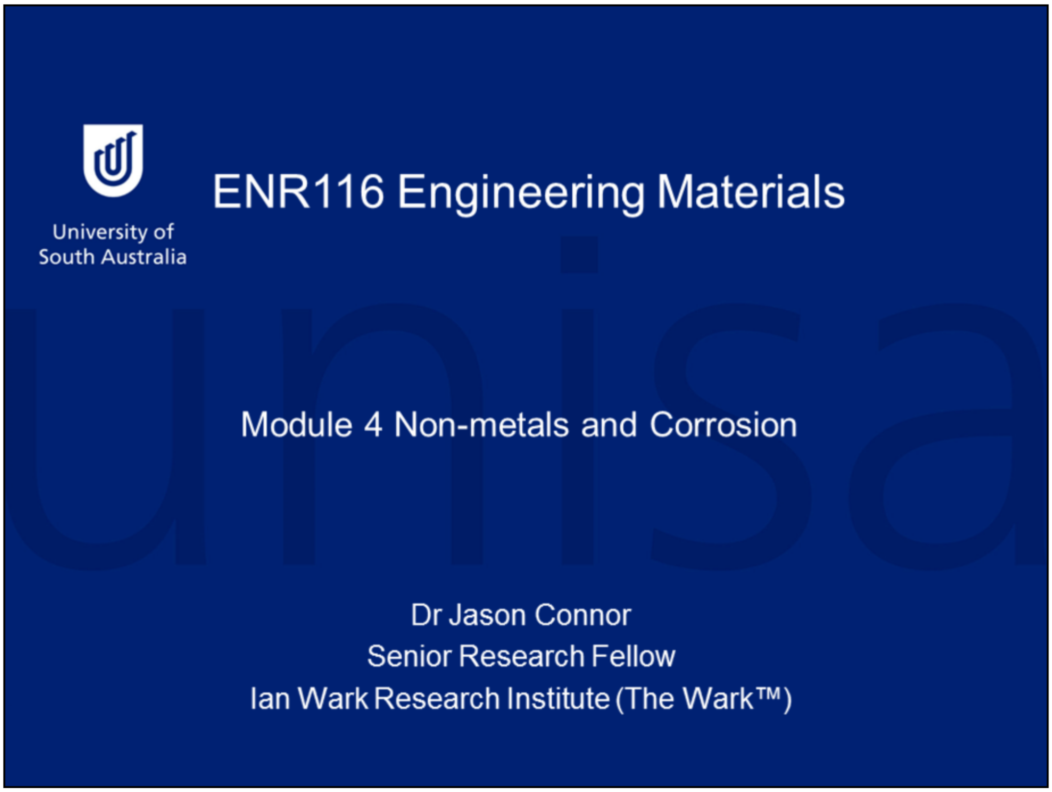

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ENR116 Engineering Materials

Module 4 Non-metals and Corrosion

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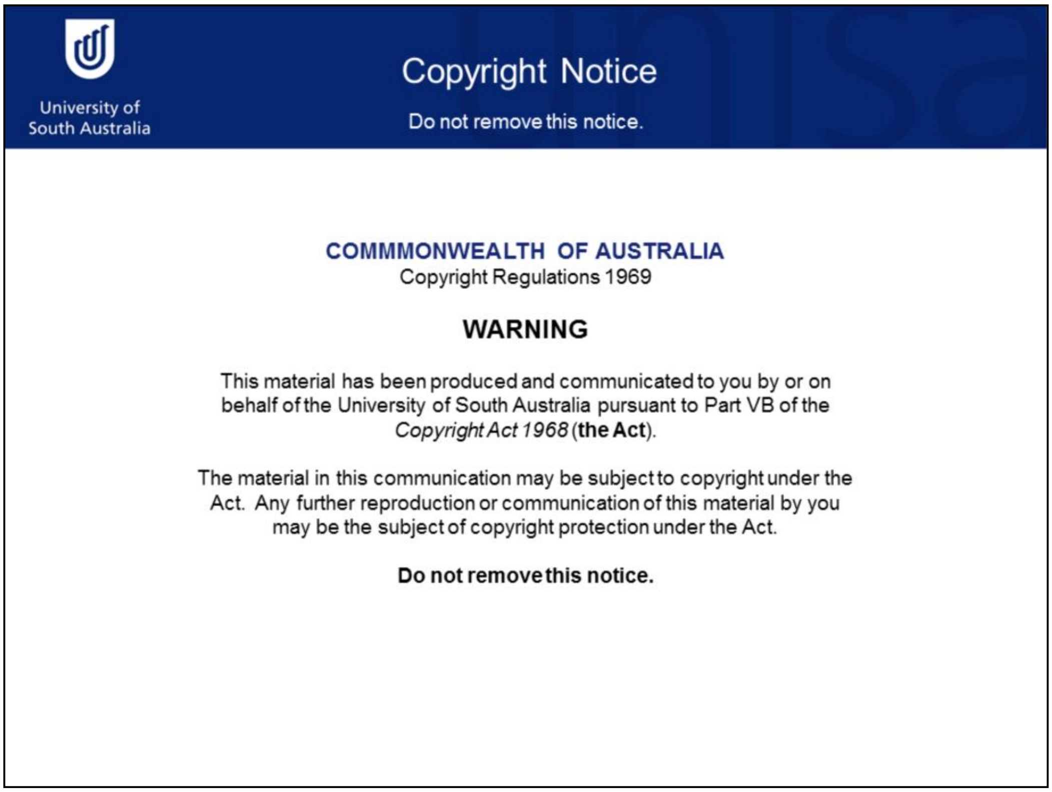

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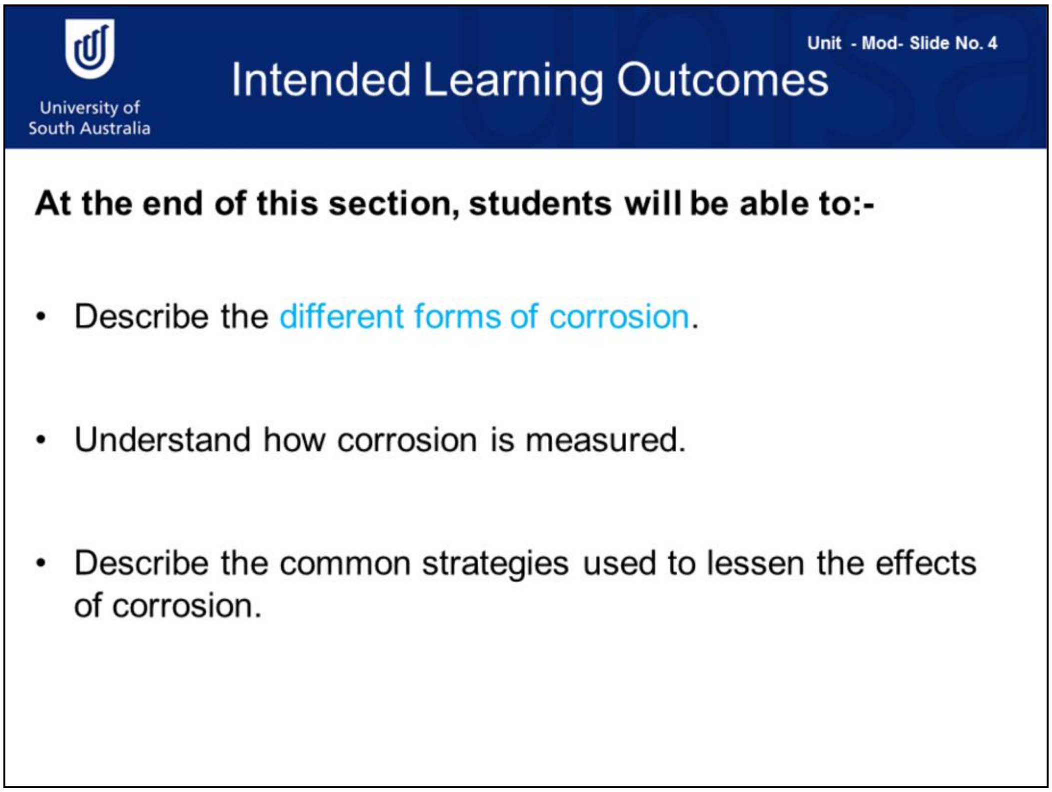
Corrosion Monitoring and Mitigation

In this lecture we will be looking at some practical aspects of corrosion and in particular some of the different types of corrosion that can occur, methods for monitoring corrosion and methods for preventing or minimising corrosion.



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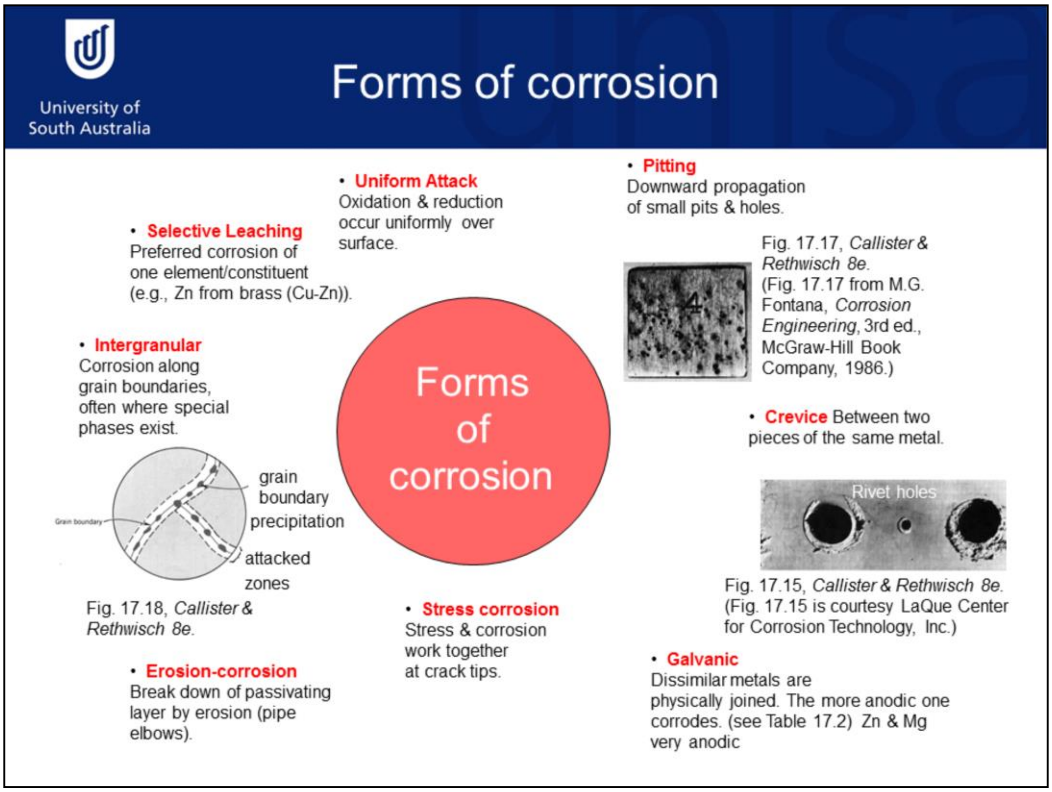
Unit - Mod- Slide No. 4

Intended Learning Outcomes

At the end of this section, students will be able to:-

- Describe the different forms of corrosion.
- Understand how corrosion is measured.
- Describe the common strategies used to lessen the effects of corrosion.

The intended learning outcomes from this presentation are to be able to describe the different forms of corrosion, understand how corrosion can be monitored and describe some common strategies for addressing corrosion problems.



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Forms of corrosion

Forms of corrosion

- **Uniform Attack** Oxidation & reduction occur uniformly over surface.
- **Selective Leaching** Preferred corrosion of one element/constituent (e.g., Zn from brass (Cu-Zn)).
- **Intergranular** Corrosion along grain boundaries, often where special phases exist.

Fig. 17.18, *Callister & Rethwisch 8e.*

- **Erosion-corrosion** Break down of passivating layer by erosion (pipe elbows).
- **Stress corrosion** Stress & corrosion work together at crack tips.
- **Pitting** Downward propagation of small pits & holes.

Fig. 17.17, *Callister & Rethwisch 8e.* (Fig. 17.17 from M.G. Fontana, *Corrosion Engineering*, 3rd ed., McGraw-Hill Book Company, 1986.)

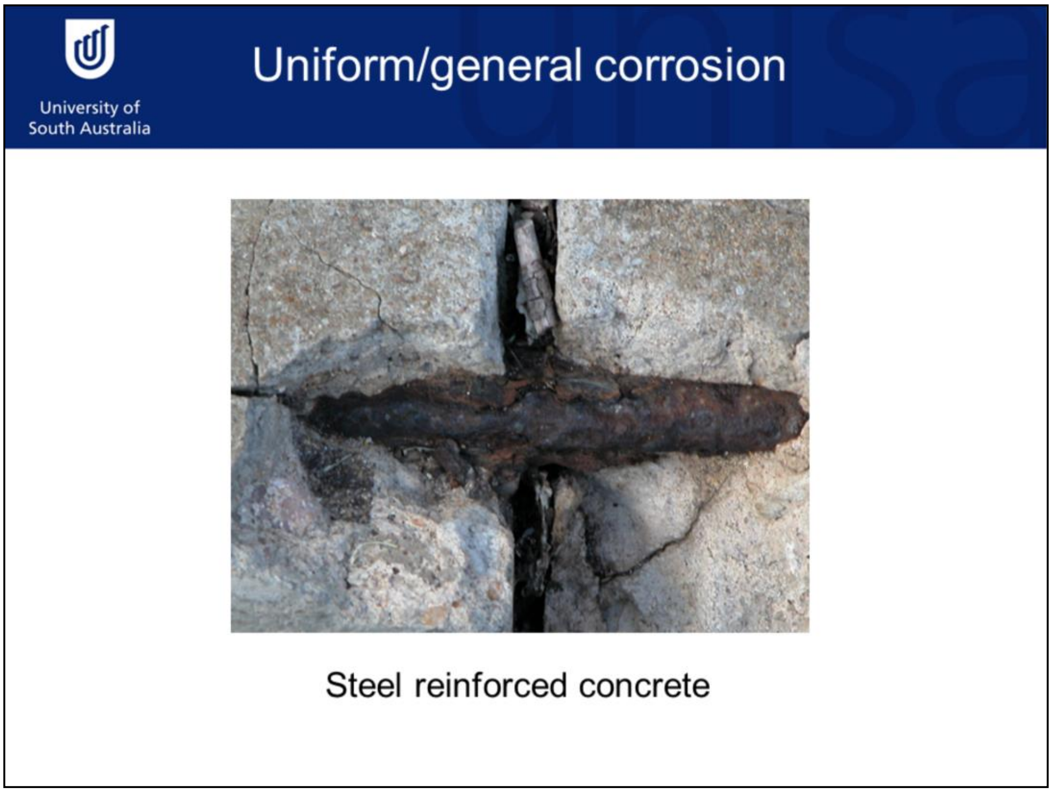
- **Crevice** Between two pieces of the same metal.

Fig. 17.15, *Callister & Rethwisch 8e.* (Fig. 17.15 is courtesy LaQue Center for Corrosion Technology, Inc.)

- **Galvanic** Dissimilar metals are physically joined. The more anodic one corrodes. (see Table 17.2) Zn & Mg very anodic

Corrosion can take a number of forms. In this slide we summarise the most common although I will not discuss all of these in detail.

The various forms of corrosion can range from uniform attack leading to general corrosion, pitting corrosion where small holes that penetrate the surface are observed, crevice corrosion where corrosion occurs underneath joints between pieces of the same metal and galvanic corrosion that occurs when dissimilar metals are joined together. Other types of corrosion that are often found in process plants are stress corrosion where stresses in the material leads to corrosion and eventual failure. Erosion corrosion, which is a result of mechanical removal of protective passive films usually by particles in a slurry but can also be related to liquid flow. Intergranular corrosion along grain boundaries and selective or preferential leaching of one of the constituents in an alloy.



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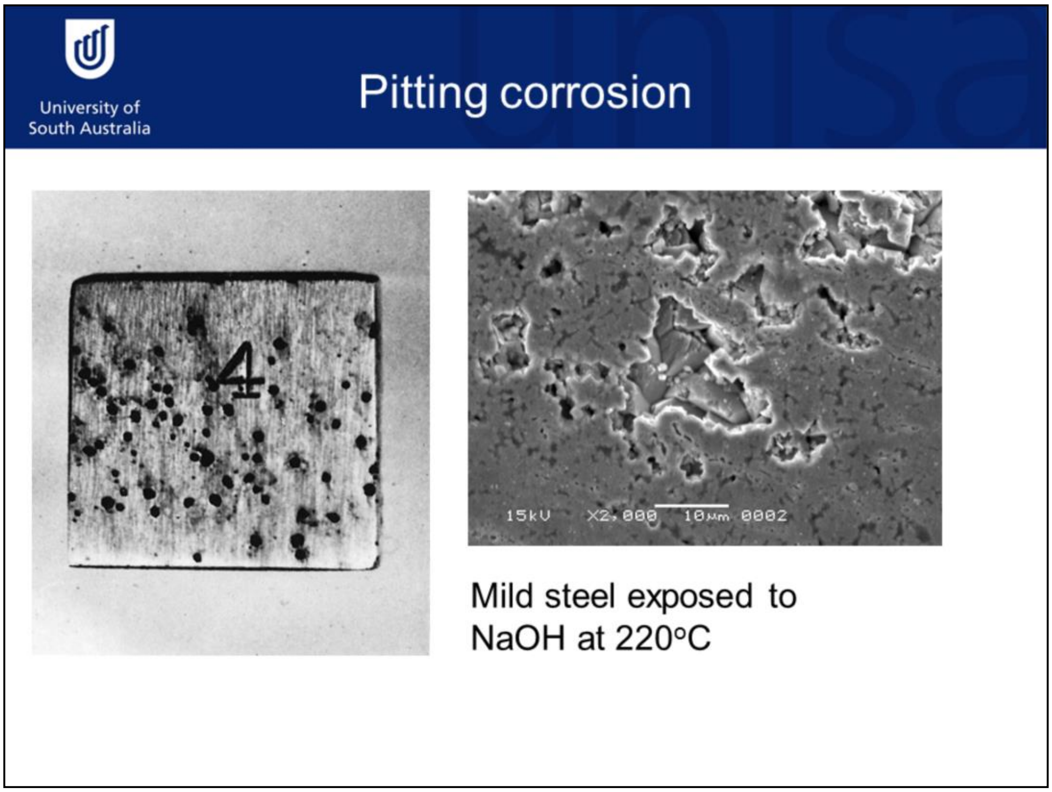
Uniform/general corrosion

Steel reinforced concrete

The type of corrosion that leads to the red oxide rust often seen on metal objects left out in the weather is normally a result of uniform attack of the metal surface. Most people are familiar with this type of corrosion and would have seen something similar to the example shown here of rusting steel reinforcing that has been exposed by damaged concrete. This type of corrosion is uniform and generally represents a low risk in terms of unexpected failure provided it is monitored.



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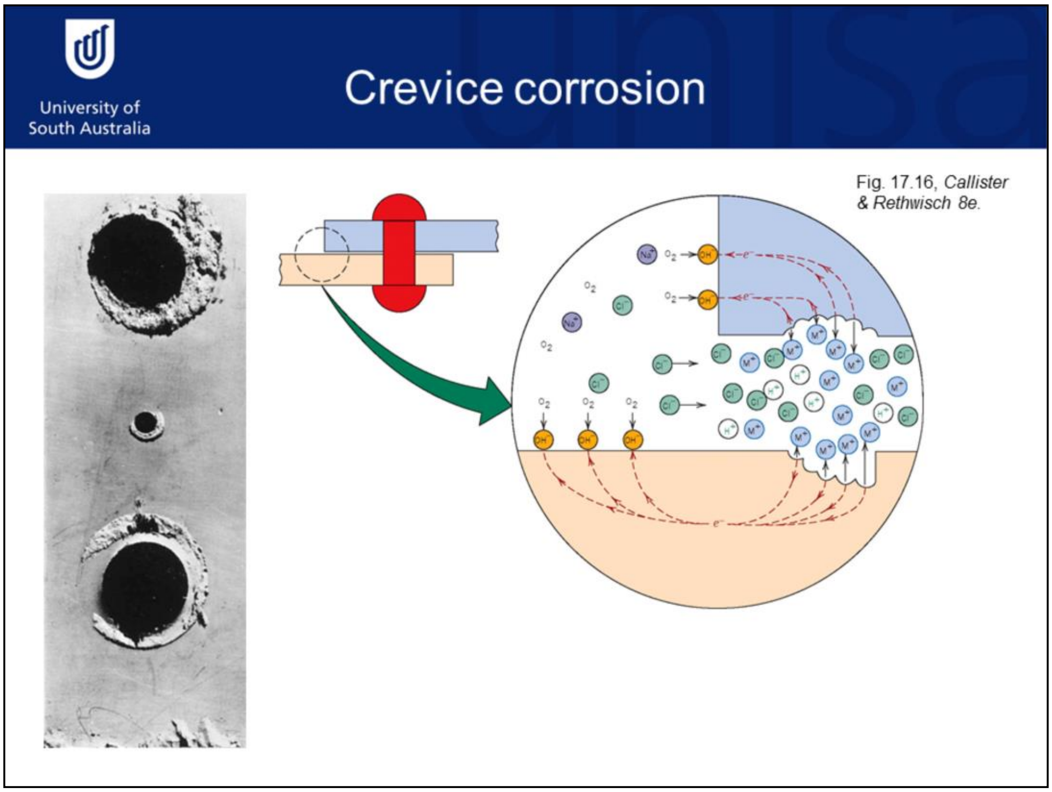
Pitting corrosion

Mild steel exposed to NaOH at 220°C

Pitting corrosion on the other hand can be quite problematic since the corrosion is very localised. It occurs because the protective passive film that protects many metals such as stainless steel and aluminium is breached. As a result the region the becomes exposed is preferentially attacked and the holes or pits tend to migrate deeper into the steel. The picture on the left shows the typical fingerprint of pitting corrosion. The image on the right shows what can happen when mild steel is exposed to NaOH at 220 C. It is a magnified view of a pit and shows breakdown of the passive layer revealing underlying surface structure.

This form of corrosion is generally difficult to detect and because it creates tiny holes in the metals it can lead to rapid failure, particularly if the metal part is operating under pressure.



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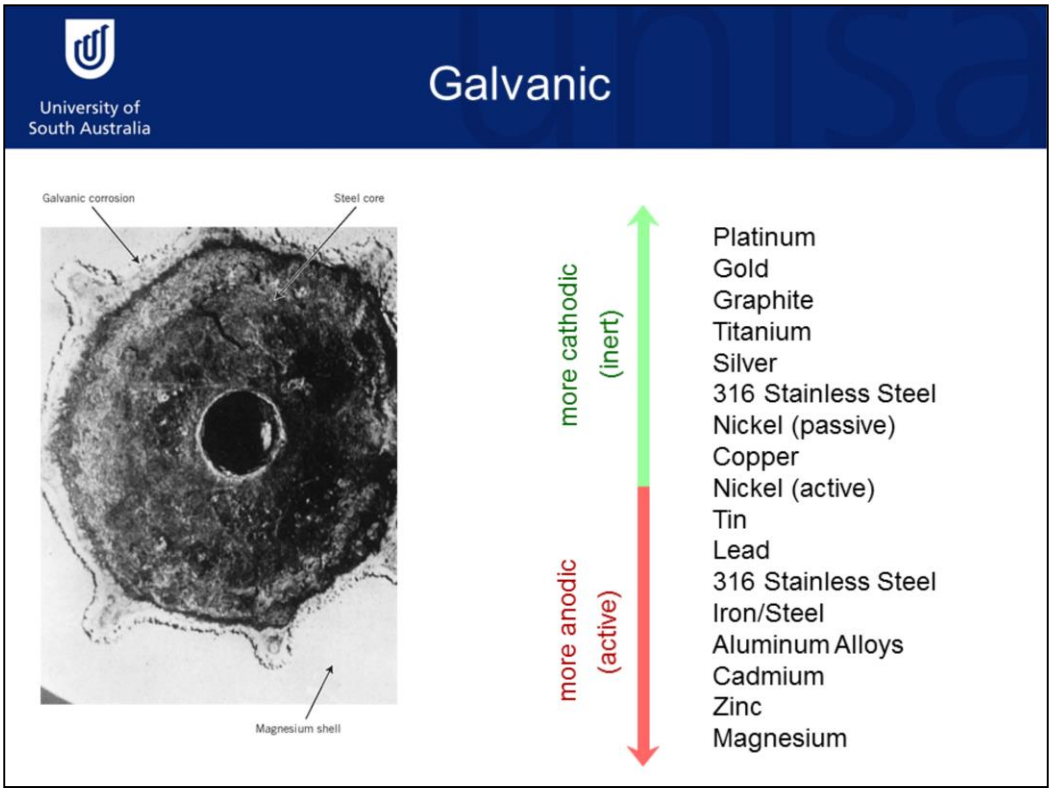
Crevice corrosion

Fig. 17.16, *Callister & Rethwisch 8e.*

Crevice corrosion is similar to pitting corrosion but is found where two pieces of metal have been joined in such a way a small gap exists at the join. In the diagram shown here, the metals have been riveted together. The region within the gap tends to be oxygen poor and you may remember from the previous lecture that when there are variations in oxygen the region low in oxygen will become the anode, and this is what happens here. The region in the crevice is anodic and oxidation takes place. The process is compounded by corrosion products blocking the crevice further, the formation of H+ ions which makes the local environment very acidic and the migration of negatively charged species like chloride ions, which cause corrosion problems in their own right, into the crevice as a result of electrostatic attraction to a region rich in positive charge. In addition the anode is much smaller than the cathode which tends to accelerate the corrosion process.

Again from a practical perspective this form of corrosion is potentially quite dangerous because it is very difficult to detect.



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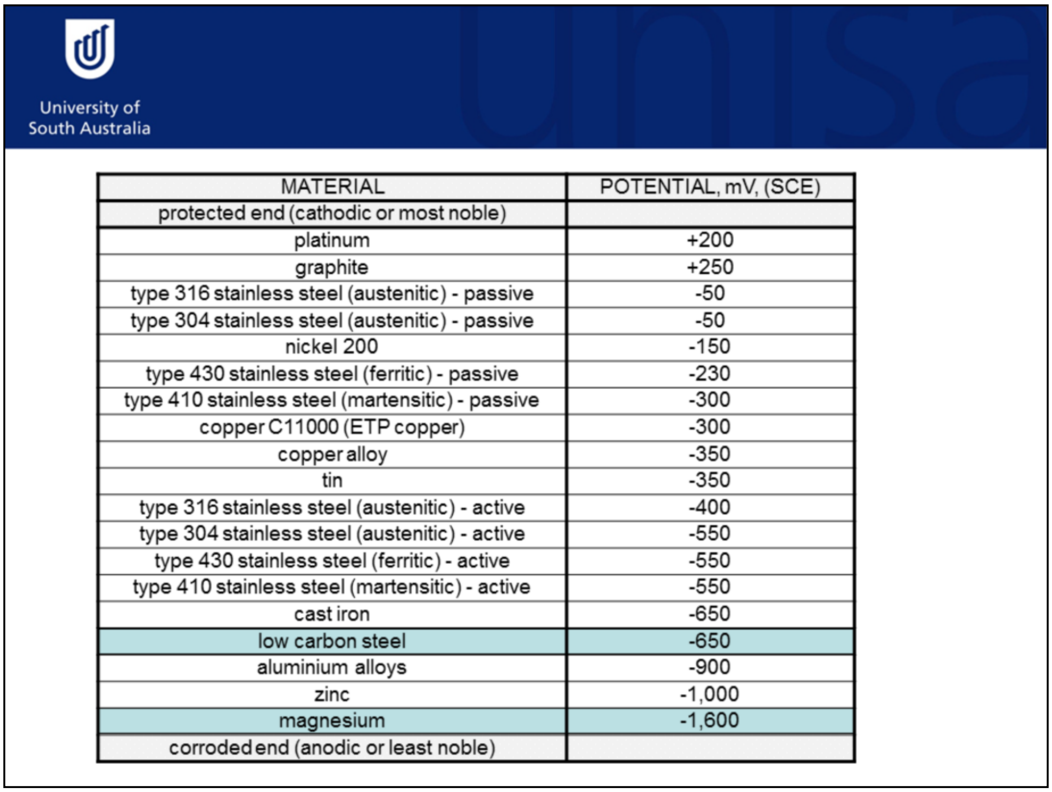
Galvanic

more cathodic (inert)

- Platinum
- Gold
- Graphite
- Titanium
- Silver
- 316 Stainless Steel
- Nickel (passive)
- Copper
- Nickel (active)
- Tin
- Lead
- 316 Stainless Steel
- Iron/Steel
- Aluminum Alloys
- Cadmium
- Zinc
- Magnesium

more anodic (active)

Galvanic corrosion of the other hand occurs when you have two different metals in contact. You may recall from the previous presentation the galvanic series in seawater. Those metals lower down the list tend to be more reactive while those further up the list more inert. If a very reactive and very inert metal are touching in a corrosive environment the more reactive metal will become the anode and corrode. The photo shows a steel core surrounded by a magnesium shell. Because the magnesium is lower down the galvanic series than the steel it will corrode in preference to the steel. The next slide assigns some numbers to the process so that you can develop a feel for the potential differences involved.



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MATERIAL	POTENTIAL, mV, (SCE)
protected end (cathodic or most noble)	
platinum	+200
graphite	+250
type 316 stainless steel (austenitic) - passive	-50
type 304 stainless steel (austenitic) - passive	-50
nickel 200	-150
type 430 stainless steel (ferritic) - passive	-230
type 410 stainless steel (martensitic) - passive	-300
copper C11000 (ETP copper)	-300
copper alloy	-350
tin	-350
type 316 stainless steel (austenitic) - active	-400
type 304 stainless steel (austenitic) - active	-550
type 430 stainless steel (ferritic) - active	-550
type 410 stainless steel (martensitic) - active	-550
cast iron	-650
low carbon steel	-650
aluminium alloys	-900
zinc	-1,000
magnesium	-1,600
corroded end (anodic or least noble)	

You will notice that the magnesium is about 1 V more negative than steel. Because the potential difference is so large there is large driving force leading to corrosion. Although galvanic corrosion is a problem it can be minimised by careful materials selection. It is desirable to keep the potential difference between the materials as small as possible. As you will see shortly, galvanic corrosion can also exploited to provide corrosion protection.

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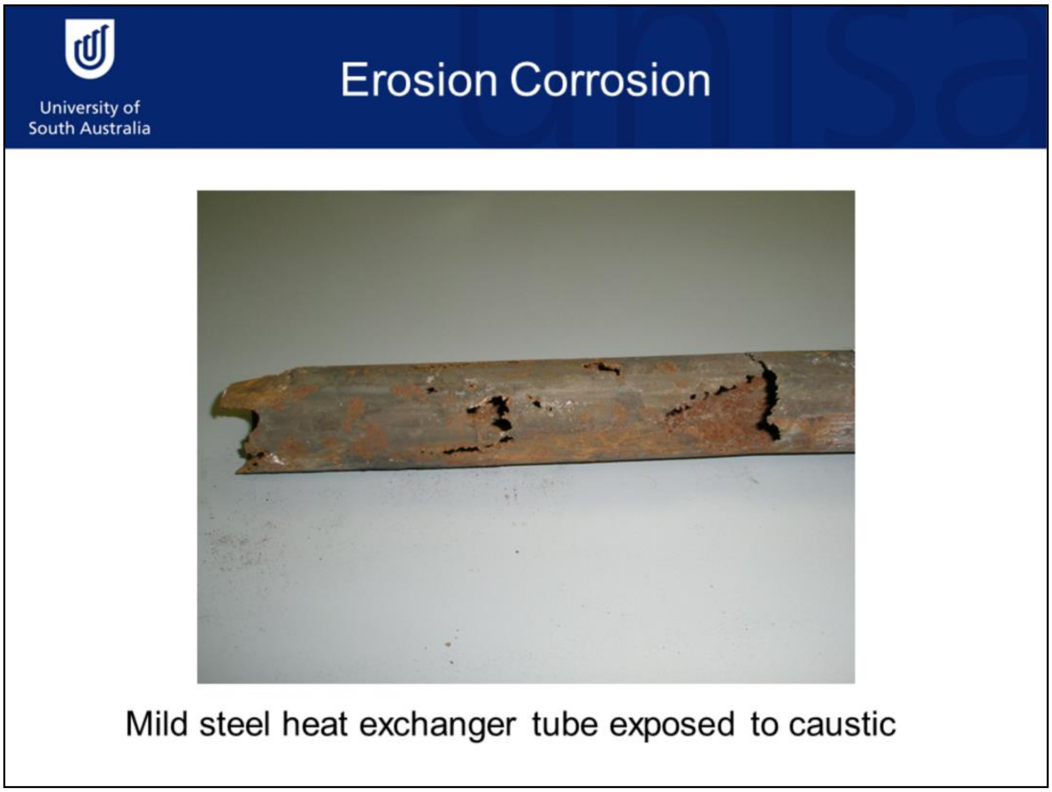
Stress corrosion cracking

The image here shows cracking around the bend of this U shaped component. Since regions under stress act as anodic sites in corrosive environments components that have residual internal stresses or stress due to applied load can become susceptible to stress corrosion cracking. It is important to note that the stress alone does not result in cracking it is because it is in a corrosive environment that cracking occurs. This form of corrosion can be catastrophic because, once formed, the cracks can propogate rapidly through a component causing it to fail. As will other forms of localised corrosion it is very difficult to detect until it is too late.



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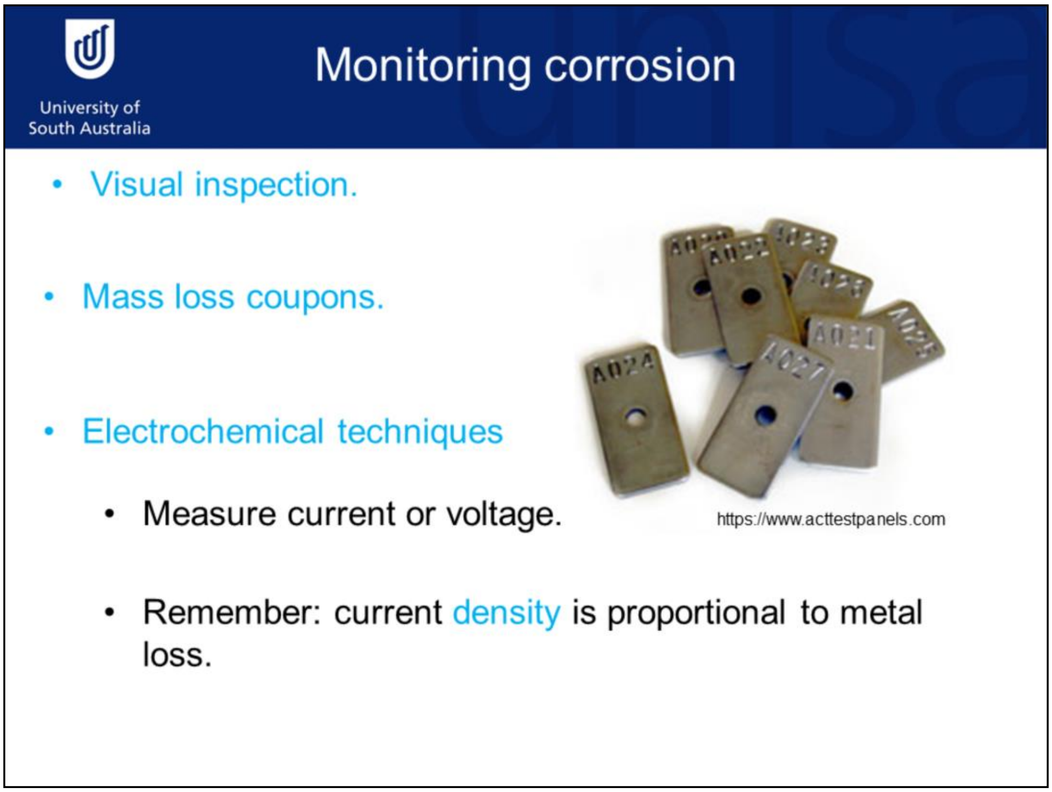
Erosion Corrosion

Mild steel heat exchanger tube exposed to caustic

Erosion corrosion occurs when particles in a slurry abrade the metal surface removing any passive protective layer present on the surface. Here you can see the result of heat exchanger tubing that has failed due to erosion corrosion.



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Monitoring corrosion

- Visual inspection.
- Mass loss coupons.
- Electrochemical techniques
  - Measure current or voltage.
  - Remember: current density is proportional to metal loss.

https://www.acttestpanels.com

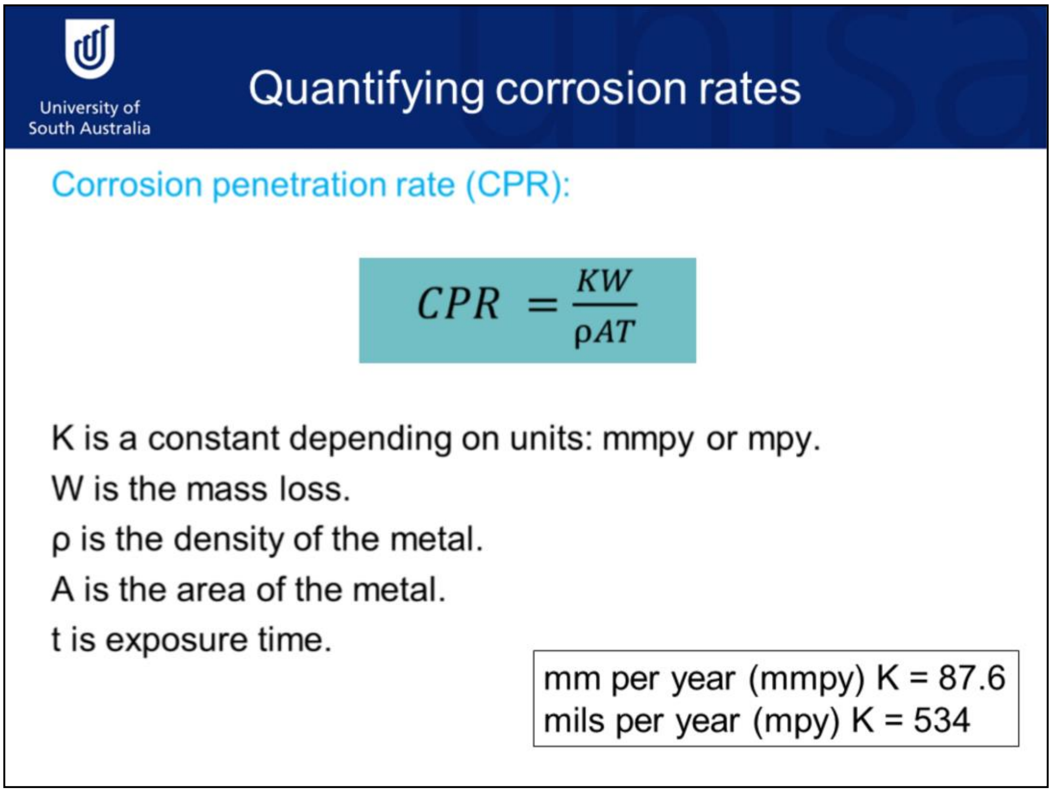
Given the potential for catastrophic failure due to corrosion the issue of monitoring corrosion is a critical one. The most obvious monitoring method is by visual inspection. This is certainly a necessary part of any corrosion monitoring program but has its limitations. In particular it is very difficult to detect very small feature that provide tell tail signs of imminent corrosion related failure.

Mass loss coupon measurements are often used to provide information about the long term effects of a corrosive environment on the metal components within that environment. Coupons are cut from a piece of metal that has the same composition as that which you wish to monitor. The coupon is then placed in the same environment as the component – for example a steel coupon may be placed inside a steel tube to monitor the metal loss of the tube due to corrosion. However, rather than remove the tube itself, the coupon is removed, and inspected, the corrosion products are carefully cleaned off the coupon and its mass measured. The change in mass from the un-corroded to the corroded coupon will provide some indication of the average corrosion rate within that process or environment. The main drawback to coupon measurements is they do not provide real time information instead only providing information about the total corrosion during the period of installation. It will not provide information on whether there were periods of high or low corrosion.

To do this some other method is usually employed. Electrochemical techniques that measure current or voltage are the most common method for achieving this. These provide a useful way of monitoring corrosion because they directly monitor the current which in turn is a measure of electron movement. Hence current density, that is the total current divided by the area, is proportional to the amount of metal lost. Electrochemical techniques can be used for quasi real time monitoring of corrosion.

One problem near all of these techniques face is they are generally unable detecting localised corrosion such as pitting. Coupon measurements will tell you pitting has occurred while electrochemical methods are normally designed for general corrosion measurements. Visual inspection can help provided the pits or cracks are visible to either the naked eye or camera arrangement used to check for corrosion.

These are just some of the measurement techniques, other methods are available but detecting small defects or cracks due to corrosion is still extremely challenging.



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Quantifying corrosion rates

Corrosion penetration rate (CPR):

$$CPR = \frac{KW}{\rho AT}$$

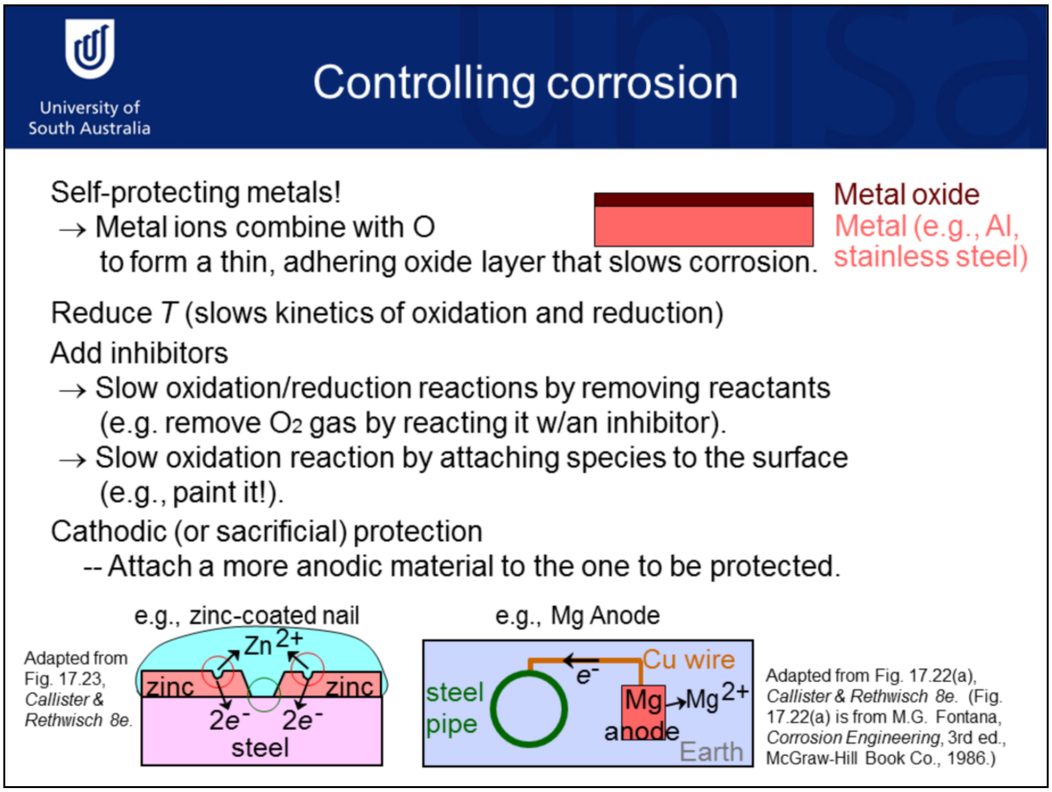
K is a constant depending on units: mmpy or mpy.
W is the mass loss.
ρ is the density of the metal.
A is the area of the metal.
t is exposure time.

mm per year (mmpy) K = 87.6
mils per year (mpy) K = 534

Corrosion rates are often expressed as a corrosion penetration rate or CPR. This provides an indication of how quickly metal is being removed as a result of corrosion.

It is proportional to the mass lost as a result of corrosion and inversely proportional to the exposure time. The proportionality constant contains information about the exposed area, metal density and a suitable conversion factor to present the data in terms of mm per year or mils per year.

Whenever presenting corrosion data as thickness changes it is very important to take care not to take the values literally. They will be indicative of the corrosion rate but because of geometry and other considerations may not accurately represent the true corrosion rate.



Controlling corrosion

Self-protecting metals!
→ Metal ions combine with O
to form a thin, adhering oxide layer that slows corrosion.

Reduce *T* (slows kinetics of oxidation and reduction)

Add inhibitors
→ Slow oxidation/reduction reactions by removing reactants
(e.g. remove O_2 gas by reacting it w/an inhibitor).
→ Slow oxidation reaction by attaching species to the surface
(e.g., paint it!).

Cathodic (or sacrificial) protection
-- Attach a more anodic material to the one to be protected.

e.g., zinc-coated nail

Adapted from Fig. 17.23, *Callister & Rethwisch 8e.*

e.g., Mg Anode

Adapted from Fig. 17.22(a), *Callister & Rethwisch 8e.* (Fig. 17.22(a) is from M.G. Fontana, *Corrosion Engineering*, 3rd ed., McGraw-Hill Book Co., 1986.)

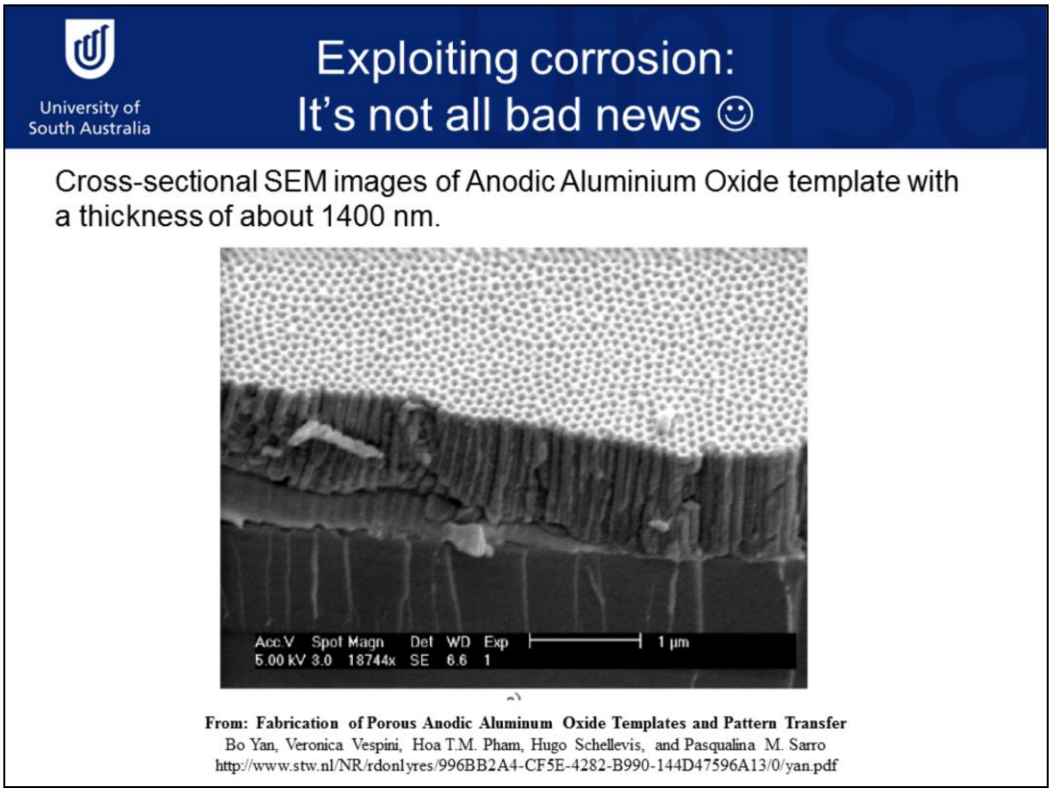
There are a number of ways to prevent or at least slow down corrosion processes. The simplest to employ is to chose metals that passivate easily and form a natural protective barrier. Typical examples include aluminium, which would be otherwise very reactive without the metal oxide film that forms on its surface, and stainless steel.

Alternatively, lowering the temperature will slow the oxidation and reduction kinetics.

In many processes it is cost effective and sometimes necessary to use ainhibitors. Inhibitors may either remove reactants or cover either anodic or cathodic materials. A good example of an inhibitor is paint.

Another method that is commonly employed to help protect metal parts involves cathodic or sacrificial protections. The idea is to exploit the galvanic series so that a sacrificial anode made of metal low in the galvanic series, for example zinc or magnesium, corrodes in preference to the cathodic metal you want to protect. You may recall that both zinc and magnesium have large negative potentials compared to most other metals which makes them perfect as anodes for cathodic protection arrangements.

Cathodic protection is often used to protect steel pipework but most people would be familiar with the zinc coated metal sheets that are used for roofs and sheds. The zinc coating is the sacrificial anode that protects the underlying structural steel.



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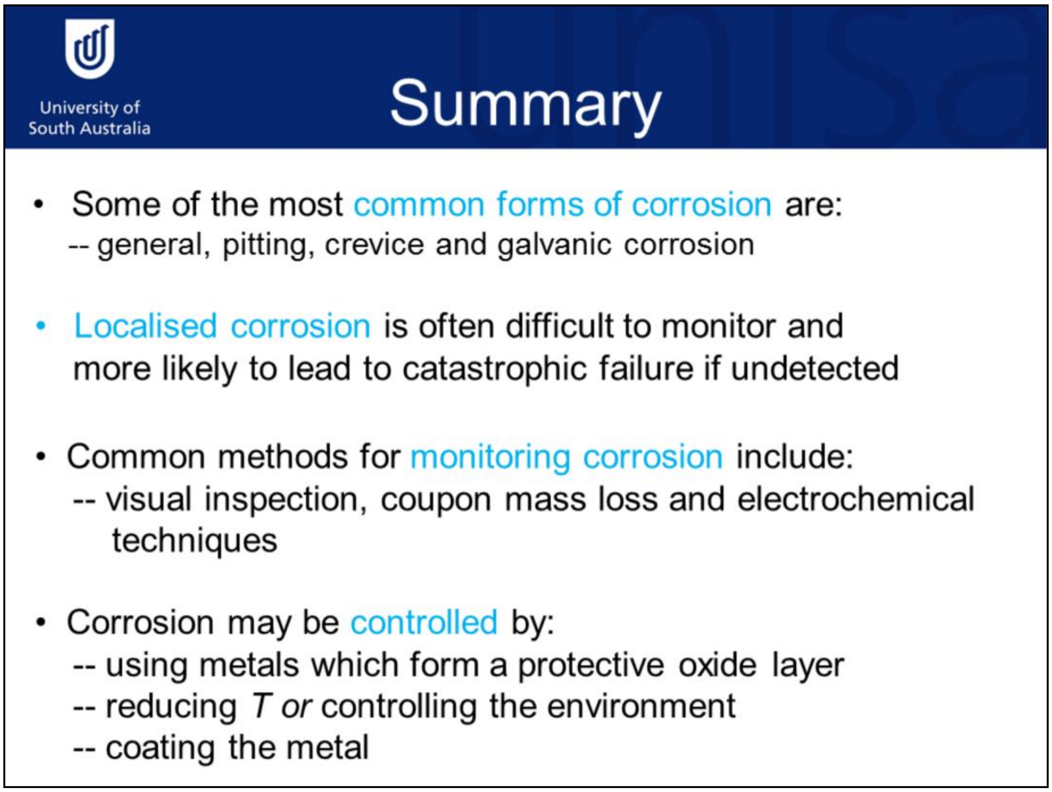
Exploiting corrosion: It’s not all bad news ☺

Cross-sectional SEM images of Anodic Aluminium Oxide template with a thickness of about 1400 nm.

From: Fabrication of Porous Anodic Aluminum Oxide Templates and Pattern Transfer
Bo Yan, Veronica Vespini, Hoa T.M. Pham, Hugo Schellevis, and Pasqualina M. Sarro
http://www.stw.nl/NR/rdonlyres/996BB2A4-CF5E-4282-B990-144D47596A13/0/yan.pdf

For most of the presentation corrosion has be presented as something that is undesirable and in many instances this is true. However, in some cases corrosion is exploited to fabricate small and delicate structures. In the picture shown here researchers deliberately anodise aluminium oxide to form a template for making high tech nano fibre structures. The anodising process is essentially a result of corrosion of the aluminium surface. In the nano fibre fabrication example the porous nature of the oxide film is exploited to provide a template for the fibre. In less high tech applications the aluminium is often anodised and the pores sealed to make the aluminium more chemically resistant for items like kitchenware.



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Summary

- Some of the most common forms of corrosion are:
  -- general, pitting, crevice and galvanic corrosion
- Localised corrosion is often difficult to monitor and more likely to lead to catastrophic failure if undetected
- Common methods for monitoring corrosion include:
  -- visual inspection, coupon mass loss and electrochemical techniques
- Corrosion may be controlled by:
  -- using metals which form a protective oxide layer
  -- reducing *T or* controlling the environment
  -- coating the metal

In this presentation we have discussed some of the most common forms of corrosion such as general, pitting, crevice and galvanic corrosion.

I have also highlighted the problems associated with localised corrosion especially because it is difficult to monitor and can lead to catastrophic failure.

I have outline some common methods for monitoring corrosion, however the list is not exhaustive and new techniques are constantly being developed to improve our ability to keep tabs on corrosion.

Finally there are a variety of ways to control corrosion ranging from taking advantage of the natural protective film that forms on many metals; reducing the temperature or controlling the environment. The other alternative is to coat the material. Finally it is important to remember that what we are trying to do is eliminate one or more of the four requirements for corrosion to take place.

Thank you