SMM 3622

Materials Technology

4.3 Corrosion

Forms of Corrosion

- ☐ Corrosion may be:

  1. General (uniform) corrosion
  2. Localised corrosion

- ☐ The worst situations occur when damage is confined to small anodic areas (localised corrosion).

- ☐ Corrosion is affected by:

  - ☐ Design details (shape), material compatibility, stress, movement (of material or fluid), surface condition and temperature.

1. Uniform (general corrosion)

- ❑ In uniform corrosion the electrochemical reactions occur at the same rate over the entire surface (corrosion occurs evenly over the entire surface of the corroding metal).

- ❑ Based on tonnage (size or weight), uniform corrosion is the most important form of corrosion.

- ❑ Uniform corrosion is usually the result of breakdown in protective coatings

- ❑ Uniform corrosion is relatively easy to measure, predict and design against.

- ❑ Uniform corrosion proceeds by a chemical / electrochemical reaction uniformly over the surface.
- ❑ This type of attack is mostly found where a metal is in contact with an acid, a humid atmosphere or a solution in general.
- ❑ The corrosion products produced may either form:

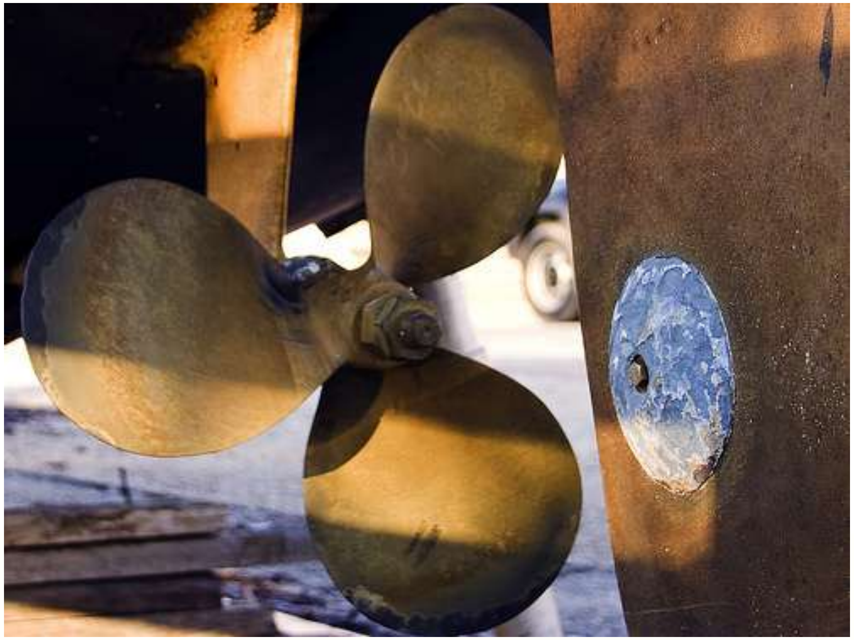
1. Protective layer on the metal (which would stop further corrosion)
2. May be readily dissolved in the environment (leading to further active corrosion)

Factors affecting uniform corrosion

1. pH
   - Low pH accelerated the cathodic reaction
   - pH affects the stability of passive films
2. Dissolved gas
   - Dissolved oxygen
3. Velocity
   - Higher velocity increases mass transfer rate
   - Accelerates erosion
4. Temperature
   - Increased temperature, will increase reaction rate

Prevention of Uniform Corrosion

1. Proper material selection
2. Change the environment (add inhibitors)
3. Cathodic protection



Cathodic Protection
bronze prop and a sacrificial zinc on the rudder.

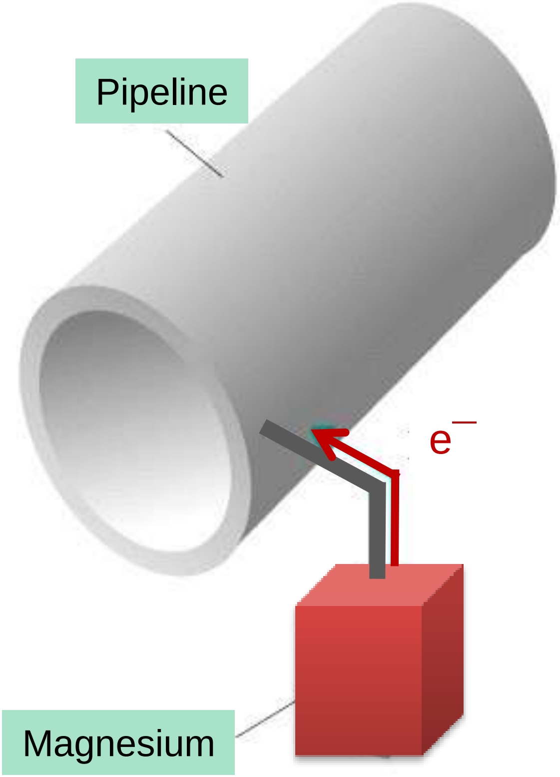
General (Uniform) corrosion

Cathodic protection

- **Cathodic protection** (**CP**) is a technique to control the corrosion of a metal surface by making it work as a cathode of an electrochemical cell.

- This is achieved by placing in contact with the metal to be protected another more easily corroded metal to act as the anode of the electrochemical cell.

- Cathodic protection systems are most commonly used to protect steel, water or fuel pipelines and storage tanks, steel pier piles, ships, offshore oil platforms and onshore oil well casings.



corrosion inhibitors

Hexamine
phenylenediamine
dimethylethanolamine
sodium nitrite

2. Localised Corrosion

- ☐ There are different types of localised corrosion:

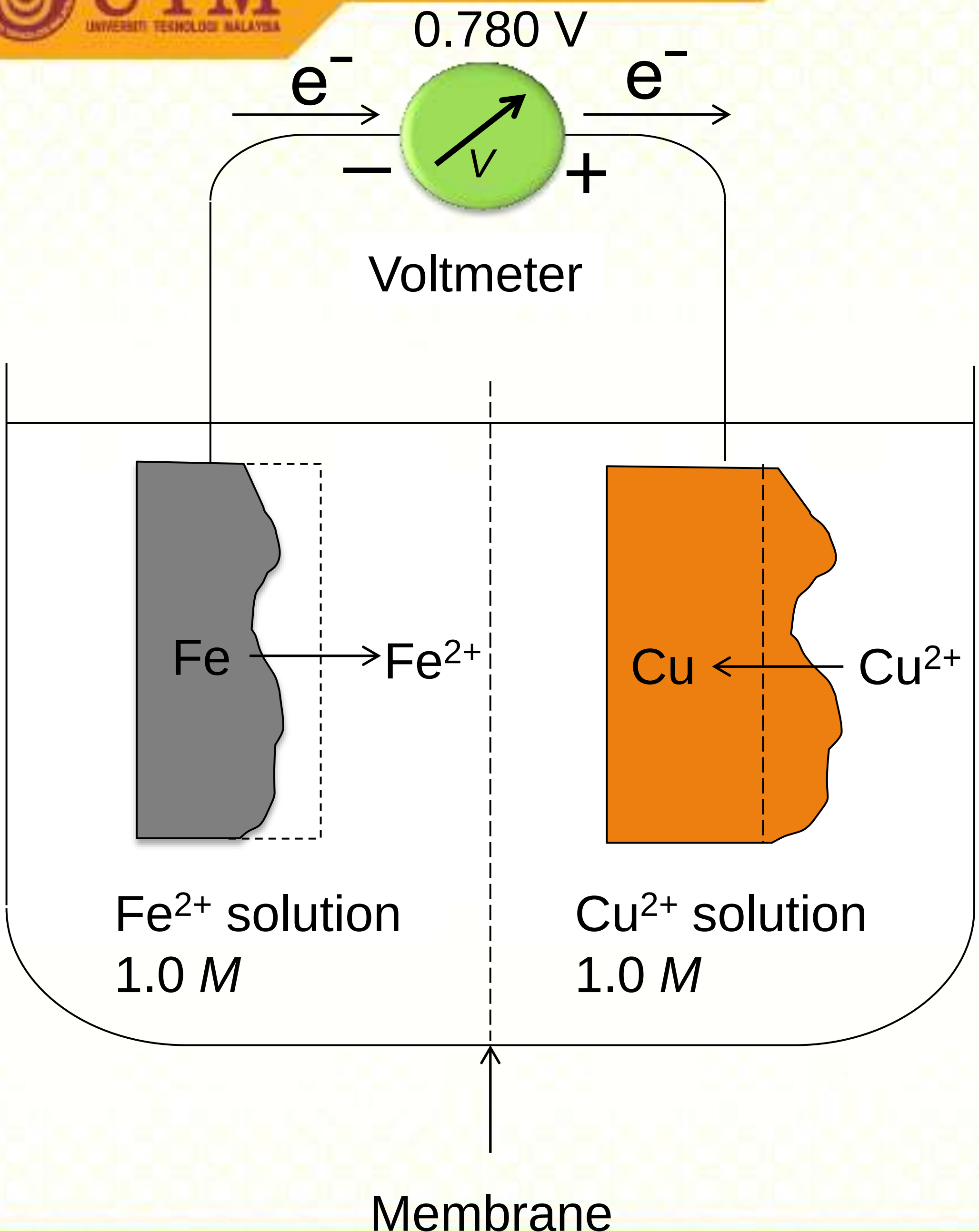
1. Galvanic corrosion
2. Pitting corrosion
3. Crevice corrosion
4. Intergranular corrosion
5. Selective leaching (dealloying)
6. Fretting corrosion
7. Cavitation corrosion
8. Erosion-corrosion
9. Environmentally induced cracking
   - ☐ Hydrogen embrittlement
   - ☐ Stress corrosion cracking (SCC)
   - ☐ Corrosion Fatigue

- ❑ Localised corrosion is due to the following factors:

1. Environment
   - Oxygen concentration
   - Chloride ion concentration
   - pH
   - flow rate
2. Material
   - Inclusions
   - Different phases
   - Grain boundaries
3. mechanical
   - Static stress
   - Cyclic stress

Galvanic Corrosion (bimetallic corrosion):

- ☐ Occurs when <u>2 different metals</u> are electrically connected in the same electrolyte
- ☐ The more active (anodic) metal corrodes faster
- ☐ The less active (anodic) metal corrodes slower and will be protected
- ☐ Driving force for corrosion the difference in electrode potential



Anodic reaction:

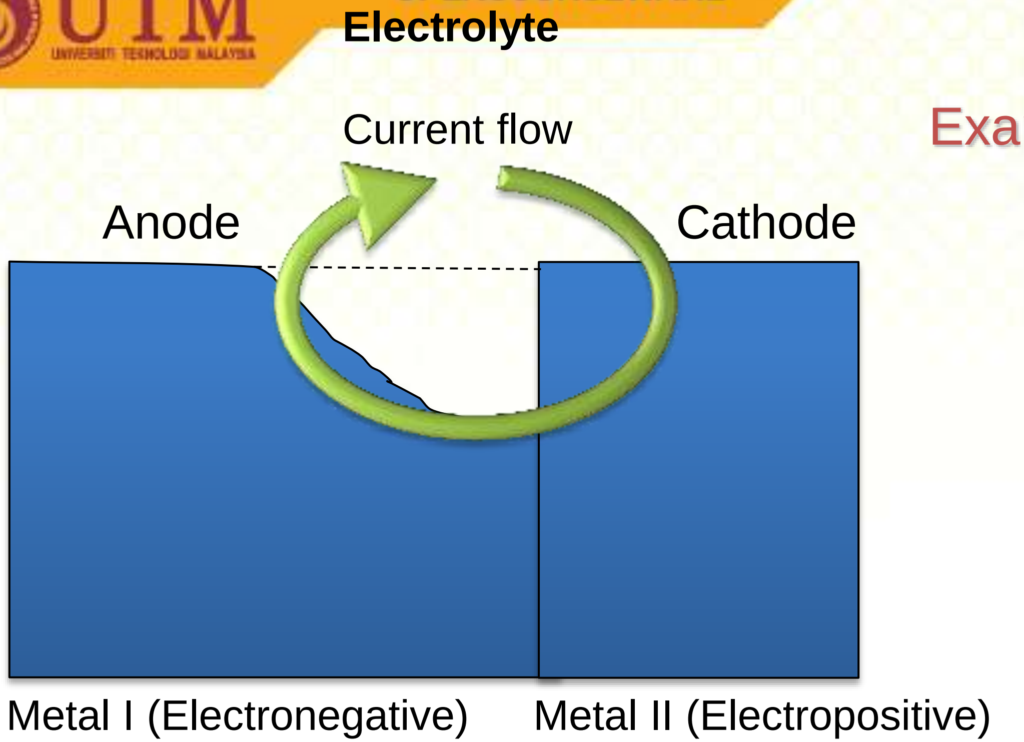
$Fe \rightarrow Fe^{+2} + 2e^-$

Cathodic reaction:

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

Overall reaction:

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



Electrolyte

Current flow

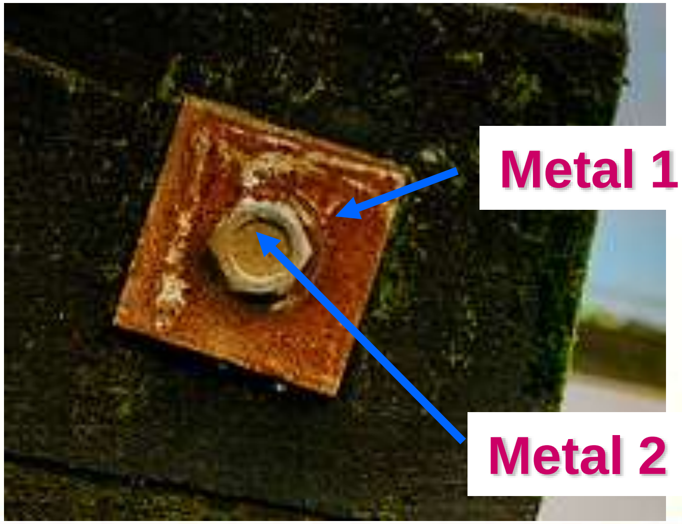
Anode

Cathode

Metal I (Electronegative)

Metal II (Electropositive)

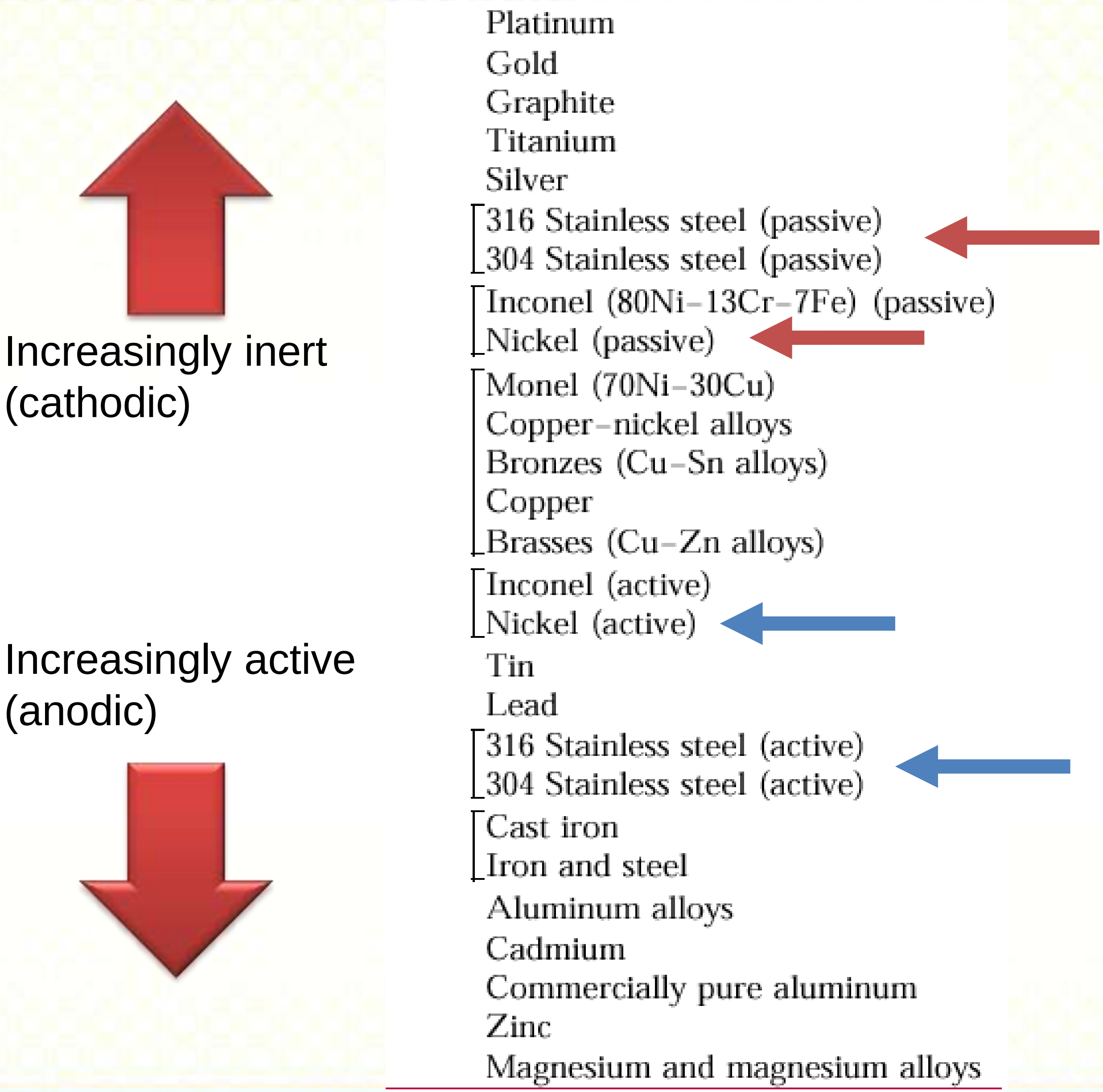
Example of galvanic corrosion



Metal 1 is more anodic

Metal 2 is less anodic

Galvanic Series in Seawater



Increasingly inert (cathodic)

Increasingly active (anodic)

Platinum
Gold
Graphite
Titanium
Silver
316 Stainless steel (passive)
304 Stainless steel (passive)
Inconel (80Ni–13Cr–7Fe) (passive)
Nickel (passive)
Monel (70Ni–30Cu)
Copper–nickel alloys
Bronzes (Cu–Sn alloys)
Copper
Brasses (Cu–Zn alloys)
Inconel (active)
Nickel (active)
Tin
Lead
316 Stainless steel (active)
304 Stainless steel (active)
Cast iron
Iron and steel
Aluminum alloys
Cadmium
Commercially pure aluminum
Zinc
Magnesium and magnesium alloys

- The galvanic series will predict which metal will corrode
- The galvanic series is similar to the “emf” but is for alloys in real environment.

Comparison between the “emf” and galvanic series

emf series	**Galvanic series**
• Is ordered by standard equilibrium potential	• Is ordered by observed behaviour in service
• Assumes activity of solution species to be = 1	• Allows for corrosion products
• Does not allow for protective corrosion products	• Can be defined for alloys
• Defined only for pure metals	• Different for every environment

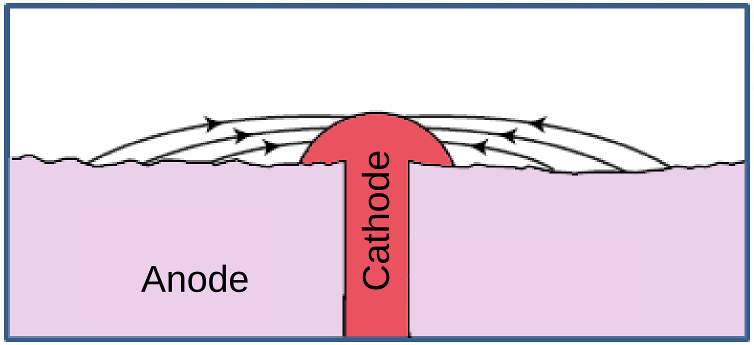
- ❑ The factors affecting the severity galvanic corrosion are:

- ❑ Size of exposed areas of the anodic metal relative to that of the cathodic metal

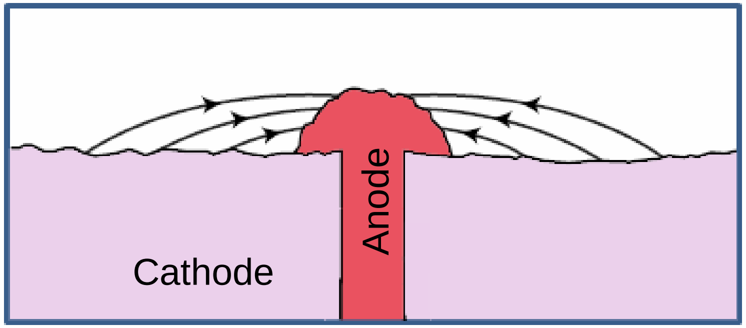
  1. **Smaller cathode relative to anode will cause small increase in corrosion of anode**
  2. **Smaller anode will suffer severe corrosion (increase of corrosion rate)**

- ❑ Difference in potential between metals (anode and cathode) in the galvanic series

- ❑ Effect of anodic polarisation on anode (some metals may passivate)



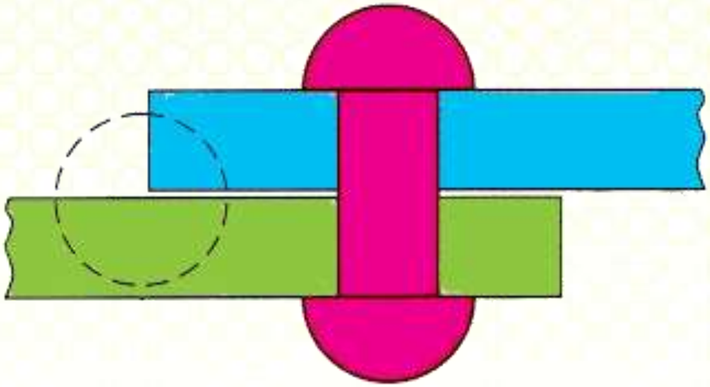
Large anode area, small cathode area showing relatively insignificant attack over a wide area of sheet



A large cathode area, small anode area showing relatively pronounced attack of the rivet head

Prevention of Galvanic Corrosion:

1. Select combinations of metals as close together as possible in the galvanic series.
2. Avoid the unfavorable area effect of a small anode and large cathode.
3. If dissimilar metal must be joined, Insulate them electrically wherever practicable.
4. Apply coatings with caution.
5. Add inhibitors, if possible, to decrease the aggressiveness of the environment.
6. Design for the use of readily replaceable anodic parts or make them thicker for longer life.
7. Install a third metal which is anodic to both metals in the galvanic contact, i.e. cathodic protection



Crevice Corrosion:

- ☐ Crevice corrosion occurs at shielded areas that contain small volume of aqueous solution

- ☐ The crevice can be a hole, a space between the surface a poorly adherent coating, another metal or even a non-metal (concrete, glass, rubber).

- ☐ Examples of such crevices are: flanged or threaded connections, shielded areas on metal surfaces (eg as a result of deposit formation), electrical connectors and sockets for integrated circuit chips on circuit boards.

☐ Liquid entry but stagnant (not flowing)

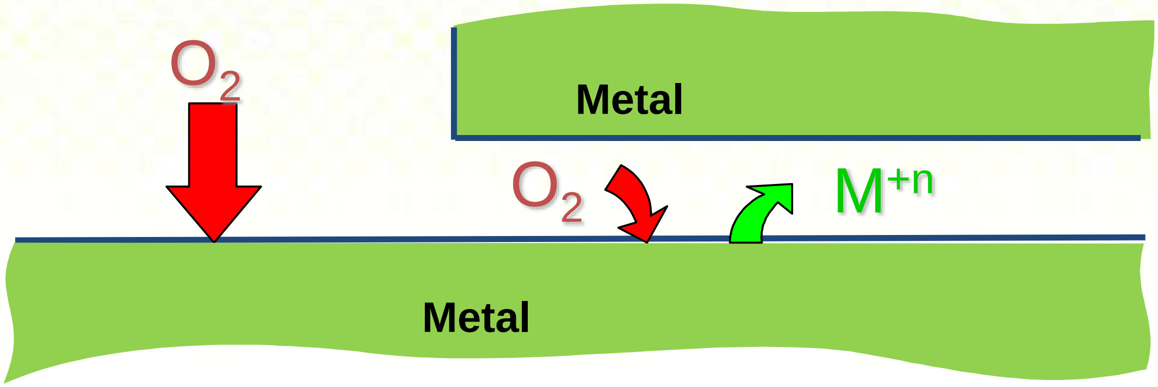
☐ Corrosion rate of crevice is higher than that on bulk

☐ Crevice corrosion is initiated by changes in local chemistry within the crevice:

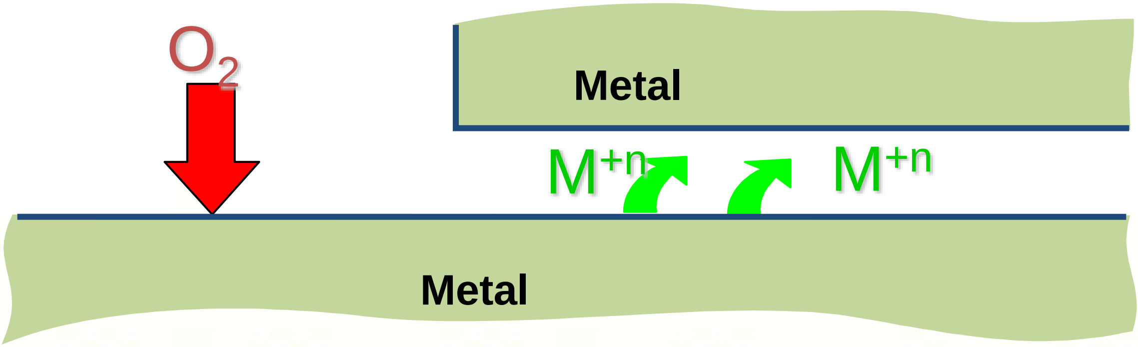
a. Depletion of oxygen in the crevice (O_2 concentration cell)
b. Depletion of inhibitor in the crevice
c. A shift to acid conditions in the crevice
d. Build-up of aggressive ion species (e.g. chloride) in the crevice

☐ Crevice corrosion occurs mainly on alloys which passivate (e.g; stainless steels)

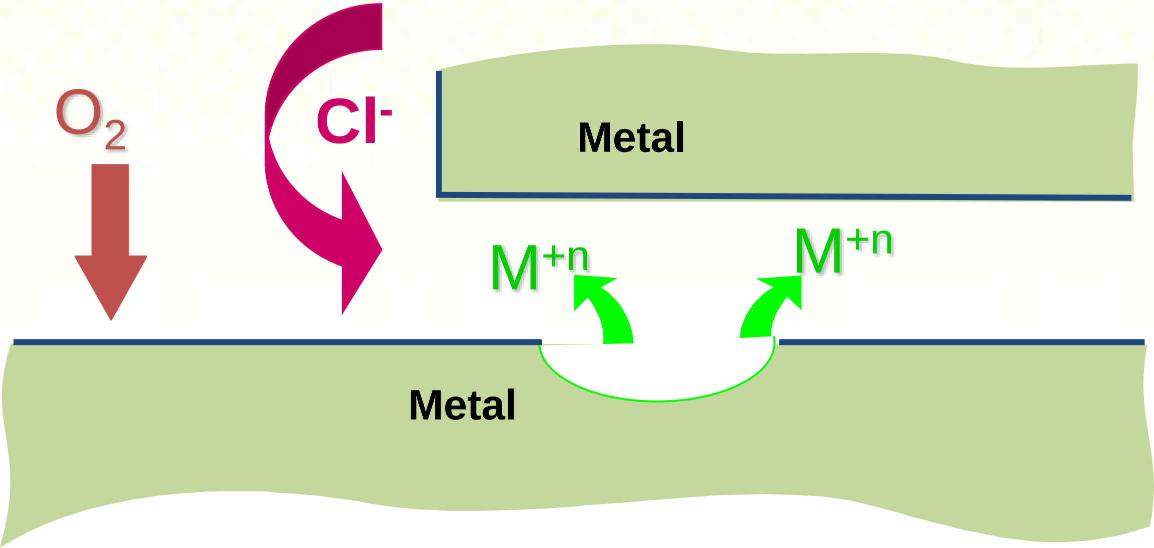
Crevice corrosion



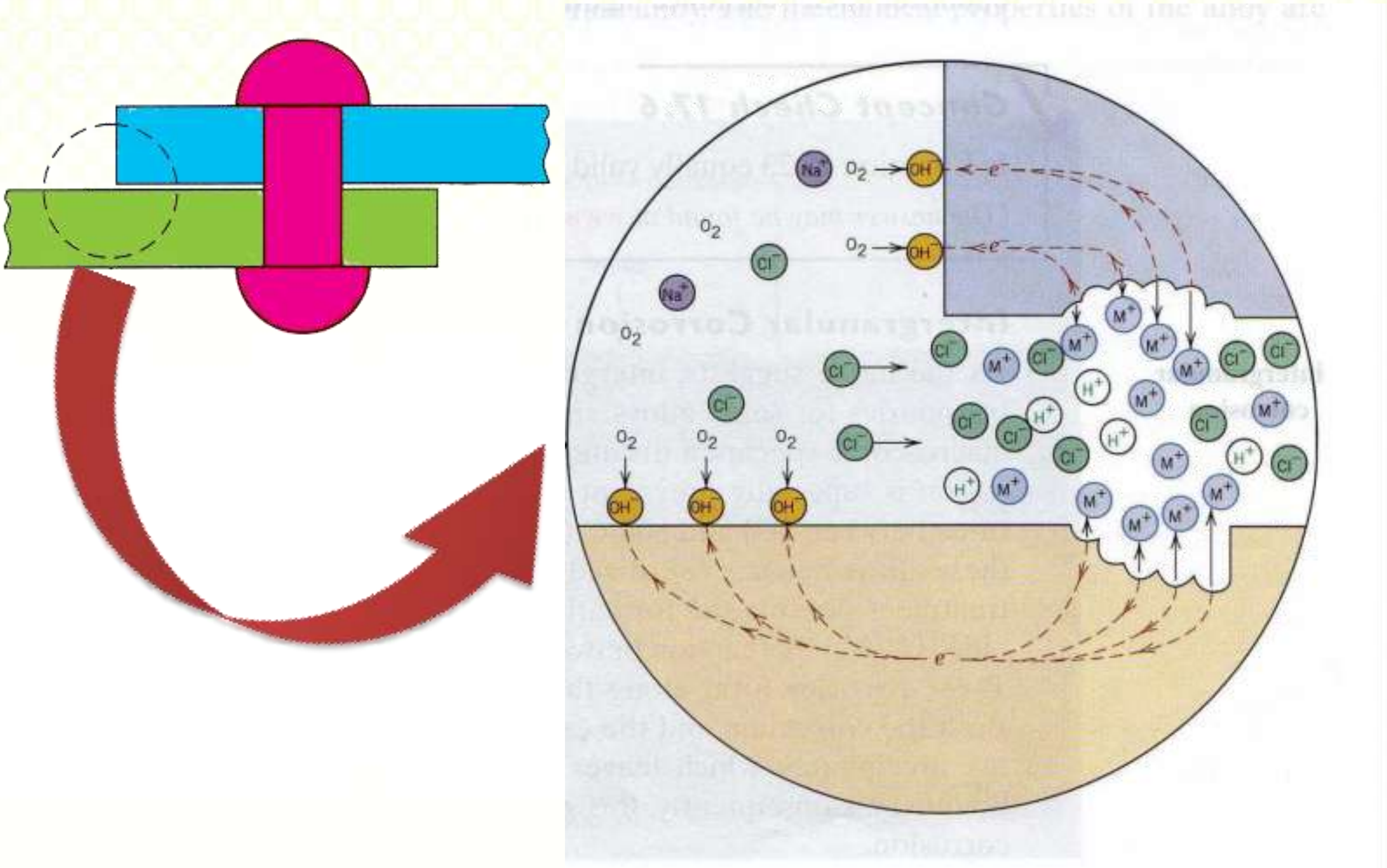
1. Anodic & cathodic reactions occur over the entire surface



2. O_2 is consumed inside the crevice by passive corrosion (depletion of O_2)



3. Attraction of Cl^- inside the crevice (charge balance)
4. pH decreases inside the crevice (more acid) - Passive film breaks down in acid and rapid active corrosion starts
5. Crevice corrosion is an "*autocatalytic process*"



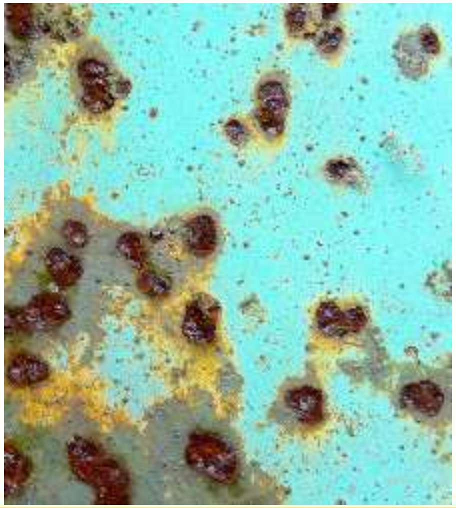
Schematic illustration of crevice corrosion between two riveted sheets.

Prevention of Crevice Corrosion:

- ❑ The most effective way of minimising crevice corrosion is the elimination of the crevice itself
- ❑ Crevice corrosion can be controlled by good design geometry (shape) to remove the crevice itself

Pitting Corrosion:

- ☐ Pitting corrosion is an intensive localised attack which results in the development of cavities or "pits" in the metal surface.
- ☐ The pits may range from deep cavities of small diameter to relatively shallow depressions.
- ☐ Quite often, the larger part of the metal surface remains virtually free from corrosion, while the corrosion pits have penetrated a significant part of the wall thickness.



- ❑ Halides such as chlorides (the main constituents of common salts), fluoride stimulate pitting.
- ❑ Stainless steels and aluminium alloys exposed to chloride containing solutions are known to suffer from pitting.
- ❑ Pitting corrosion is one of the most dangerous form of corrosion **"Weight loss is very small but grave consequences"**
- ❑ Pitting is considered to be more dangerous than uniform corrosion damage because it is more difficult to detect, predict and design against.

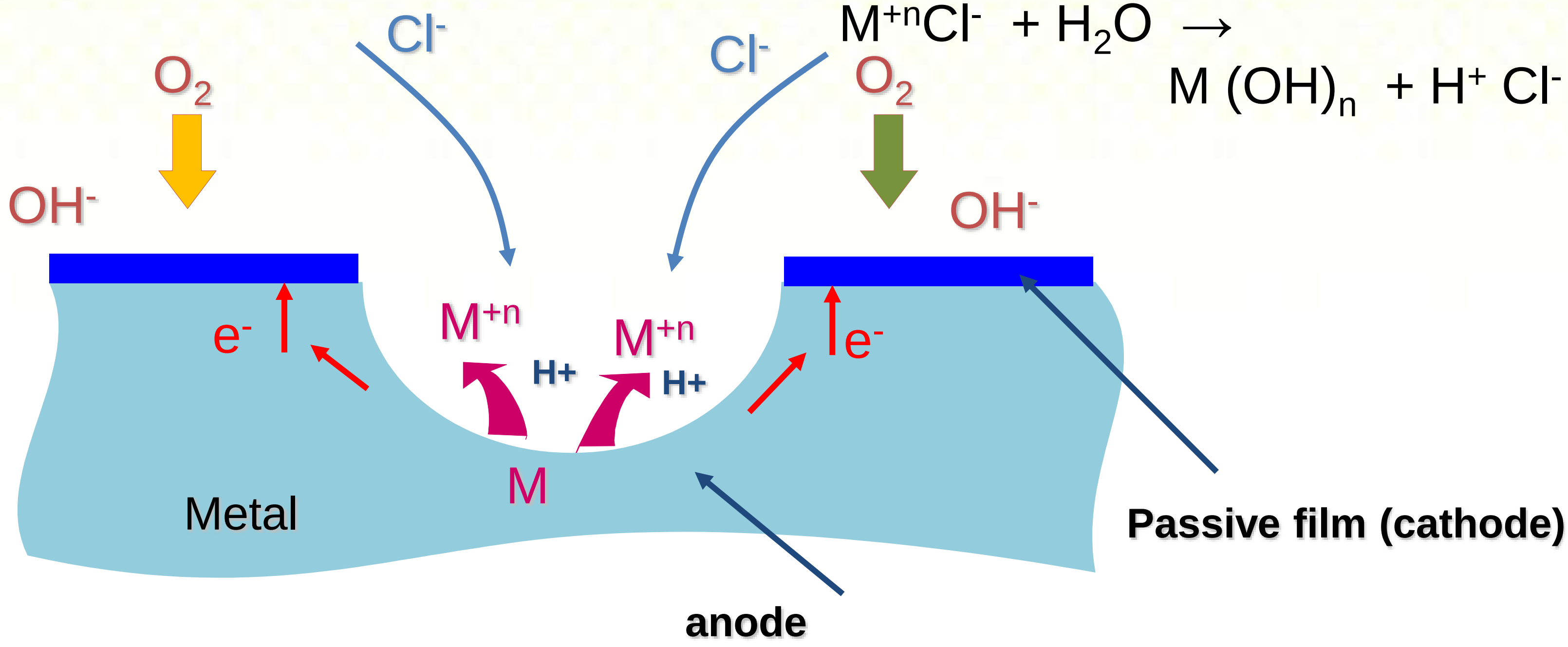
- ☐ Pitting corrosion is initiated by:

1. Local breakdown of protective passive film
    - ☐ Factors that can cause breakdown of a passive film: acidity, low dissolved O_2 concentrations, high concentrations of Cl^-

2. Localised damage to, or poor application of a protective coating
3. Compositional heterogeneity (presence of inclusion, segregation or precipitates)

Mechanism of pitting corrosion:

- ❑ Generally, the mechanism of pitting corrosion can be summarised as follows:



$$M^{+n}Cl^{-} + H_2O \rightarrow M(OH)_n + H^{+}Cl^{-}$$

1. Local breakdown of passive film (initiation) – act as anode
2. The unbroken film (protective film) acts as cathode
3. Pits develop at the anodic region.
4. Presence of Cl^- reduces the pH inside the electrolyte of the growing pit to about 1 (acidic) – increase corrosion (autocatalytic process)

Prevention of Pitting Corrosion:

1. Decrease the aggressiveness of the environment
   - ☐ By decreasing the Cl^- content, acidity and temperature
2. Increase the resistance of materials
3. The best protection against pitting corrosion is to select a material with adequate pitting resistance