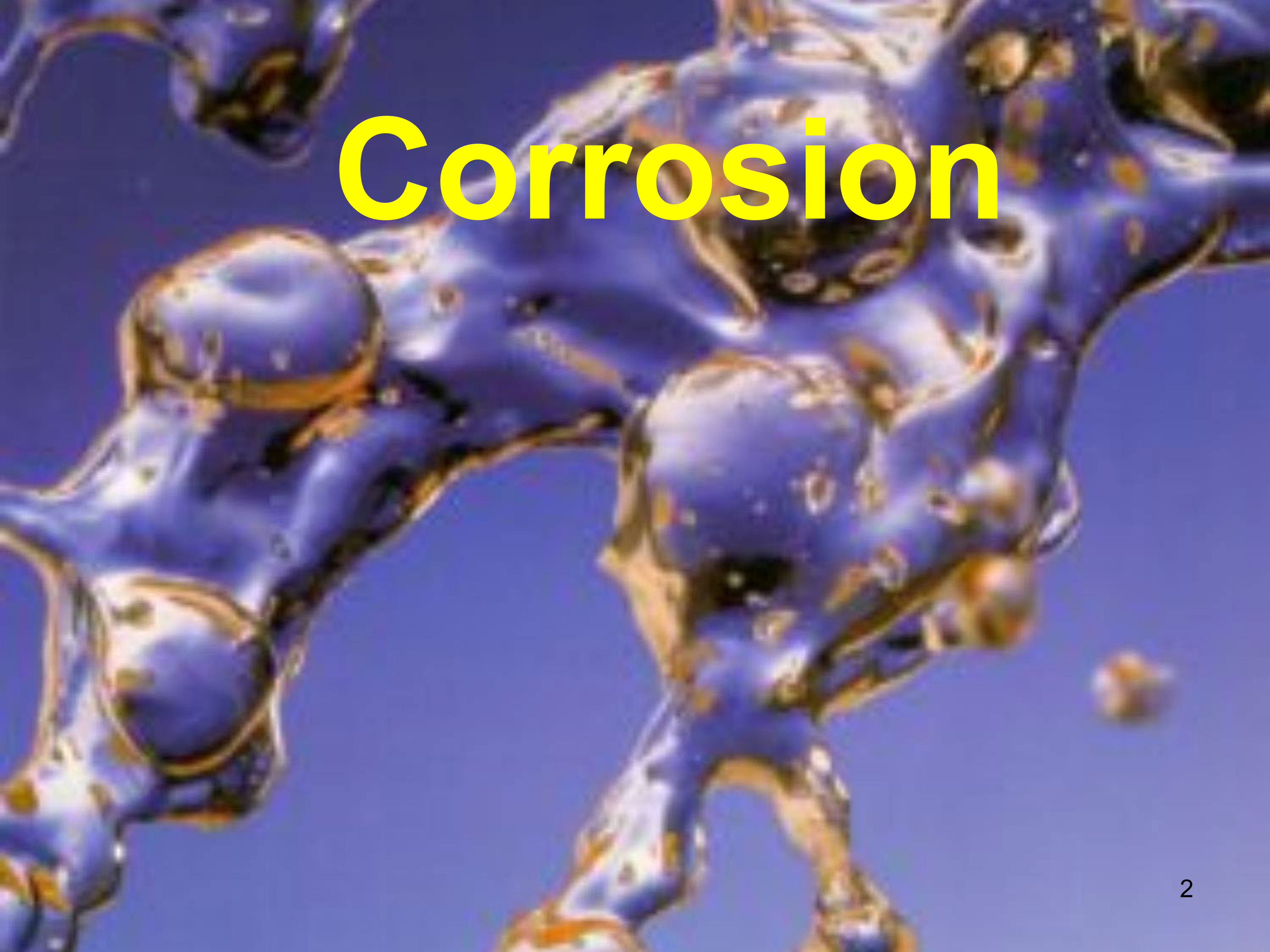
Material & Thermodynamic Science



Corrosion



Introduction

Corrosion and degradation of materials is at an economic level one of the most significant material problems today. The annual cost to Australia is estimated at hundreds of millions of dollars.

So, what is Corrosion?

To most of us we think corrosion means rust. That is, a by-product of the corrosion of ferrous metals. But non-ferrous metals can also corrode.

Corrosion may be defined as the deterioration of a material or its properties by reaction with its environment.

Why Study Corrosion?

- Materials are precious resources
- Engineering design is incomplete without knowledge of corrosion
- Applying knowledge of corrosion protection can minimize disasters
- Corrosion – contaminate products such as pharmaceutical, food and dairy products or luxury items like soap
- Corrosion products – threat to the environment
- Artificial implants for the human body!!!

Corrosion - Metals

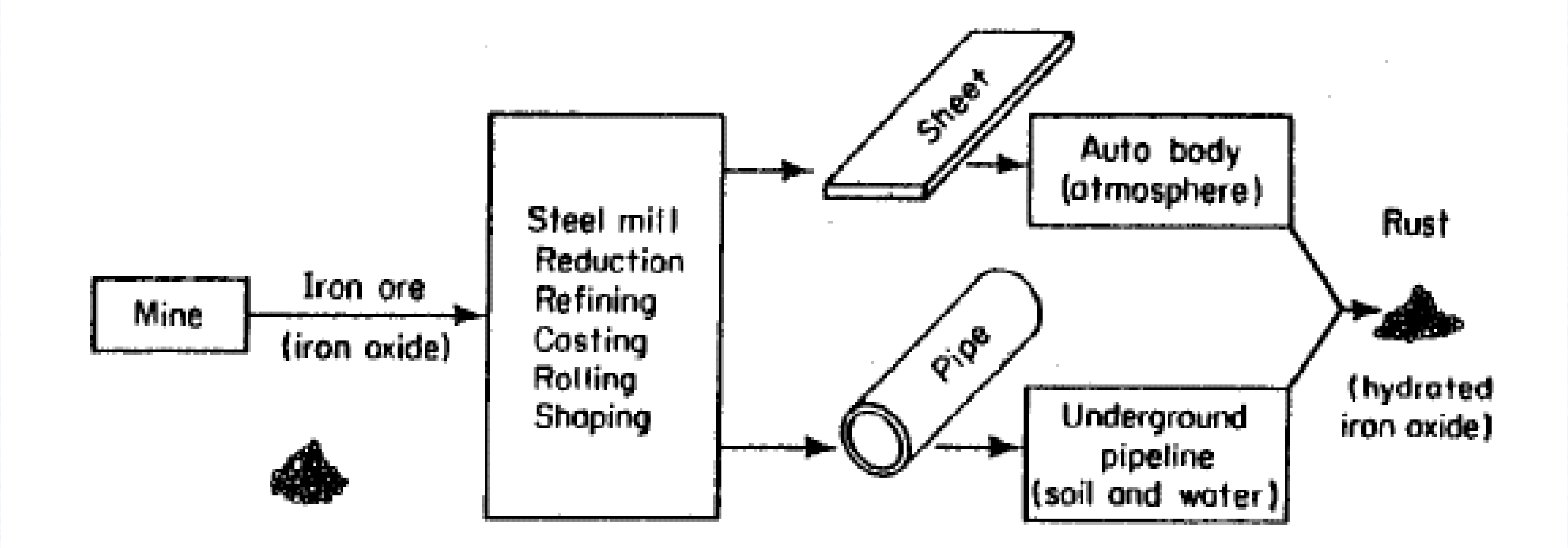
Corrosion occurs when metals react with oxygen, water, and other substances in the environment.

Most metals exist in nature as oxides, sulphides or some other metallic compound – called ‘ores’. For example, iron is mined as iron oxide.

The extraction and refining of these ores requires a large amount of energy. These refining processes result in a significant increase in the ‘free energy’ of the atoms.

Corrosion is the natural tendency for the metal to lose this energy and revert to the energy state in which it existed in nature as an ore. For example, the corrosion of iron will produce iron oxide.

Corrosion - Iron



Corrosion - Polymers

Corrosion can also occur in Polymers.

Corrosion in polymers is usually referred to as <u>degradation</u>.

Polymers degrade as a result of the bonds between the organic molecules been affected by the environment. This results in a loss of the normal properties of the polymer.

For example, rubber will develop a crazed cracking after a period of exposure in the atmosphere due to the attack on the organic bonds by ozone in the air.

However, in this lesson we will focus on **<u>corrosion in metals</u>**.

Metallic Corrosion – Chemical Reactions

Metallic corrosion is electrochemical corrosion – it involves the release and flow of electrons.

In electrochemical corrosion atoms of the metal are **oxidised** to form metal ions and electrons. The ions leave the metal and are dissolved in the electrolyte.

The electrons flow through to another place where they are consumed in another chemical reaction called **reduction**.

Chemical reactions which involve electron transfer are called **Red**uction / **Ox**idation reactions – Redox reactions.

A redox reaction is really two reactions happening at the same time:

- A reduction reaction and..
- An oxidation reaction

Let us look at an example….

Metallic Corrosion – Redox Reactions

Oxidation

A metal is oxidised when its atoms lose one or more electrons to form metal ions:

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

Iron is oxidised to iron ions and electrons. This can occur when iron reacts with hydrochloric acid (HCl):

$$Fe + 2HCl \rightarrow FeCl_2 + H_2$$

This is a corrosion reaction and can be represented ionically as:

$$Fe + 2H^+ \rightarrow Fe^{2+} + H_2$$

In this reaction the electrons lost by the iron are taken up by the hydrogen ions to give molecules of hydrogen gas.

Metallic Corrosion – Redox Reactions

Reduction

Reduction is the opposite to oxidation and indicates a gain of electrons. A metal is reduced if one or more electrons is placed back into the shell of a metal ion.

For example:

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

Iron ions gain two electrons to form metallic iron.

Iron ore is reduced to iron when it is heated in the presence of carbon:

$$2Fe_2O_3 + 3C + \text{heat} \rightarrow 4Fe + 3CO_2$$

Metallic Corrosion – Redox Reactions

Reduction

In the corrosion of iron reaction referred to earlier;

$$Fe + 2HCl \rightarrow FeCl_2 + H_2$$

There is also a reduction – the hydrogen ions from HCl are reduced to hydrogen molecules:

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

In the reduction of iron reaction:

$$2Fe_2O_3 + 3C + \text{heat} \rightarrow 4Fe + 3CO_2$$

The electrons for the reduction of the iron ions come from the oxidation of carbon to carbon dioxide.

So, whenever oxidation occurs it must be accompanied by reduction

This becomes important when we study corrosion and corrosion prevention.

Metallic Corrosion – Redox Reactions

The areas where the oxidation and reduction processes occur are called the **anode** and **cathode**.

The **anode** is that metal, or surface part of metal, at which corrosion or **oxidation** is occurring.

The **cathode** is that metal surface at which a **reduction** reaction occurs.

There are three conditions which must be present for corrosion to occur:

1. There must be an electrolyte present.

2. An anode and a cathode must be formed.

3. There must be chemical reactions at both the anode and the cathode.

Let us examine these three key points..

Metallic Corrosion – Electrolytes

An electrolyte is a liquid that conducts electricity. This conduction occurs by the migration of ions.

Pure water is a poor electrolyte (because it is a poor conductor). However, most domestic water contains minerals and metals and hence it becomes a good electrolyte

Humidity, pollution and salt create the electrolyte for atmospheric corrosion.

In dry central areas of Australia rusting of iron is almost negligible due to the very low humidity.

In coastal regions where there is both salt and high humidity (due to sea spray) rusting of iron occurs very rapidly.

Formation of Anode and Cathode

There are three principal ways by which an anode or cathode may be formed:

- An external electromotive force (EMF)
- Different metals in contact
- Chemical concentration effects in the electrolyte

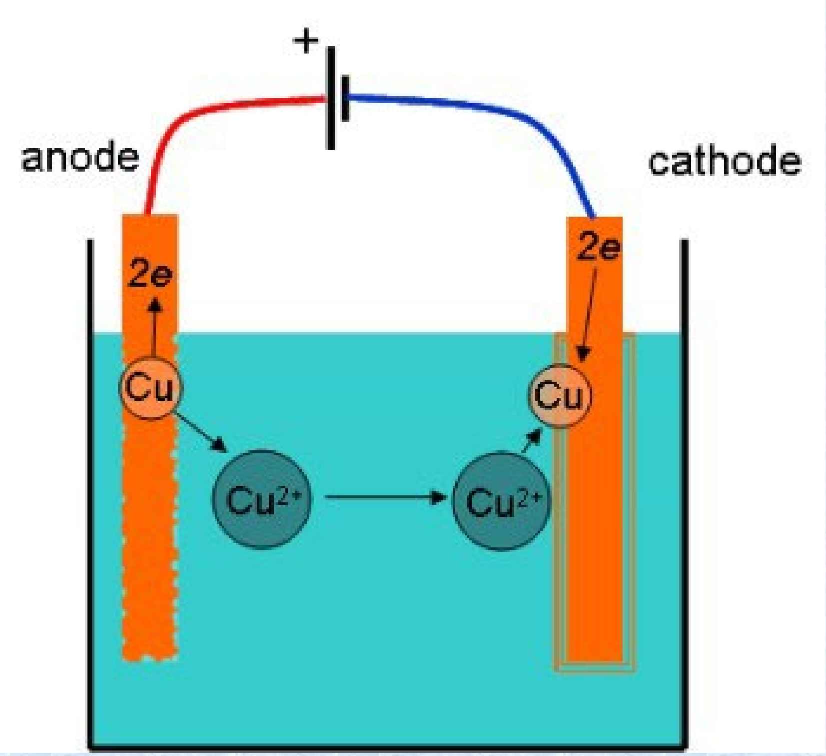
External EMF

If a system is connected to a battery or some other DC power supply, an anode and a cathode will be formed.

The area at which **current enters** the system is the **cathode** (by convention this is the **negative** charged electrode or terminal). The cathode attracts **cations**.

The area at which **current leaves** the system is the **anode** (by convention this is the **positive** charged electrode or terminal).

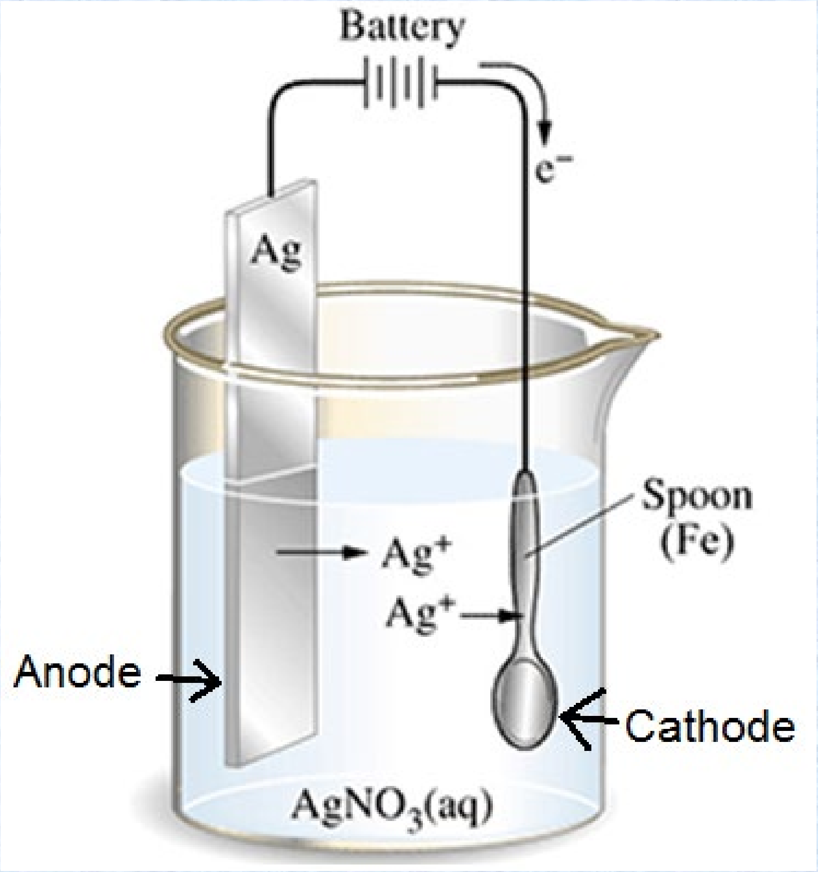
The anode attracts **anions**.



Electroplating

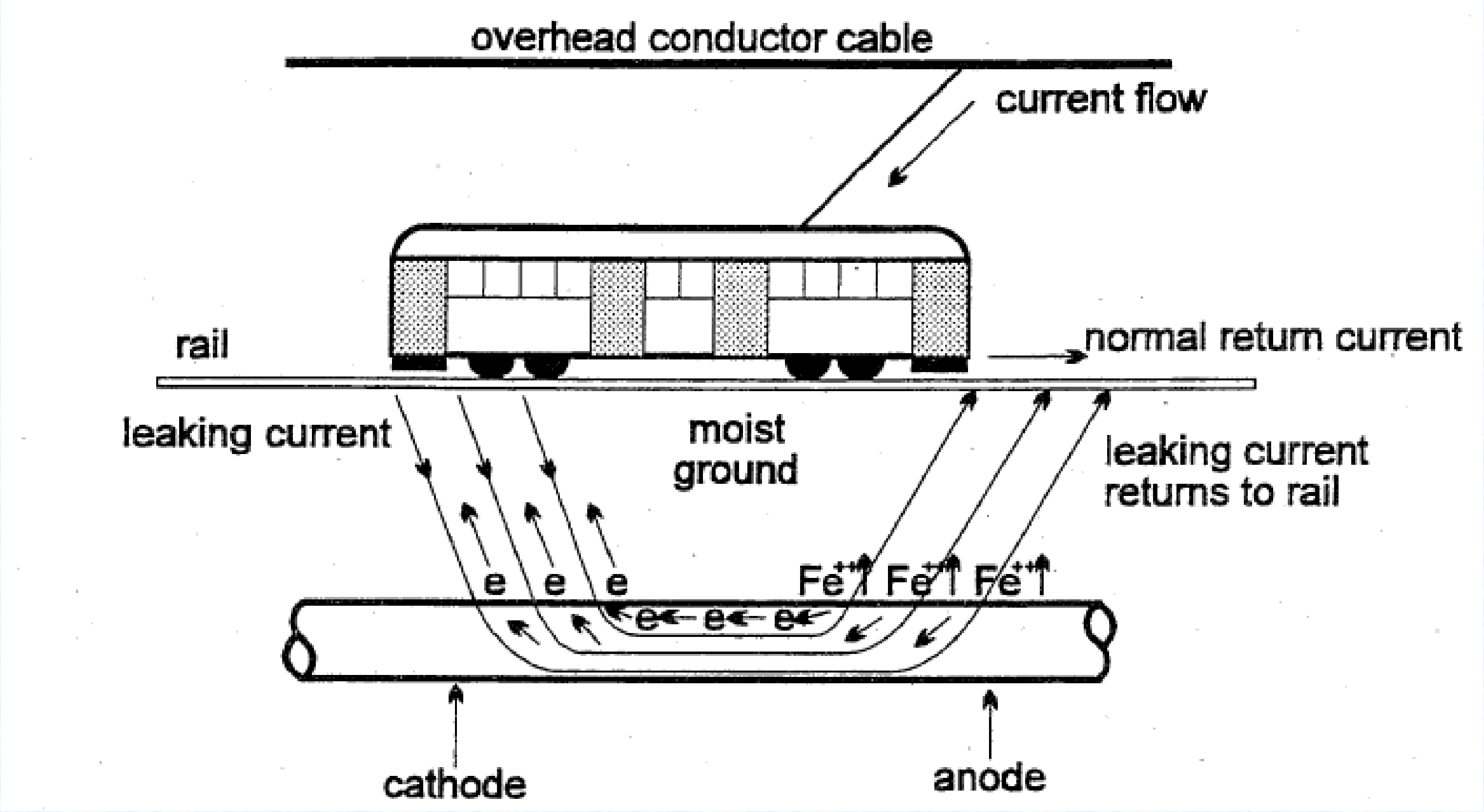
This principle is used in electroplating where the workpiece (a spoon) is the cathode and the metal (silver) to be plated onto the workpiece is the anode of a plating cell.

In this cell, silver is dissolved (corroded) from the anode and then plated onto the cathode (the spoon).



Corrosion due to Stray Currents

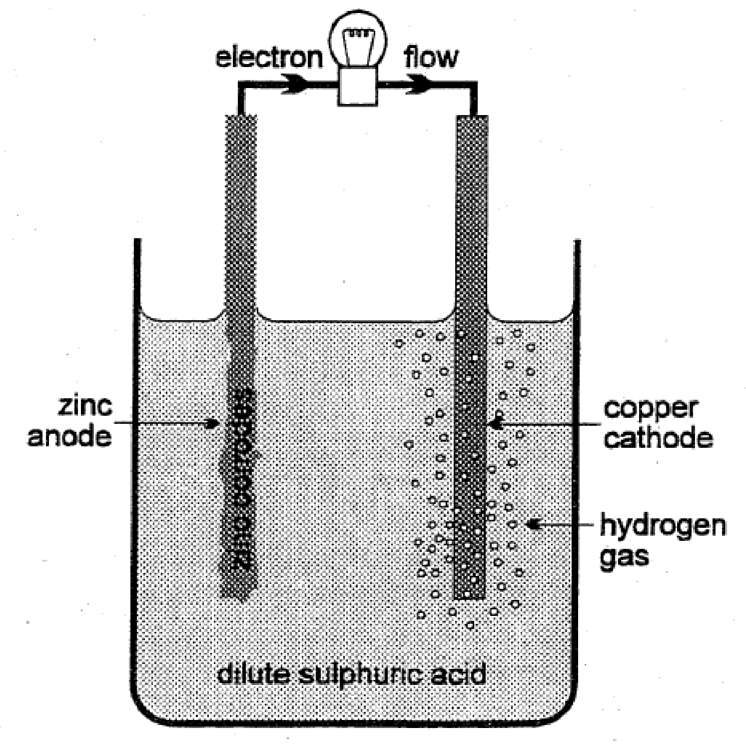
In some situations, corrosion arises from stray current or leakage current from some direct current system to a buried pipeline. Look at the example below of stray currents originating from tram lines:



Different metals in contact

If two different metals are connected electrically in an electrolyte, a potential difference will exist and one metal will become anodic (and corrode) while the other metal becomes a cathode. This type of corrosion is called **galvanic corrosion**.

If we immerse a plate of copper and a plate of zinc in sulphuric acid, a galvanic cell will be created with sufficient current generated to power a small torch lamp.

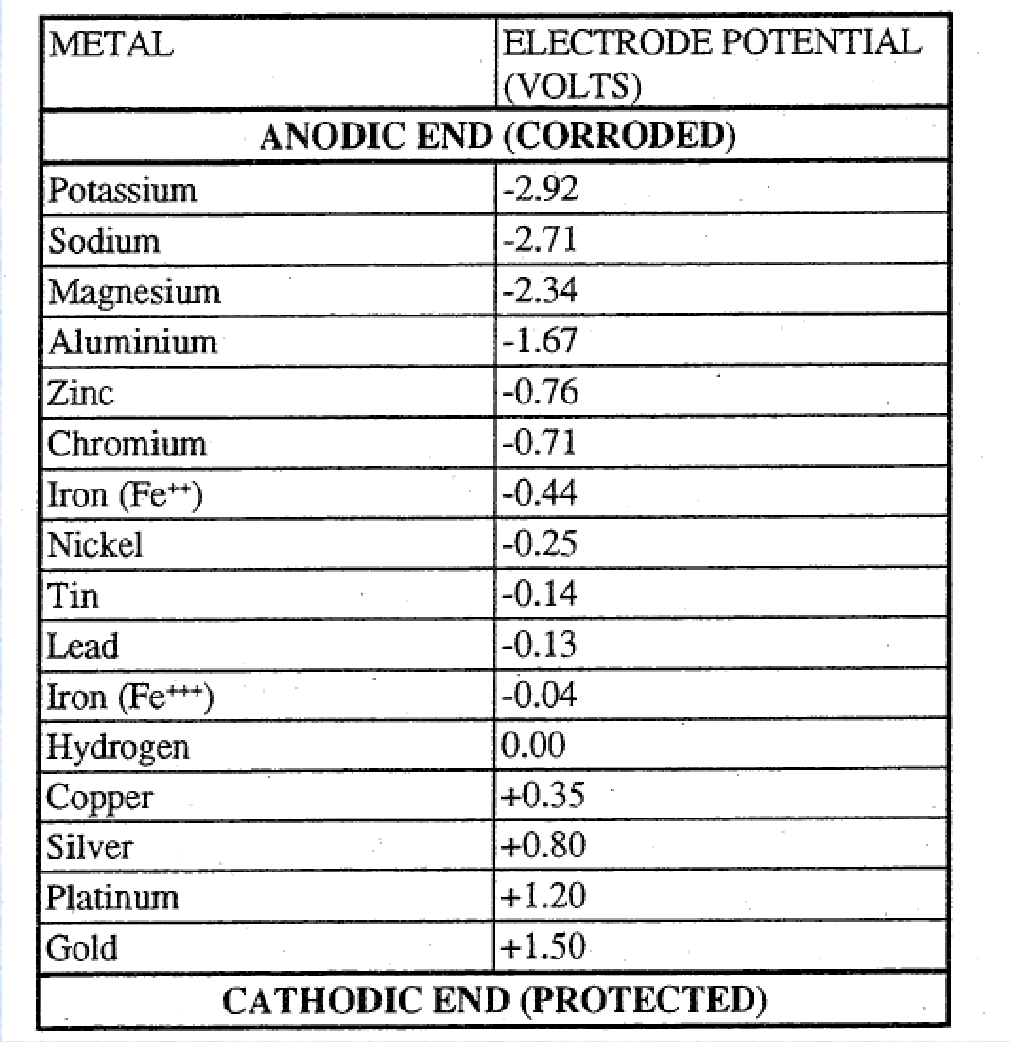


Redox Potentials

The corrosion resistance of pure metals is determined by their position in a table called the **Electrochemical Series.**

The electrochemical series lists the potential of a metal in contact with a solution containing ions of the same metal, measured relative to a standard hydrogen electrode.

These electrode potentials are sometimes called **redox potentials** – the more negative the value the greater is the tendency for corrosion.



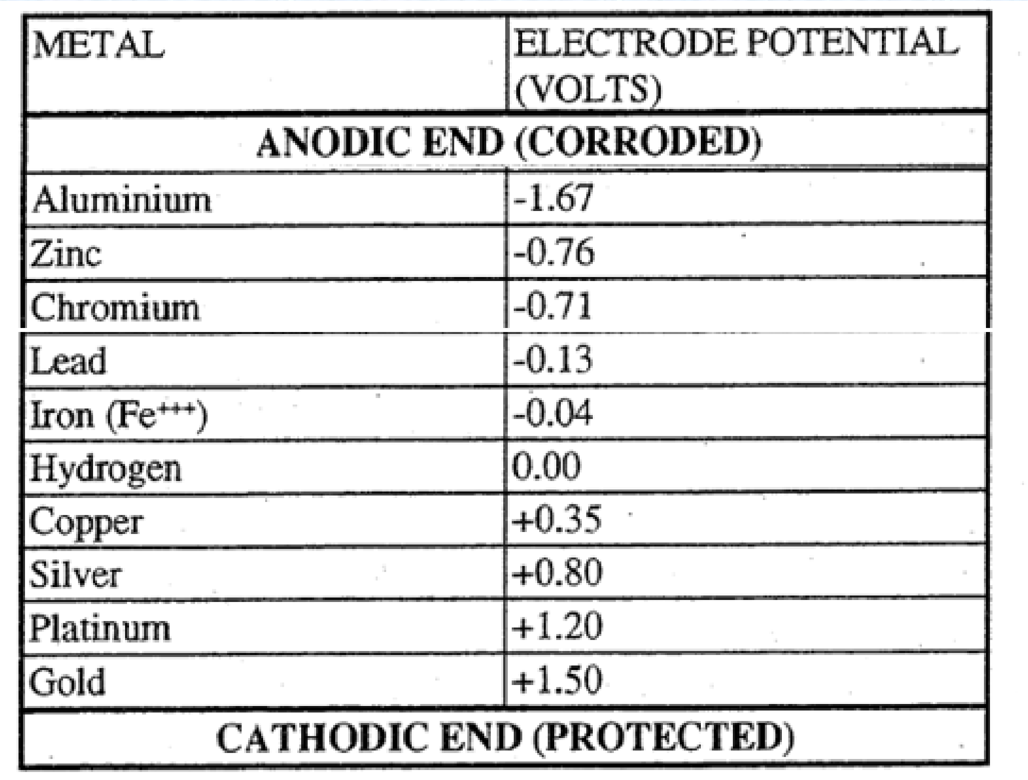
METAL	ELECTRODE POTENTIAL (VOLTS)
ANODIC END (CORRODED)	
Potassium	-2.92
Sodium	-2.71
Magnesium	-2.34
Aluminium	-1.67
Zinc	-0.76
Chromium	-0.71
Iron (Fe^{++})	-0.44
Nickel	-0.25
Tin	-0.14
Lead	-0.13
Iron (Fe^{+++})	-0.04
Hydrogen	0.00
Copper	+0.35
Silver	+0.80
Platinum	+1.20
Gold	+1.50
CATHODIC END (PROTECTED)	

Redox Potentials

The theoretical potential between any two metal/metal ion half cells can be determined from the algebraic difference in potentials from this table.

For example, a copper/copper sulphate – zinc/zinc sulphate cell would give:

Potential Difference = 0.35 – (-0.76) = 1.11 volts



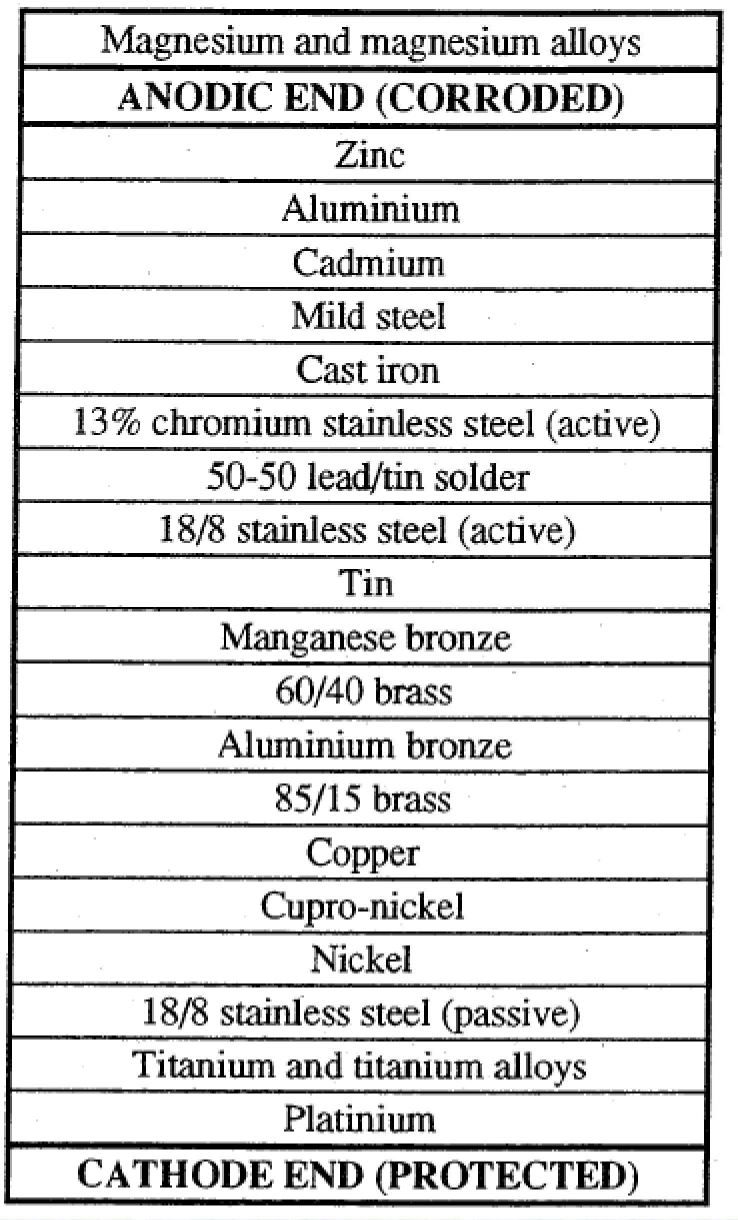
METAL	ELECTRODE POTENTIAL (VOLTS)
ANODIC END (CORRODED)	
Aluminium	-1.67
Zinc	-0.76
Chromium	-0.71
Lead	-0.13
Iron (Fe^{+++})	-0.04
Hydrogen	0.00
Copper	+0.35
Silver	+0.80
Platinum	+1.20
Gold	+1.50
CATHODIC END (PROTECTED)	

Galvanic Series of metals and alloys

Also, a table can be produced for metals and alloys showing their potential relative to the hydrogen electrode in any electrolyte – such as sea water.

This table is useful in determining the galvanic protection of metals. For example, zinc is coated onto steel to provide a form of corrosion protection.

Zinc will corrode in preference to steel and thus protect the integrity of the steel.



Magnesium and magnesium alloys
ANODIC END (CORRODED)
Zinc
Aluminium
Cadmium
Mild steel
Cast iron
13% chromium stainless steel (active)
50-50 lead/tin solder
18/8 stainless steel (active)
Tin
Manganese bronze
60/40 brass
Aluminium bronze
85/15 brass
Copper
Cupro-nickel
Nickel
18/8 stainless steel (passive)
Titanium and titanium alloys
Platinium
CATHODE END (PROTECTED)

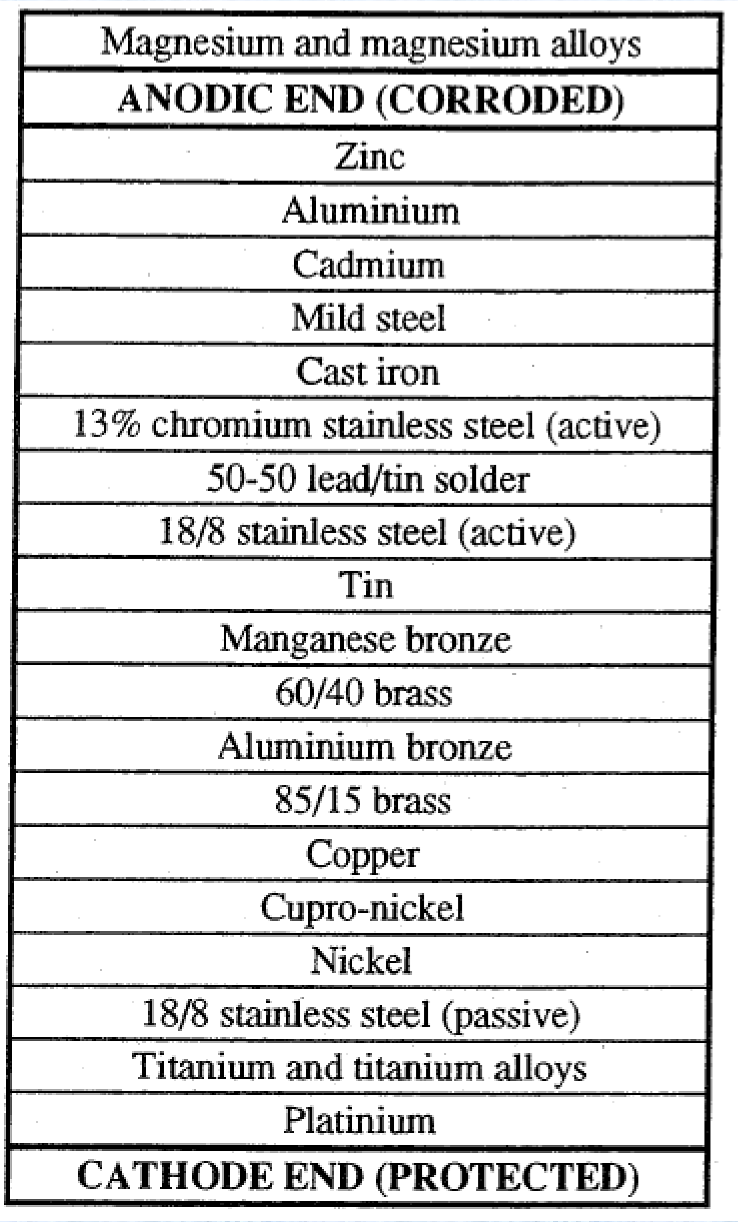
Galvanic corrosion rates

The rate of galvanic corrosion is often determined by the relative areas of the anode and cathode.

If the anode is small compared to the cathode the driving force for attack on the anode is great and corrosion of the anode will be rapid.

For example, an aluminium bolt in large steel plates will corrode very quickly.

However, a steel bolt in large aluminium plates will have little effect on the aluminium because the anode is so large compared with the cathode.

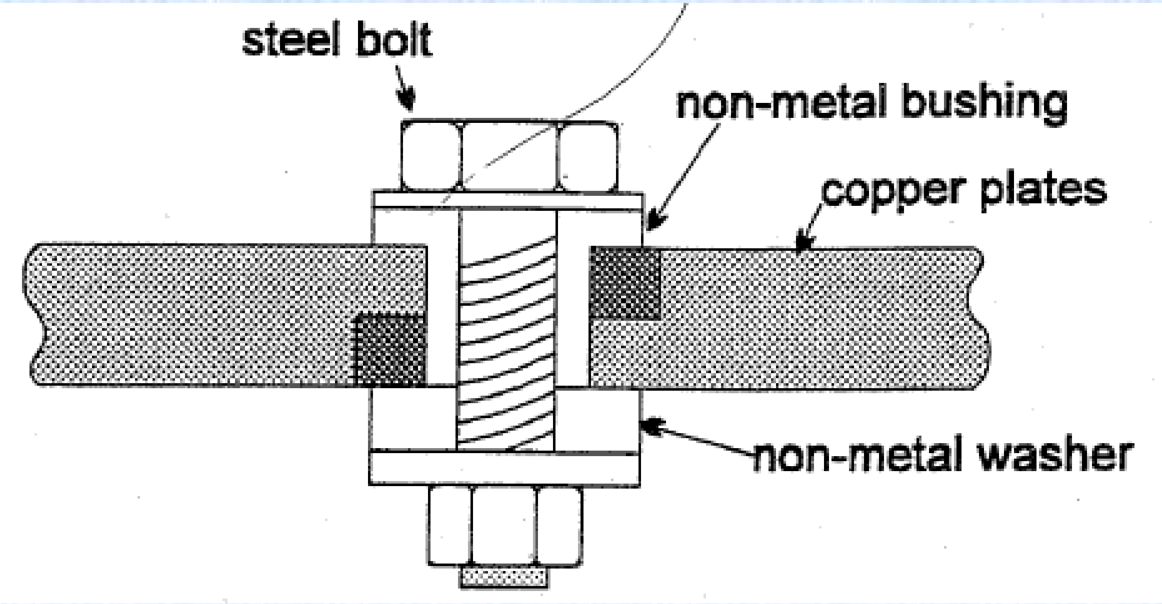


Magnesium and magnesium alloys
ANODIC END (CORRODED)
Zinc
Aluminium
Cadmium
Mild steel
Cast iron
13% chromium stainless steel (active)
50-50 lead/tin solder
18/8 stainless steel (active)
Tin
Manganese bronze
60/40 brass
Aluminium bronze
85/15 brass
Copper
Cupro-nickel
Nickel
18/8 stainless steel (passive)
Titanium and titanium alloys
Platinium
CATHODE END (PROTECTED)

Minimising Galvanic Corrosion

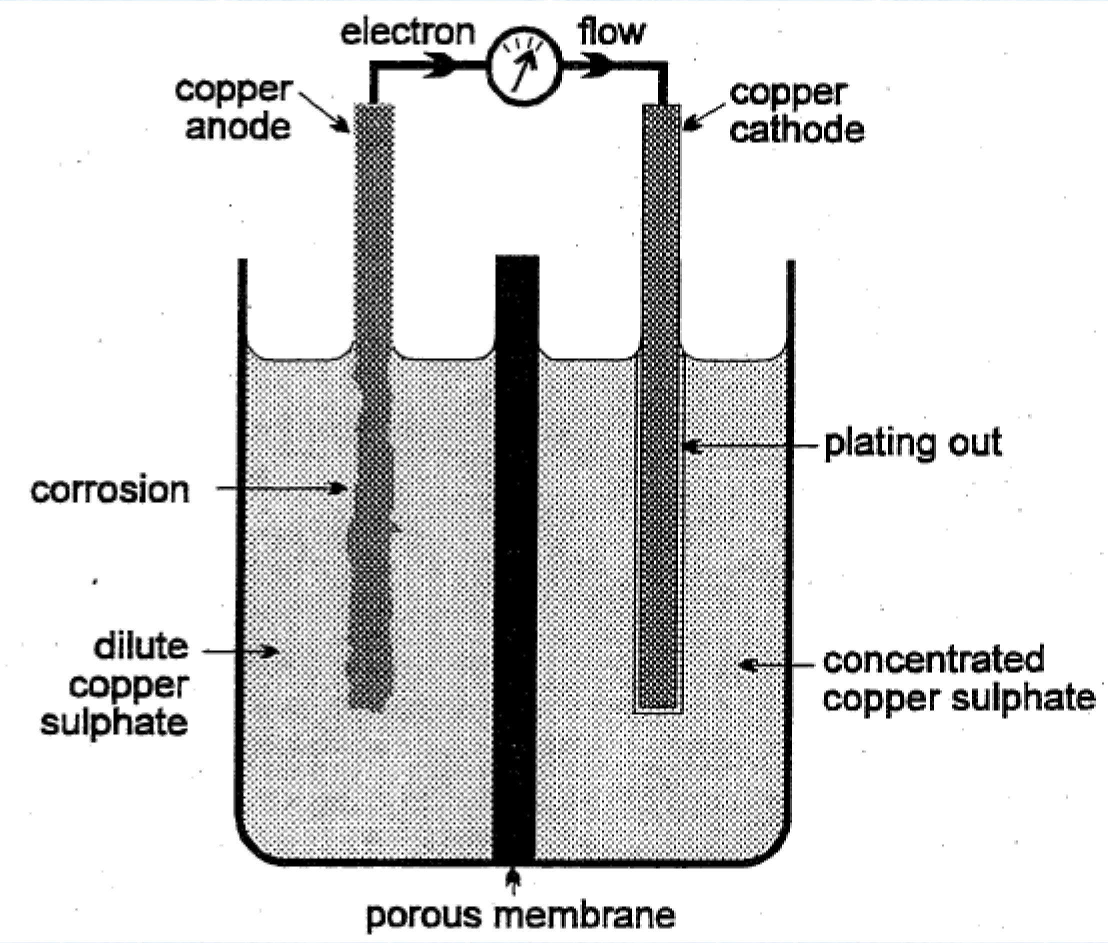
Galvanic corrosion is minimised by avoiding the use of different metals in situations where an electrolyte is present.

If this is not possible, then parts should be assembled so that there is no electrical path between the metals to allow current flow – such as using insulating washers as shown in the diagram below:



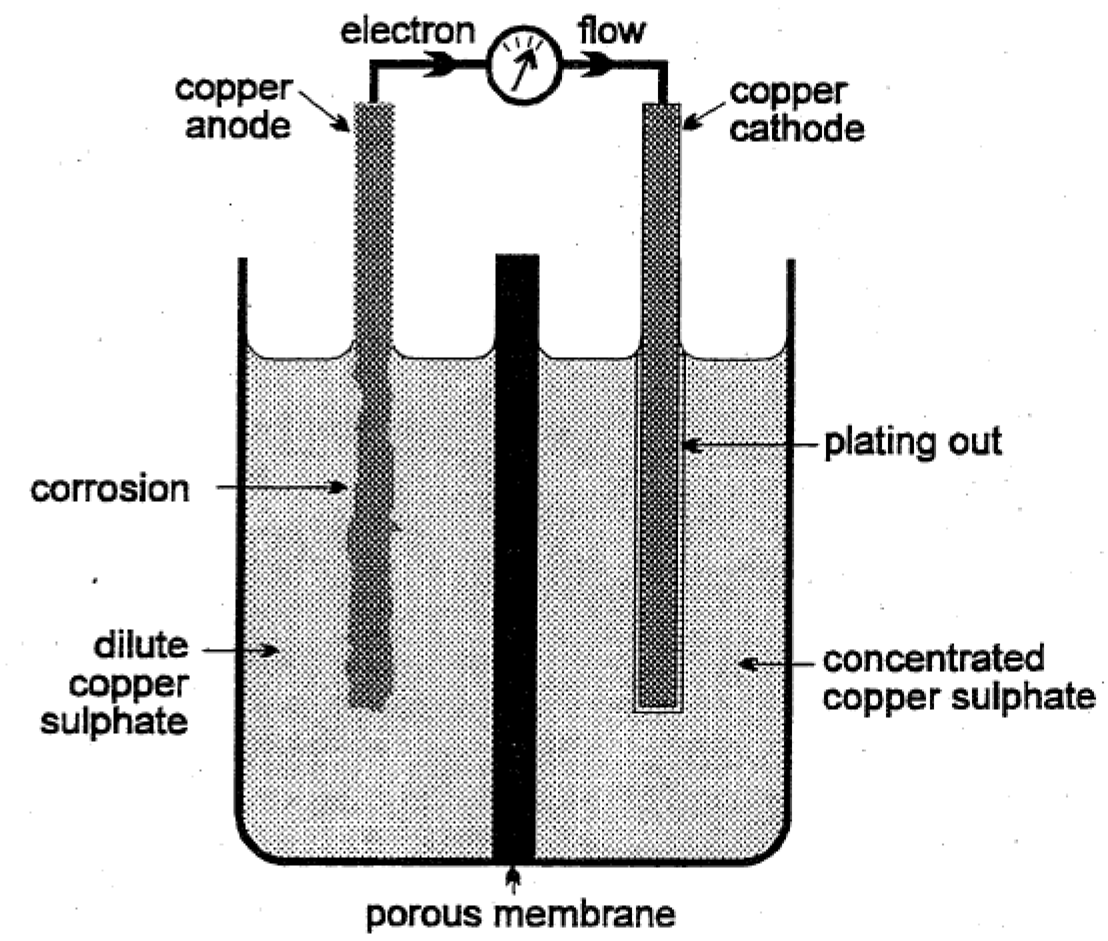
Chemical Concentration Effects

The electrode potential of a metal in a solution of its own ions varies with the concentration of ions in solution. Thus variations in concentration of an electrolyte at different parts of the same metal will produce differences in potential. This type of cell is called a **Concentration Cell**.



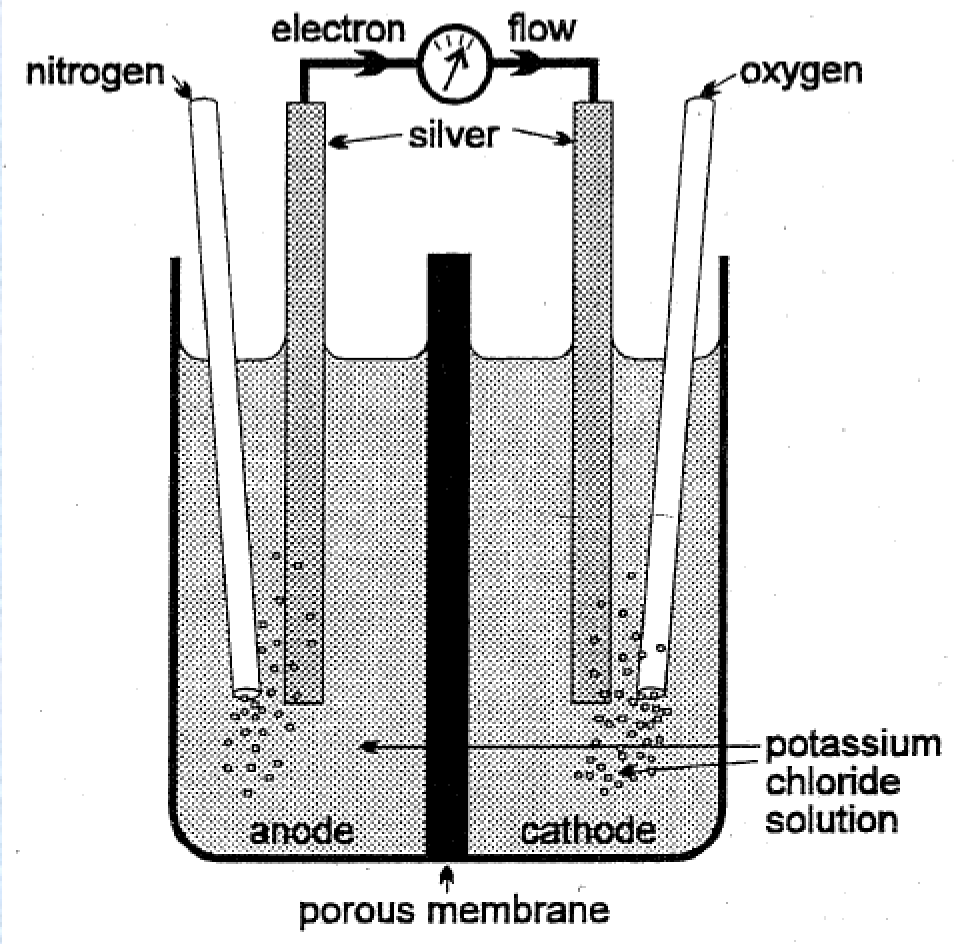
Concentration Cell

In this concentration cell, the electrode in the dilute copper sulphate solution becomes anodic and corrodes. At the cathode, copper is electroplated on to the electrode. These reactions will continue until the copper ion solution in both solutions becomes equal – at which stage there will be no potential difference.



Differential Aeration Cell

A common type of concentration cell is due to differences in oxygen concentration in aqueous liquids – called a **Differential Aeration** cell. In the cell shown below, nitrogen bubbled through the left hand half of the cell causes this side to be deprived of oxygen and thus becomes anodic (corrosion occurs).



Differential Aeration due to depth

Differential Aeration has been observed at different depths in aqueous solutions and even over the area beneath a drop of electrolyte on the surface of a metal. Remember, corrosion occurs at the anode where there is a <u>deficiency</u> of oxygen.

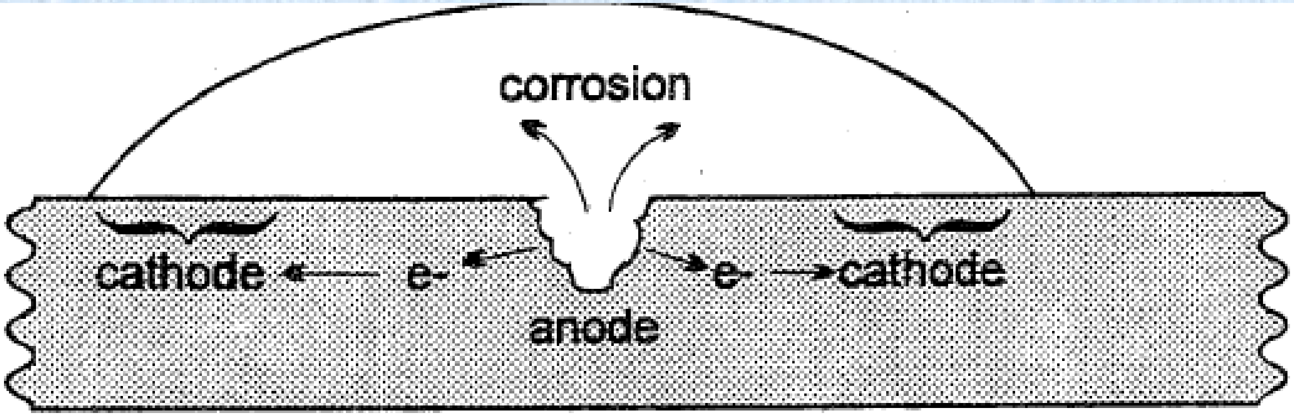


Fig 8.8 Differential aeration beneath a droplet of water

Differential Aeration due to depth

Differential Aeration has been observed at different depths in aqueous solutions and even over the area beneath a drop of electrolyte on the surface of a metal. Remember, corrosion occurs at the anode where there is a <u>deficiency</u> of oxygen.

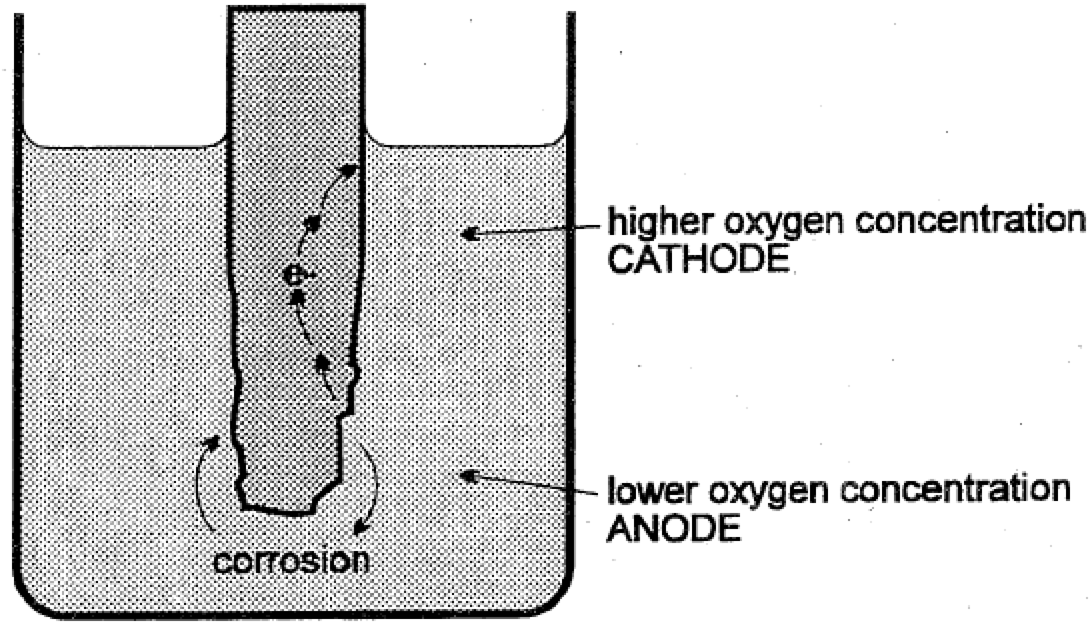


Fig 8.9 Differential aeration due to depth

Differential Aeration – crevice corrosion

In crevice corrosion a difference in oxygen concentration occurs between the root of the crack and the area near the metal surface.

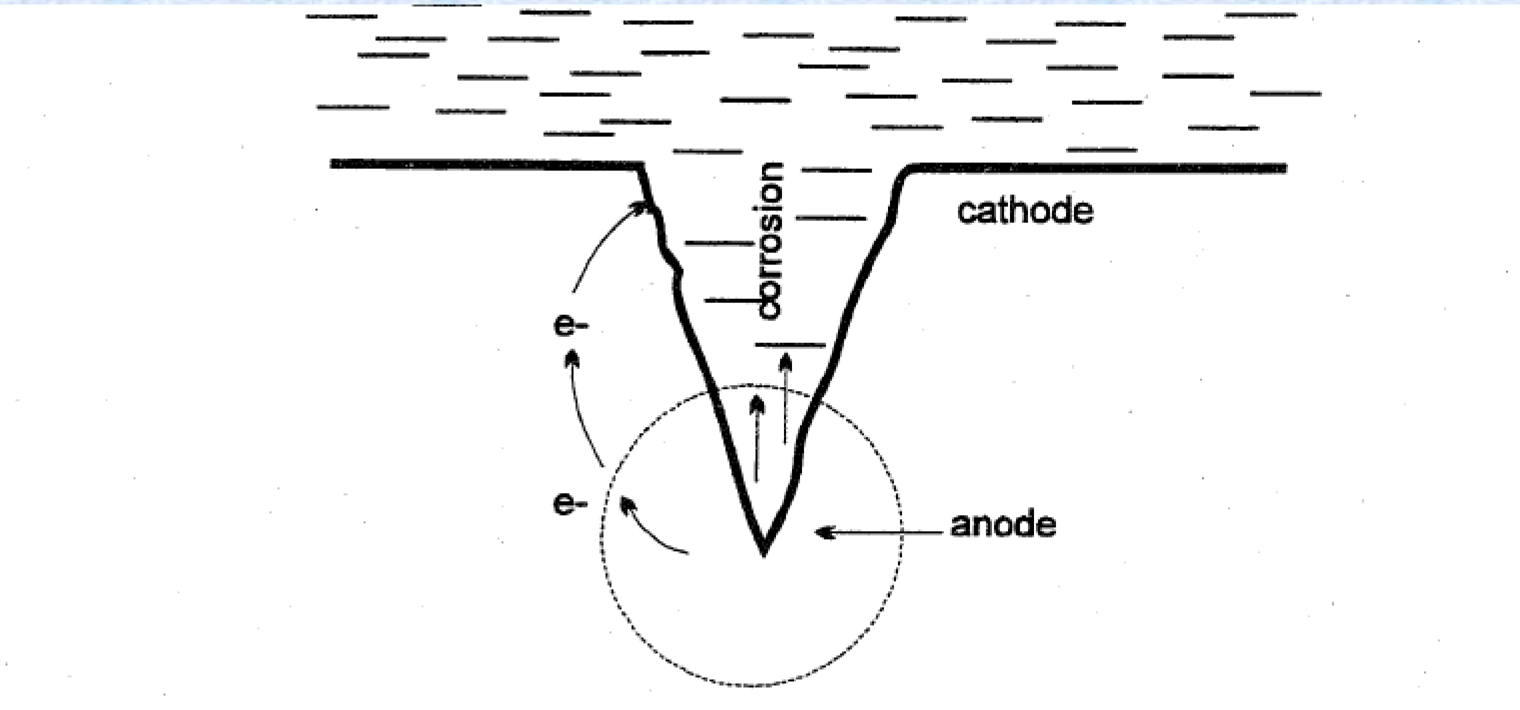


Fig 8.10 Crevice Corrosion

Chemical Reactions at the Anode and Cathode

In an electrochemical (corrosion) cell oxidation occurs at the anode and reduction occurs at the cathode.

At the anode, metal goes into solution as metal ions. The typical reaction for a metal M would be:

$$M \rightarrow M^{n+} + n\,e^{-}$$

At the cathode, there are two main types of cathode reactions.

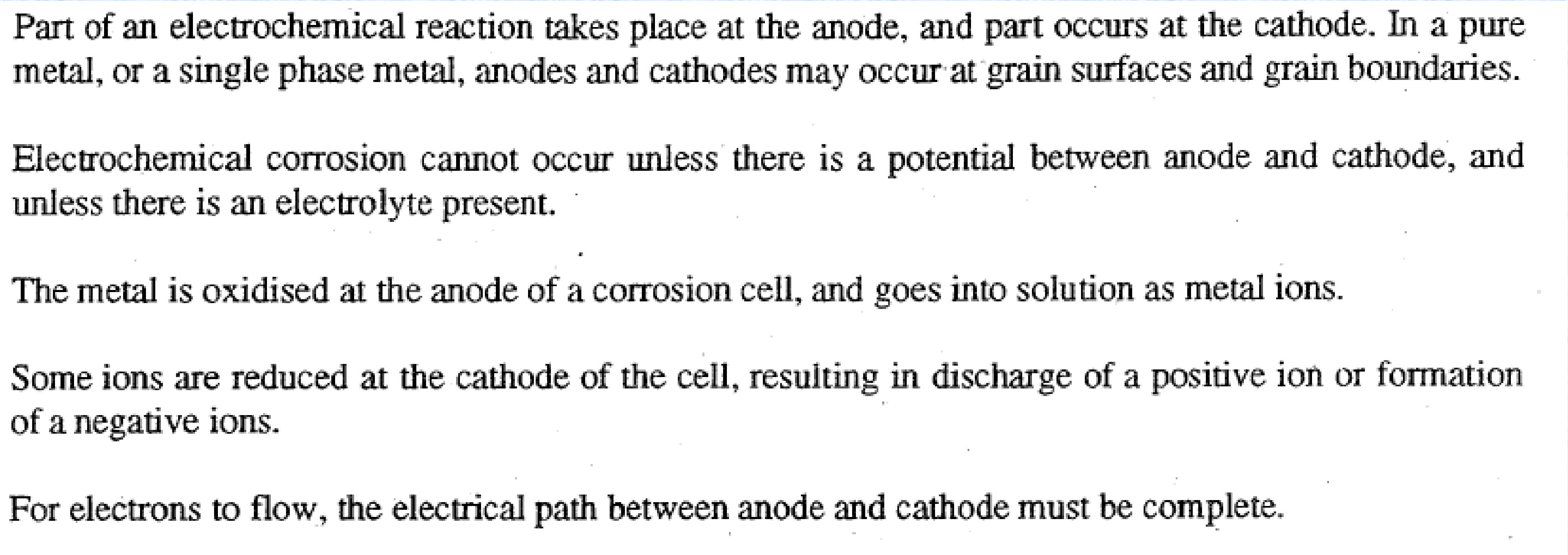
1. The discharge of a positive ion:

$$M^{n+} + n\,e^{-} \rightarrow M$$

2. The formation of negative ions:

$$X^{-} + n\,e^{-} \rightarrow X^{n-}$$

Summary of some key points



Part of an electrochemical reaction takes place at the anode, and part occurs at the cathode. In a pure metal, or a single phase metal, anodes and cathodes may occur at grain surfaces and grain boundaries.

Electrochemical corrosion cannot occur unless there is a potential between anode and cathode, and unless there is an electrolyte present.

The metal is oxidised at the anode of a corrosion cell, and goes into solution as metal ions.

Some ions are reduced at the cathode of the cell, resulting in discharge of a positive ion or formation of a negative ions.

For electrons to flow, the electrical path between anode and cathode must be complete.

Factors Affecting Corrosion

There are two main factors that contribute to corrosion:

1. Material Properties
2. Environmental conditions

Material Properties

Redox potentials as indicated in the Electrochemical Series table provide a guide to determining if a corrosion process is likely. For example, gold has a redox potential of +1.5 v. This is near the cathodic end and is hence very immune to corrosion in most electrolytes.

Metallurgical factors also affect the potential of a metal to corrode.

For example:

- The presence of inclusions and precipitates. Inclusions can be defects in the metal and impurities. Sometimes inclusions can reduce the tendency of corrosion in a material. Wrought iron, which contains siliceous slag inclusions, is more corrosion resistant that steel.
- The effect of ‘cold’ work. Performing bending and other forms of ‘cold’ work can create local stresses which in turn will affect its corrosion properties.

Environmental Factors

The nature and composition of the environment plays a major role in the selection of a materials. Environments are often classified as:

- Acid, Neutral or Base
- Salts
- Aqueous or Gaseous
- Organic or Inorganic
- Industrial, Rural or Seaboard (Saline)

Another environment factor affecting corrosion is temperature. Increasing the temperature generally increases the rate of corrosion.

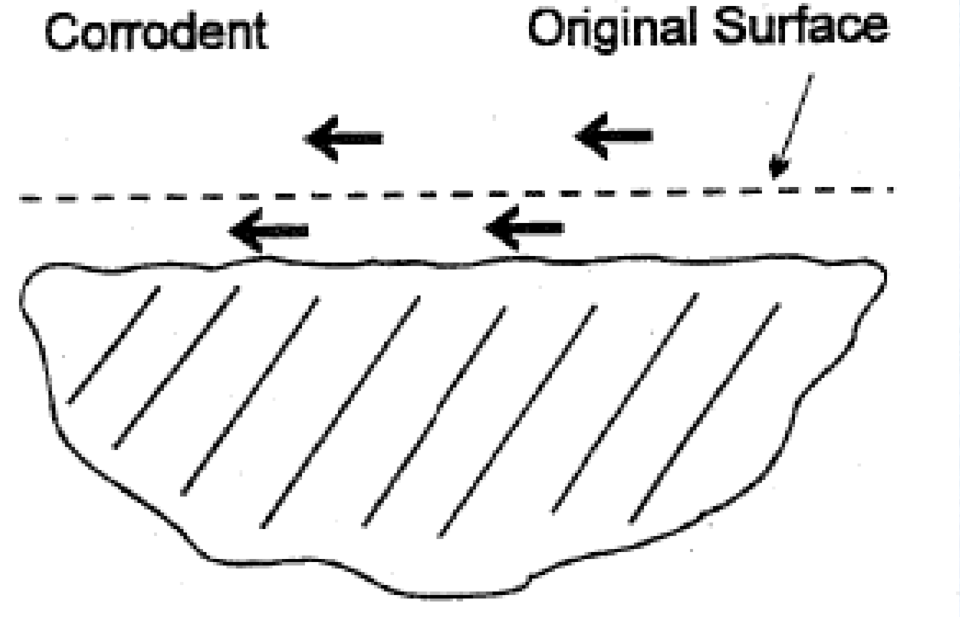
As mentioned previously, aeration also affects corrosion rate. Generally, aeration decreases corrosion rates on passive metals.

Remember, corrosion occurs at the anode where there is a deficiency of oxygen.

Corrosion Systems – Uniform Corrosion

Uniform corrosion is the simplest from of corrosion in which all exposed surfaces undergo a uniform rate of destruction.

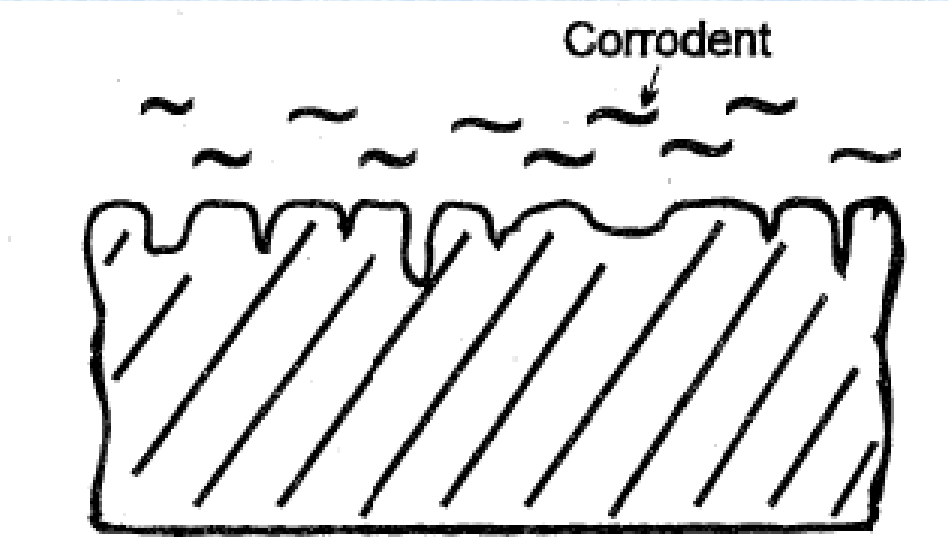
Rusting of steel in an example of uniform corrosion.



Corrosion Systems – Pitting Corrosion

Pitting corrosion is a localised corrosion characterised by surface cavities.

Once a pit starts, it becomes self propagating because of concentration cell effects.

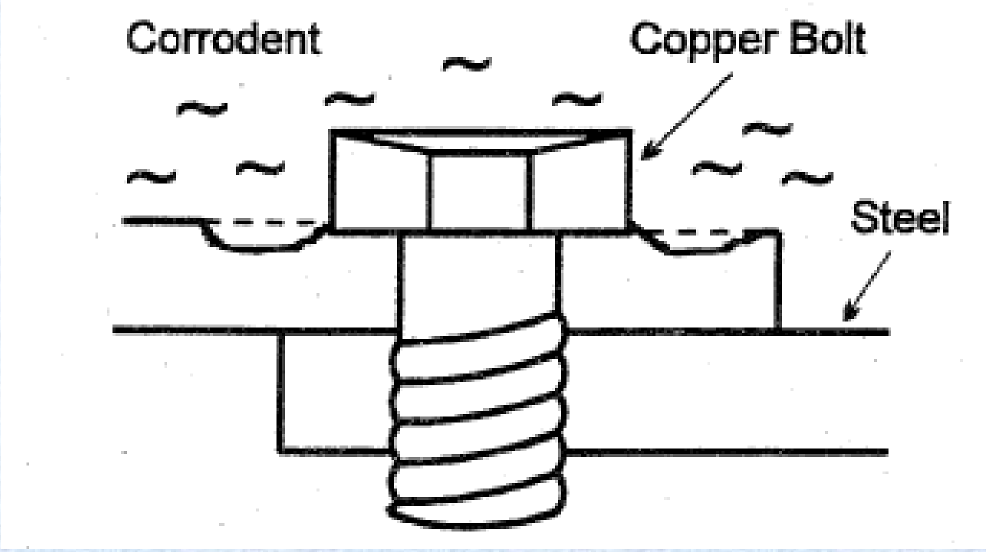


Corrosion Systems – Galvanic Corrosion

Galvanic corrosion is a form of corrosion that results when two dissimilar metals are connected together in an electrolyte, so that one metals becomes anodic and corrodes by galvanic action.

An important factor in galvanic corrosion is the size of the anodic and cathodic metals.

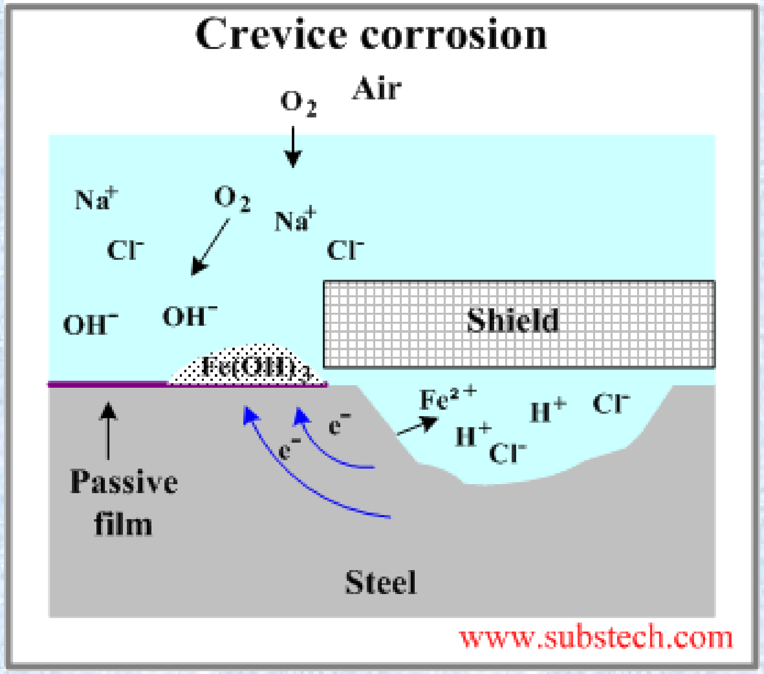
A copper bolt in a steel plate will cause the steel plate to corrode (refer back to the Electrochemical Series table of redox potentials) not the copper bolt.



Corrosion Systems – Crevice Corrosion

Crevice corrosion results from differences in concentration of both ions and dissolved gases, particularly oxygen, in an electrolyte. These effects can result in pitting attack and crevice.

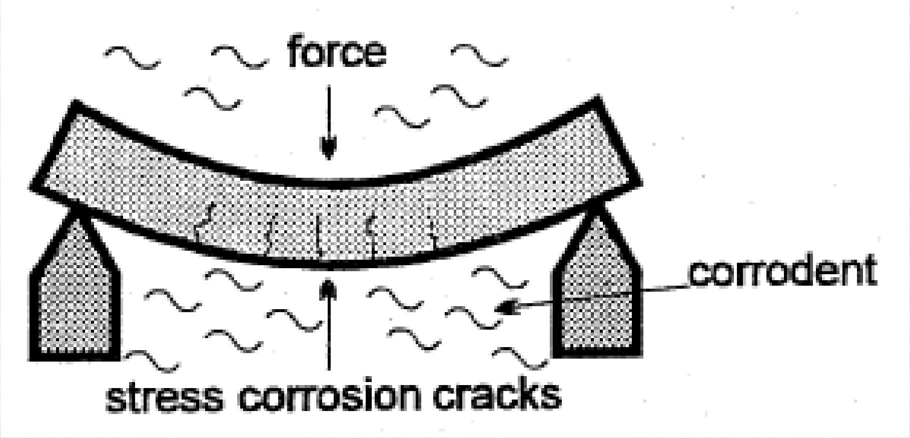
Crevice corrosion can develop in surface cracks on the metal or between overlapping metal joints. This can happen in bolted pipe flanges and under the heads of bolts and rivets.



Corrosion Systems – Stress Corrosion

Stress corrosion can occur in metal that has been ‘cold’ worked – that is, bent, stretched or formed without heating. It can also occur in metals under constant stress, such as a tanks containing liquid under pressure.

The effect of stress is to cause grain boundaries in the metal to become anodic to the rest of the structure so that corrosion takes place at these boundaries.



Corrosion Systems – Intergranular Corrosion

Integranular corrosion is corrosion attack that occurs preferentially along the grain boundaries in certain metals. It results from segregation, or depletion, of certain alloying elements at the grain boundaries. This lowers the corrosion resistance of the boundary and creates anodic areas at these zones – causing anodic corrosion.

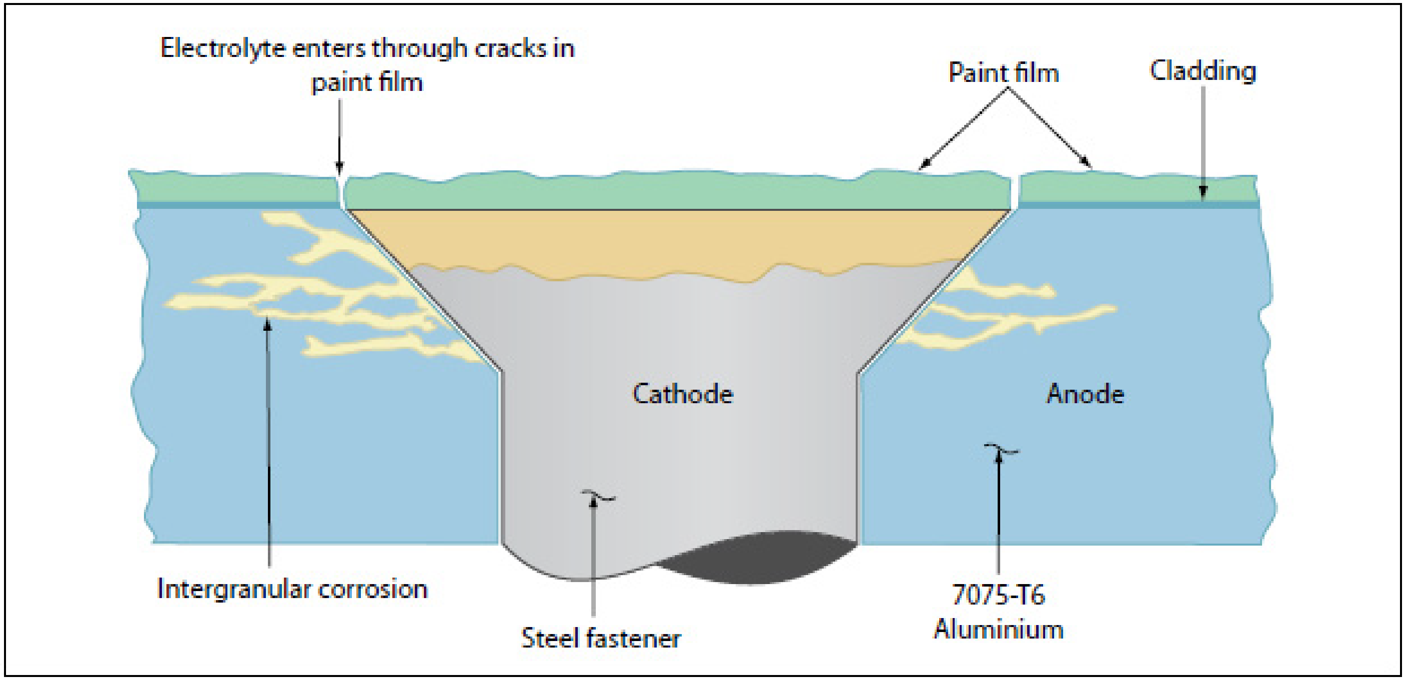


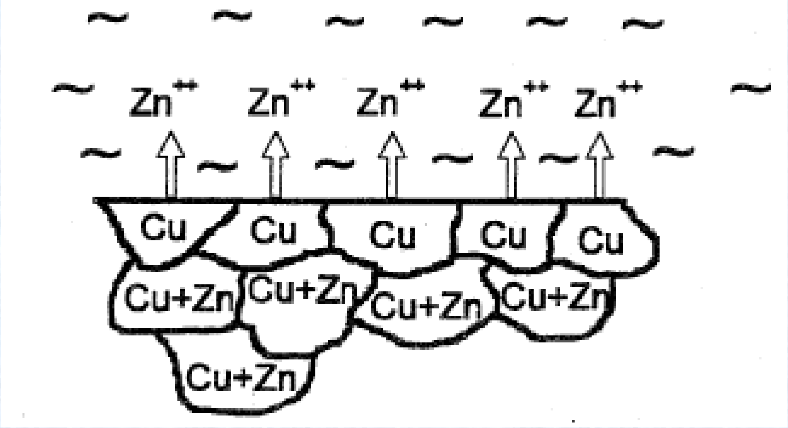
Figure 6-8. Intergranular corrosion of 7075-T6 aluminum adjacent to steel fastener.

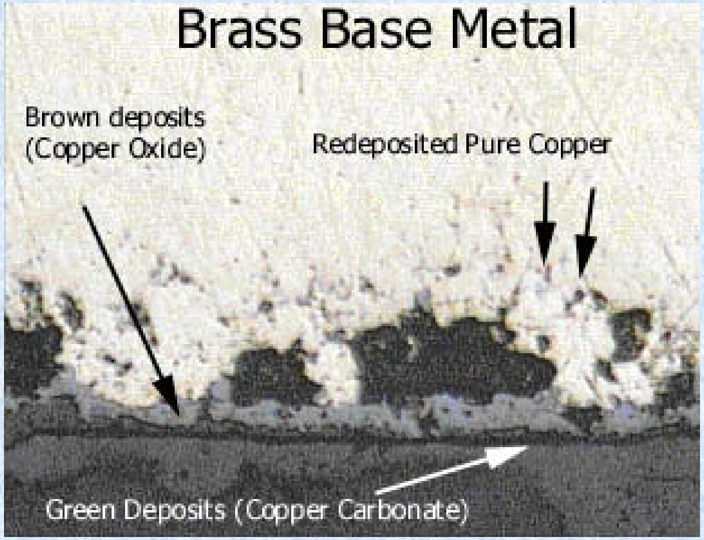
Corrosion Systems – De-Alloying Corrosion

De-alloying corrosion is a process in which one constituent of a metal alloy is preferentially attacked and removed.

De-alloying is most common in the yellow copper-zinc alloys or brasses, where it is known as dezincification. The process occurs by anodic dissolution of the brass which results in both copper and zinc ions entering the electrolyte.

The galvanic conditions are such that the copper ions are immediately reduced and plate back out as copper with the end result that zinc is removed from the alloy.



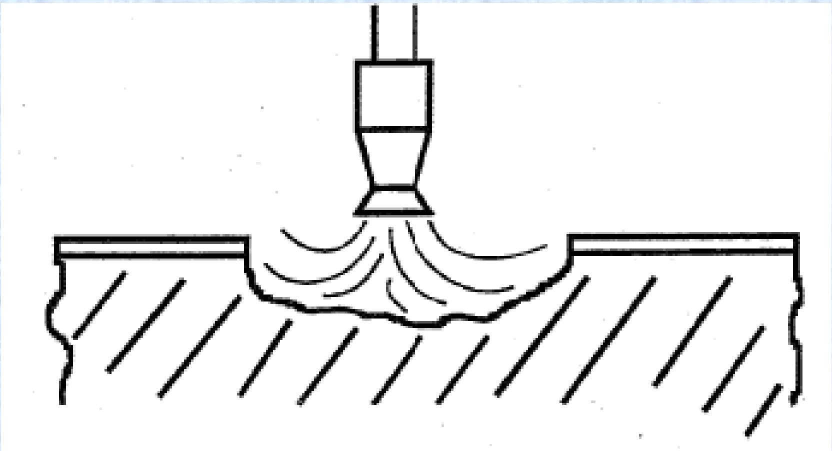


Corrosion Systems – Fretting Corrosion

Fretting corrosion results from the rubbing action due to the relative motion between two metal surfaces. It usually occurs under bearings, gears, and hubs that have been pressed onto shafts, and on machines components where there are small amounts of rubbing from vibrations.

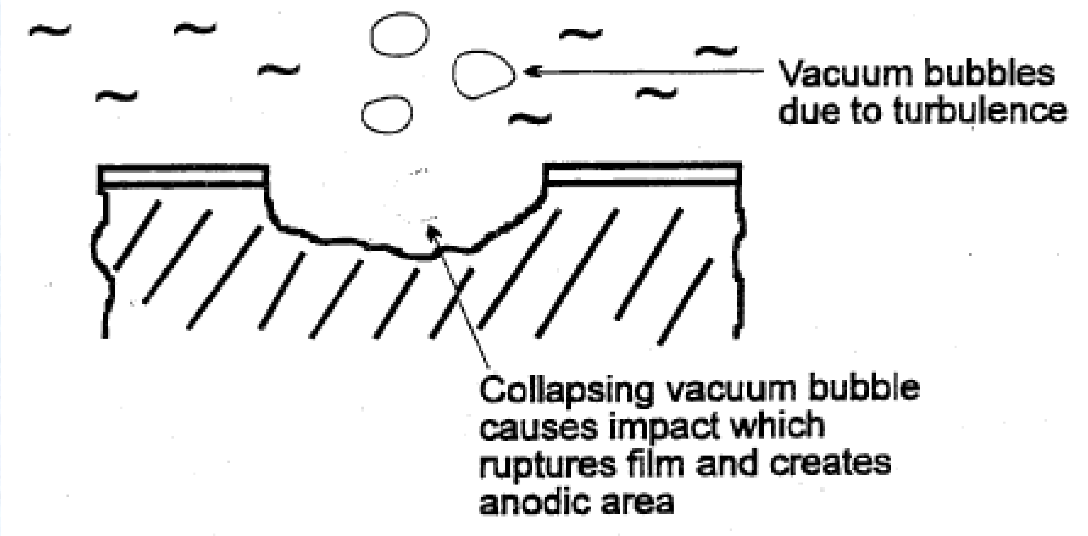
Corrosion Systems – Impingement & Cavitation

Impingement and cavitation corrosion results from the high relative movement between liquid and solid materials. Impingement corrosion is the removal of material by a stream of fluid. The constant impingement by the stream breaks down the protective film on a metal surface and creates an anodic area which corrodes.



Corrosion Systems – Impingement & Cavitation

In Impingement and cavitation corrosion, the cavitation is the result of imploding vacuum bubbles in a fluid. These bubbles are created by turbulence in the flowing fluid. The bubbles collapse when they strike the metal surface causing a sever impact on the surface. Galvanic corrosion then occurs at the damaged anodic area. Impingement and cavitation corrosion is very common on marine propellers.



Corrosion Protection

The methods most commonly used to prevent or minimise the effects of corrosion are:

- Modification to the environment
- Modification to the metal
- Use of protective coatings
- Cathodic protection

Corrosion Protection – Environment Control

Aqueous corrosion can often be minimised or prevented by the addition of **Inhibitors** (polarising agents) to the electrolyte, or by removal of the corrosion **Stimulators**.

For example, in the car Inhibitors are added to the car radiator to minimise corrosion attack of the alloy engine block.

In neutral solutions, corrosion rates are largely controlled by the oxygen concentration. De-aeration removes this corrosion stimulator and so minimises corrosion attack. Several techniques can be used to remove the dissolved oxygen – for example; purging with an inert gas like Nitrogen.

Atmospheric corrosion is determined by humidity and gaseous or solid contaminants in the environment. In some cases the air can be ‘dried’ to reduce corrosion effects due to humidity. However, where atmospheric corrosion is significant, protection generally involves treatment of the metal to shield it from the atmosphere.

Corrosion Protection – Modification of the metal

It is often possible to modify the properties of the metal by mixing it with other metals to create an alloy that is corrosion resistant.

In acid conditions, resistance to attack can be obtained by the use of a noble metal, such as gold or platinum (expensive!) or by using an alloy that has similar noble behaviour.

Also, alloys based upon nickel have demonstrated good resistance to acid in low oxygen environments.

In alkaline conditions, magnesium and silver based alloys all exhibit good corrosion resistance. Iron and aluminium based alloys are generally unsuitable.

Stainless steels are an example of a series of alloyed ferrous metals that contain 12% to 25% chromium and 20% nickel, in which the alloys are added to enhance the corrosion resistance of the metal.

Corrosion Protection – Protective coatings

Metallic coatings:

Metallic coatings on steel are usually coatings of noble metals (gold, silver etc.) each of which has a superior corrosion resistance to steel and hence can shield the steel from its corrosive environment.

Metallic coatings are applied in a variety of ways, including:

Cladding – Sheet metal is ‘sandwiched’ or roll bonded together.

Dipping – Iron and steel parts are sometimes coated by dipping into a bath of liquid metal.

Metal spraying – this involves using ‘atomised’ particles of molten metals sprayed onto the material to be protected.

Electrodeposition – sometimes called “electroplating” is the most widely used method for coating metals. Parts to be electroplated are immersed in an electrolyte – with the sample to be coated made the cathode and the anode is the pure metal which is being deposited.

Corrosion Protection – Galvanic protection

Galvanic protection is extensively used in the protection of marine structures, ships, tanks and buried pipelines immersed or buried in electrically conducting liquids and soils.

In galvanic protection 'sacrificial' anodes are electrically connected to the material to be protected from corrosion via insulated conductors. Due to the flow of electrons, the anode will corrode in preference to the cathode material.

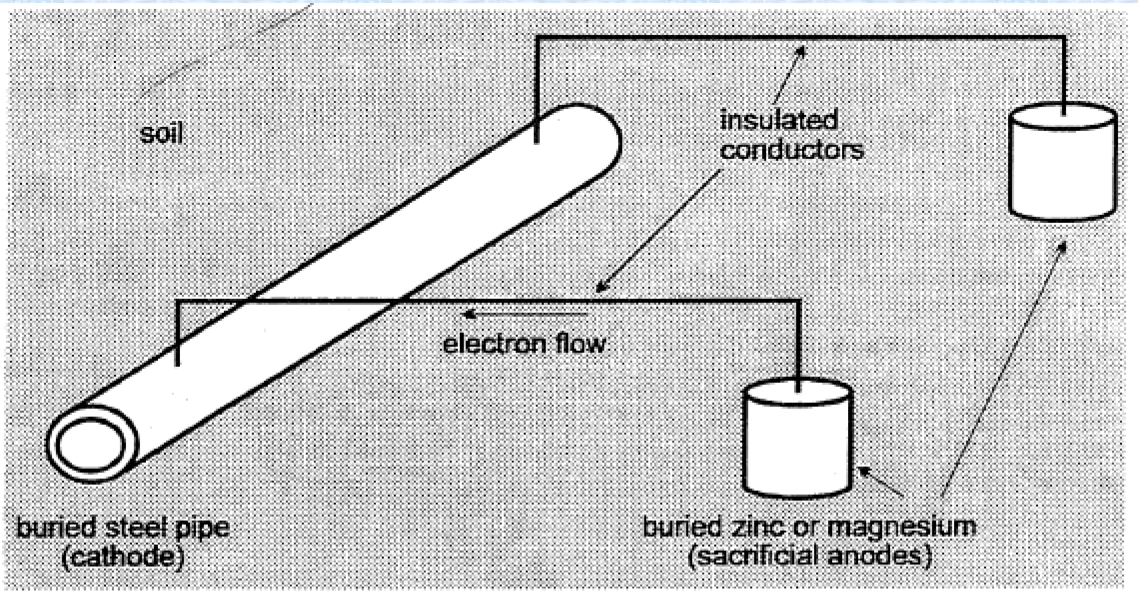
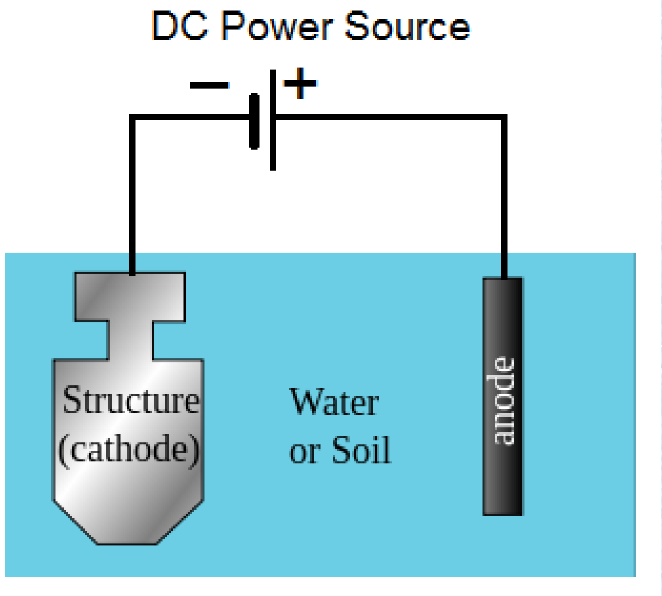


Fig 8.22 Galvanic Protection using sacrificial anode

Corrosion Protection – Cathodic protection

Another method of providing galvanic protection is the impressed current method. This is called **Cathodic Protection**. A DC source is used as a supply of electrons to protect the corroding metal; the metal to be protected is connected to the negative terminal of the DC supply. The positive terminal of the DC supply is connected to the anode. The anode is usually made from non-corroding metal, such as platinised titanium, to maximise life of the anode.



www.fadingvictoria.com

Corrosion Testing of Metals

There are numerous tests and methods of establishing the corrosion properties of a material. The following are a selection of some laboratory tests that can be performed to establish the level of corrosion resistance:

Simple Immersion – A sample of the metal is immersed in the environment within a suitable container – if necessary the container may be heated

Galvanic Cells – the metal is connected into a galvanic cell to measure corrosion potential and current relative to another metal.

Corrosion Testing of Metals

Crevice Corrosion Susceptibility – This can be measured by placing a rubber band around the metal and immersing it in the corrosive liquid.

Stress Corrosion Tests – In this test the sample is bent under stress to induce residual stress and then restrained in the bent position. It is then immersed in the liquid for sufficient time to determine the metal’s susceptibility to stress corrosion.