BFF1113
Engineering Materials

DR. NOOR MAZNI ISMAIL
FACULTY OF MANUFACTURING ENGINEERING

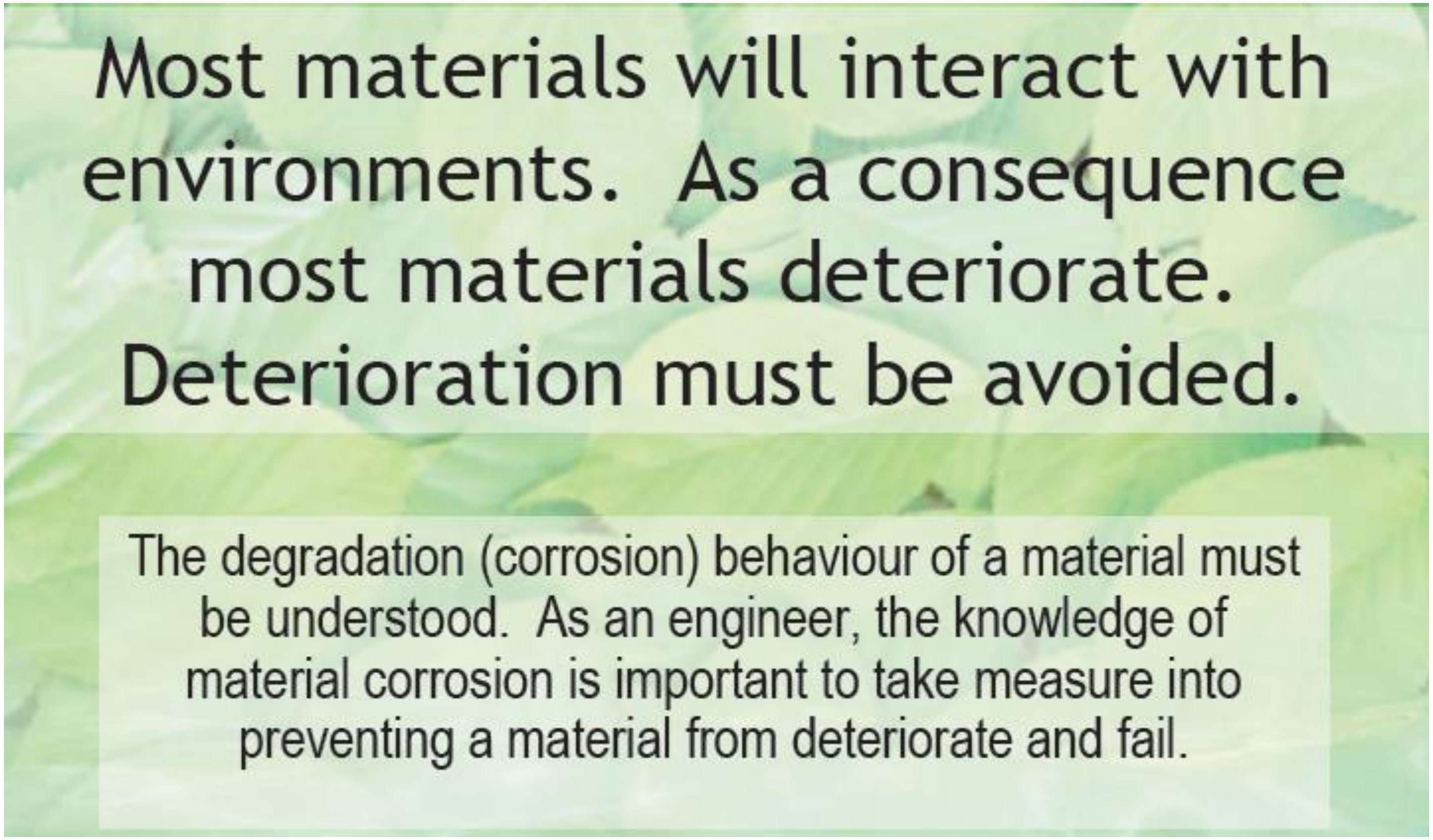
Course Guidelines:

1. Introduction to Engineering Materials
2. Bonding and Properties
3. Crystal Structures & Properties
4. Imperfection in Solids
5. Mechanical Properties of Materials
6. Physical Properties of Materials
7. Failure & Fundamental of Fracture
8. Metal Alloys
9. Phase Diagram
10. Phase Transformation – Heat Treatment
11. Processing and Application of Metals
12. Ceramic Materials
13. Polymer Materials
14. Composite Materials
15. **Corrosion & Degradation of Materials**
16. Environment and Sustainability

Corrosion & Degradation of Material

ISSUES TO ADDRESS...

- Why does corrosion occur?
- What metals are most likely to corrode?
- How do temperature and environment affect corrosion rate?
- How do we suppress corrosion?



Most materials will interact with environments. As a consequence most materials deteriorate. Deterioration must be avoided.

The degradation (corrosion) behaviour of a material must be understood. As an engineer, the knowledge of material corrosion is important to take measure into preventing a material from deteriorate and fail.

How do metals deteriorate?

Material loss by dissolution (corrosion) or by the formation of nonmetallic scale or film (oxidation)

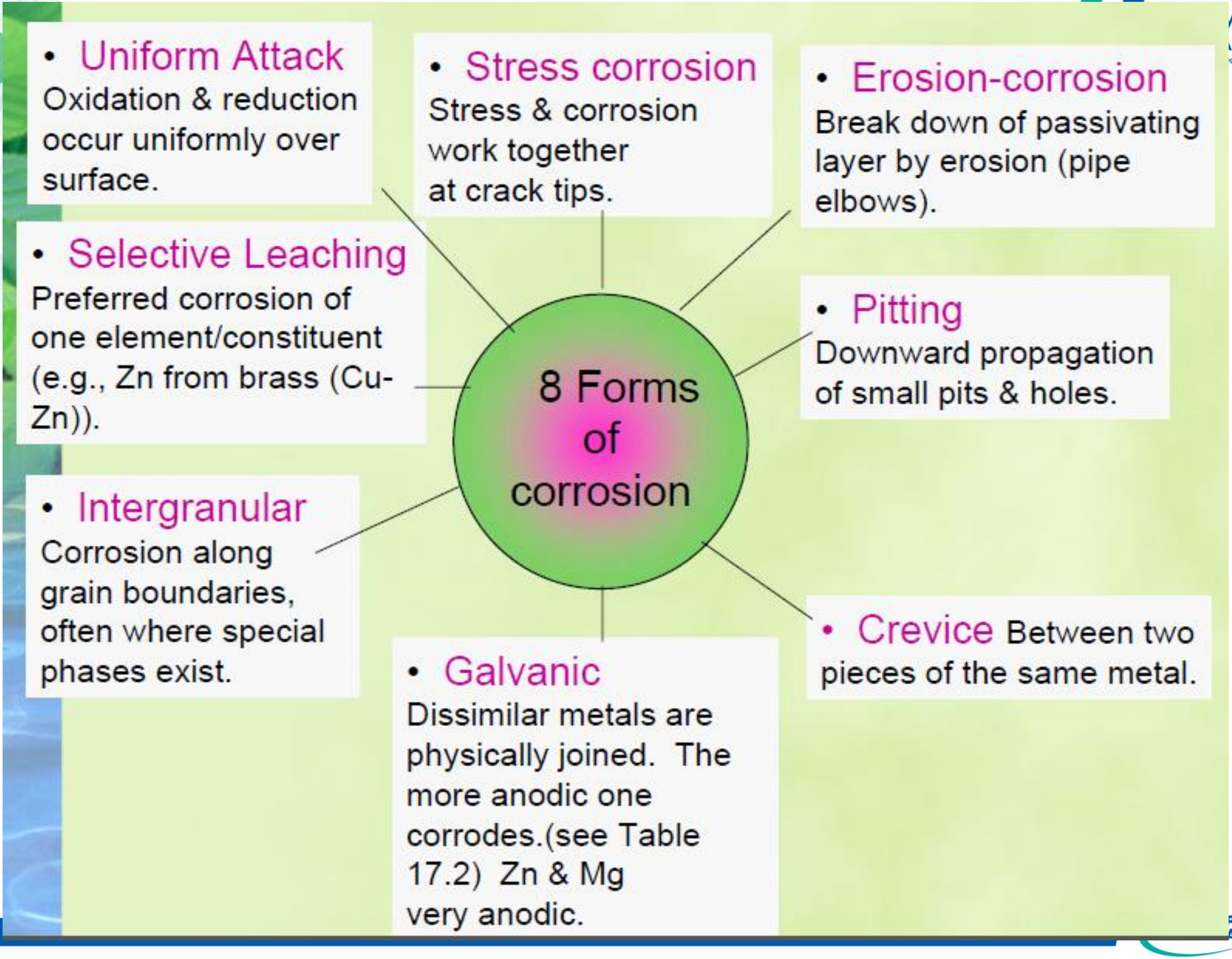
How do ceramics deteriorate?

Ceramics are often resistance to corrosion. But at severe environment ceramics can deteriorate (corrosion)

How do polymers deteriorate?

Polymer degrades by absorbing liquid exposed to it and swell. Electromagnetic radiation (UV) can alter polymer molecules

CORROSION
of
metals



8 Forms of corrosion

- **Uniform Attack**
  Oxidation & reduction occur uniformly over surface.

- **Stress corrosion**
  Stress & corrosion work together at crack tips.

- **Erosion-corrosion**
  Break down of passivating layer by erosion (pipe elbows).

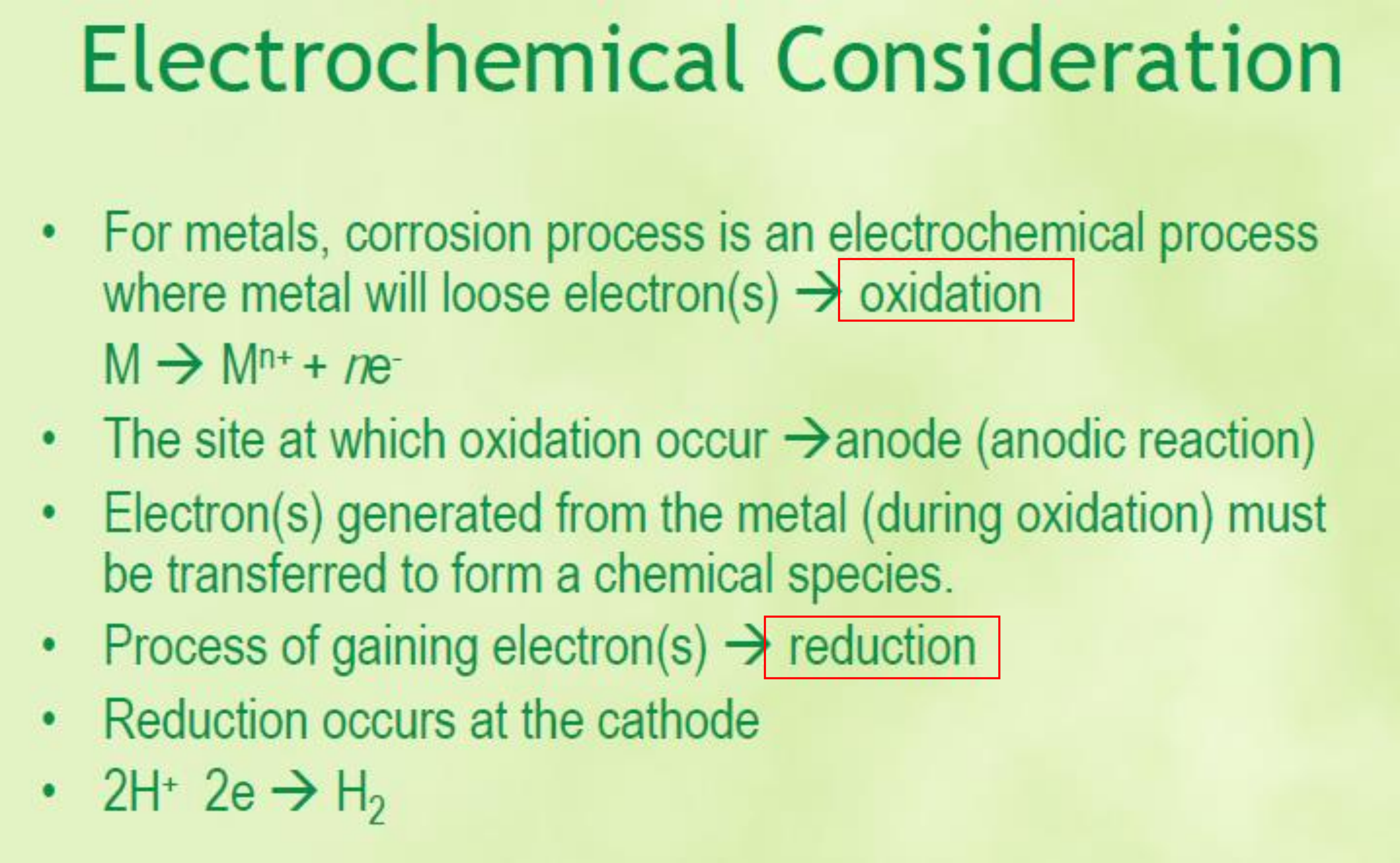
- **Selective Leaching**
  Preferred corrosion of one element/constituent (e.g., Zn from brass (Cu-Zn)).

- **Pitting**
  Downward propagation of small pits & holes.

- **Intergranular**
  Corrosion along grain boundaries, often where special phases exist.

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

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



Electrochemical Consideration

- For metals, corrosion process is an electrochemical process where metal will loose electron(s) → oxidation

  $M \rightarrow M^{n+} + ne^-$
- The site at which oxidation occur → anode (anodic reaction)
- Electron(s) generated from the metal (during oxidation) must be transferred to form a chemical species.
- Process of gaining electron(s) → reduction
- Reduction occurs at the cathode
- $2H^+ \ 2e \rightarrow H_2$

The corrosion of metallic materials in terms of electrochemical reactions that take place in aqueous solutions.

CORROSION RATES

A simple test for measuring corrosion is the weight loss method. The method involves exposing a clean weighed piece of the metal or alloy to the corrosive environment for a specified time followed by cleaning to remove corrosion products and weighing the piece to determine the loss of weight.

The corrosion rate, or the rate of material removal as a consequence of the chemical action, can be expressed as the **corrosion penetration rate (CPR)**, or the thickness loss of material per unit of time:

The rate of corrosion (R) or (CPR) is calculated as:

$$R = KW/(\rho At)$$

where K is a constant, W (mg) is the weight loss of the metal after exposure time t, A is the surface area of the metal exposed, and ρ is the density of the metal (in g/cm^3).
The constant K = 534 for CPR in mpy, and 87.6 for mm/yr (unit of A is in cm)

Passivity – a layer of passivation:

Under particular environments, some active metals and alloys may turn inert, known as passivity. It is usually observed in metals such as Cr, Ni, Ti and their alloys.

Passivity is inherited as a result of formation of a thin and highly adherent oxide film on the metal surface. For example: stainless steels are highly resistant to corrosion in many environments, except in hard sea water. For steels, Cr forms a protective layer.

Aluminium is also observed to passive in many environments. This is due to formation thin oxide layer.

Noted that OXIDATION of metals is also possible in gaseous atmosphere, normally air, wherein an oxide layer or scale forms on the surface of the metal.

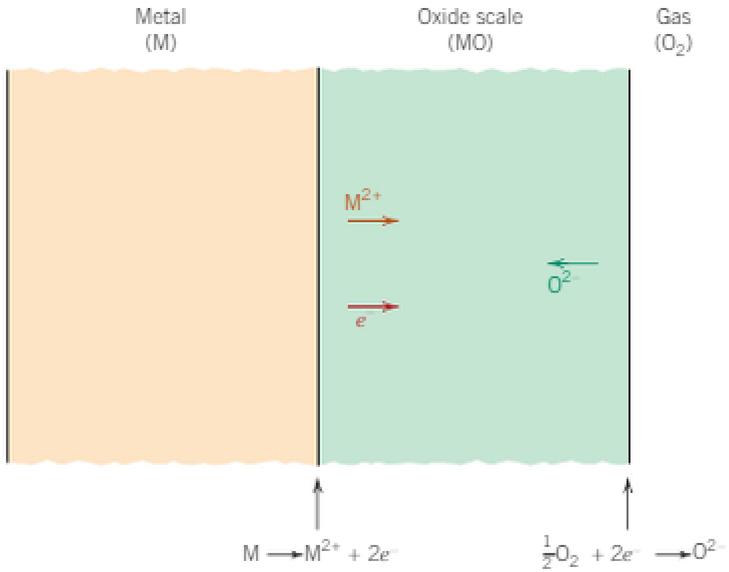
RATE OF OXIDATION or the rate of film thickness increase, and the tendency of the film to protect the metal from further oxidation are related to the relative volumes of the oxide and metal.

The ratio of this volumes, termed the ***Pilling-Bedworth ratio***, can be determined from the following expression:

$$R_{PB} = \frac{V_{oxide}}{V_{metal}} = \frac{M_{oxide} \cdot \rho_{metal}}{n \cdot M_{metal} \cdot \rho_{oxide}}$$

where:

- R_{PB} is the Pilling–Bedworth ratio,
- M – the atomic or molecular mass,
- n – number of atoms of metal per one molecule of the oxide
- ρ – density, and
- V – the molar volume.



$$M + \tfrac{1}{2}O_2 \longrightarrow MO \qquad aM + \frac{b}{2}O_2 \longrightarrow M_aO_b$$

EXAMPLE:

Metal	Metal Density (g/cm³)	Metal molar mass (g/mol)	Metal Oxide	Oxide molar mass (g/mol)	Oxide Density (g/cm³)
Zr	6.51	91.22	ZrO_2	123.22	5.89
Sn	7.30	118.71	SnO_2	150.71	6.95
Bi	9.80	208.98	Bi_2O_3	465.96	8.90

$$\mathrm{Zr} + \mathrm{O_2} \rightarrow \mathrm{ZrO_2}$$

$$\text{P – B ratio} = \frac{A_{\mathrm{ZrO_2}}\,\rho_{\mathrm{Zr}}}{A_{\mathrm{Zr}}\,\rho_{\mathrm{ZrO_2}}}$$

$$= \frac{(123.22\ \mathrm{g/mol})(6.51\ \mathrm{g/cm^3})}{(91.22\ \mathrm{g/mol})(5.89\ \mathrm{g/cm^3})} = 1.49$$

$$2\mathrm{Bi} + \frac{3}{2}\mathrm{O_2} \rightarrow \mathrm{Bi_2O_3}$$

$$\text{P – B ratio} = \frac{A_{\mathrm{Bi_2O_3}}\,\rho_{\mathrm{Bi}}}{(2)\,A_{\mathrm{Bi}}\,\rho_{\mathrm{Bi_2O_3}}}$$

$$= \frac{(465.96\ \mathrm{g/mol})(9.80\ \mathrm{g/cm^3})}{(2)(208.98\ \mathrm{g/mol})(8.90\ \mathrm{g/cm^3})} = 1.23$$

By using the P-B ratio, it can be determined if it is possible for the metal to undergo passivation in the presence of dry air by building a protective oxide film.

Using the P-B ratio as the basis for gauging protective films, the following can be assumed:

- **If the P-B ratio is less than 1, the oxide film is too thin and will most likely break down, such as in magnesium.**

- **If the P-B ratio is grater than 2, the oxide film chips off and offers no protection, such as in iron.**

- **If the P-B ratio is greater than 1, but less than 2, the oxide film is passivating and offers protection from surface oxidation such as in titanium, aluminum and chromium.**

Corrosion Prevention in General- 1. Materials Selections & Design

1. Correct type of materials
    - Limit use of polymers in presence of strong inorganic acids.
    - Ceramics have better corrosion resistance but are brittle
2. Choose a right metal once the working environment has been detected. Use a less active metal (galvanic series and emf) but not always possible as inert metals are expensive
3. Avoid dissimilar metals that can cause galvanic corrosion
4. Provide allowance for corrosion of thickness
5. Allow complete drainage
6. Make sure parts can be replaced
7. Weld rather than rivet

CATHODIC PROTECTION is a technique used to control the corrosion of a metal surface by making it the cathode of an electrochemical cell. A simple method of protection connects protected metal to a more easily corroded "sacrificial metal" to act as the anode.

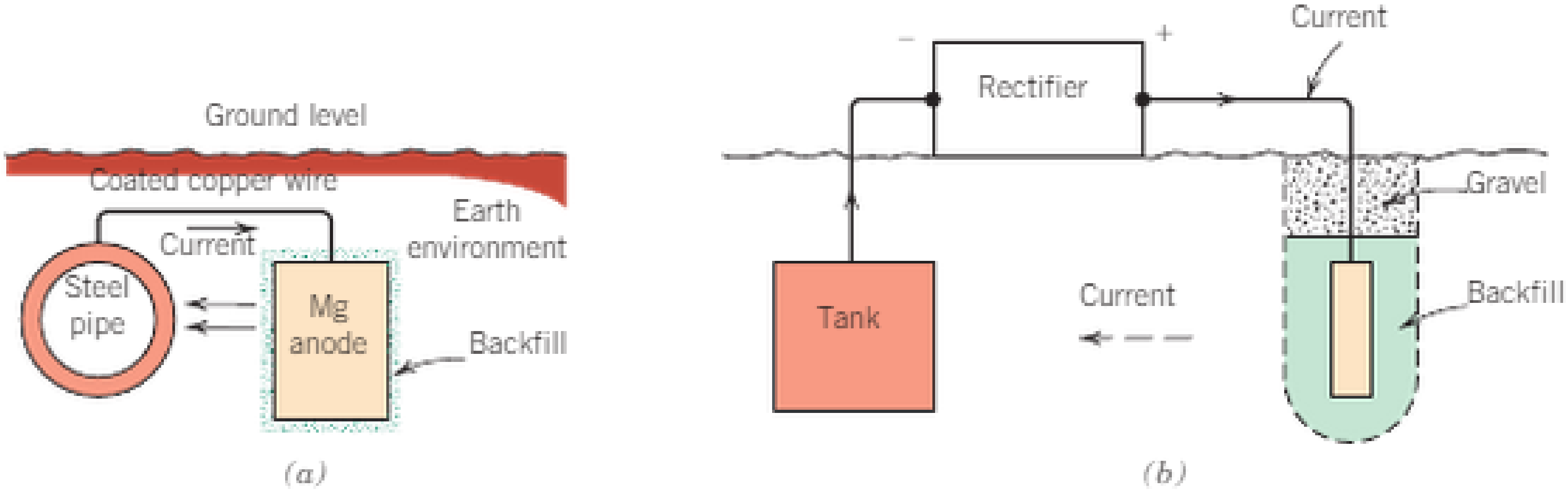
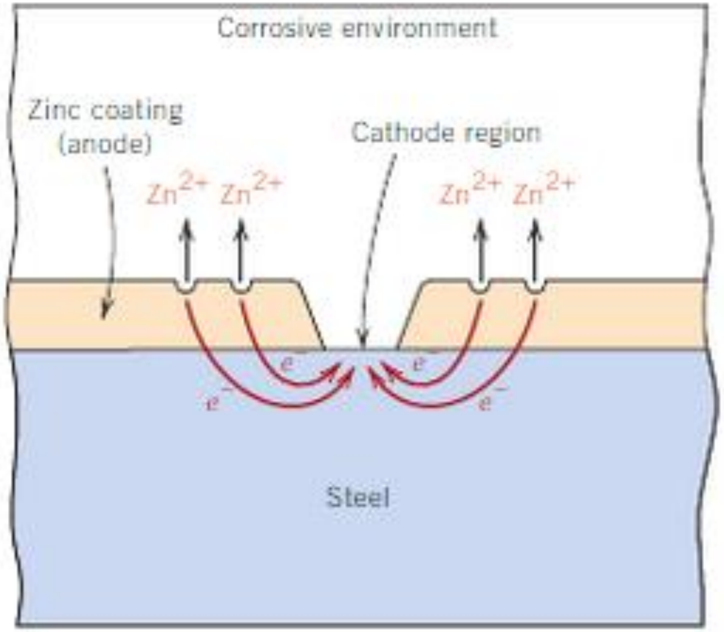


Figure 17.22 Cathodic protection of (*a*) an underground pipeline using a magnesium sacrificial anode, and (*b*) an underground tank using an impressed current. (From M. G. Fontana, *Corrosion Engineering*, 3rd edition. Copyright © 1986 by McGraw-Hill Book Company. Reproduced with permission.)



The white patches visible on the ship's hull are zinc block sacrificial anodes.

Zinc sacrificial anode *(rounded object)* screwed to the underside of the hull of a small boat.

Galvanic sacrificial anode attached to the hull of a ship, showing corrosion.

Corrosion Prevention
2. Environment

1. Change the environment e.g. lowering the fluid temperature, pressure, concentration and velocity
2. Add inhibitors (when added to the environment will decrease corrosion)
   - Inhibitors are retarding catalyst
   - Inhibitors form a protective coating on metals
   - Inhibitors react with the active species in the environment and reduces activity
3. Avoid having species that will corrode metals in the environment (e.g. oxygen, chlorine) → remove oxygen if possible

Corrosion Protection
3. Coatings

- Coatings are physical barriers
- Protective coatings, metallic, ceramics or polymer coatings
  - Metallic Coatings: Used to protect metal by separating from corrosive environment and serving as anode.
    - Coating applied through electroplating or roll bonding.
  - Inorganic coatings: Coating with steel and glass.
    - Steel is coated with porcelain and lined with glass.
  - Organic coatings: Organic polymers (paints and varnishes) are used for coatings.
    - Serve as barrier but should be applied carefully.

DETERIORATION
of
ceramics

- **Ceramic** materials are relatively **resistant to corrosion**, however ceramics do get deteriorated during their service under extreme temperatures or in rather extreme environments; the process is frequently also called corrosion.

- Ceramics are indeed much more environmentally stable, as compared to any other group of engineering materials, e.g. metals or plastics. Still, the potential for ceramics as corrosion resistant engineering structural materials are far from being fully realized, because of:
  - \- mechanical non-reliability of structural ceramic components
  - \- difficult design with brittle materials
  - \- a shortage of information and standardization of ceramics
  - \- human reluctance to use non-ductile materials

DEGRADATION
of
polymers

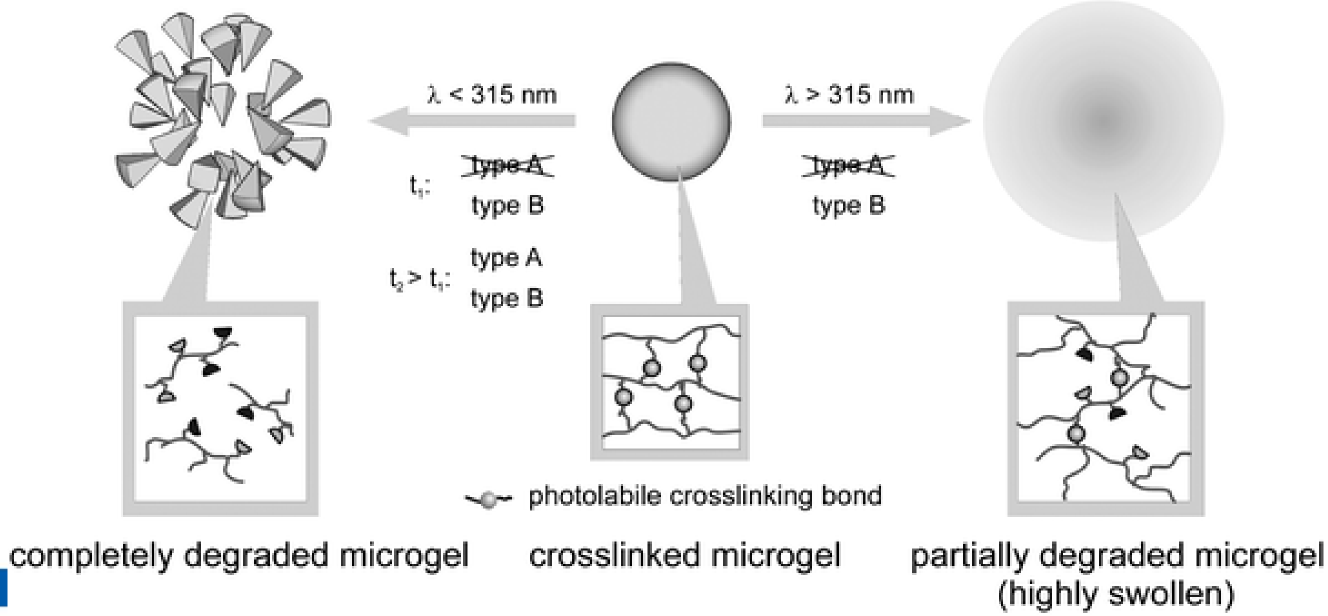
Degradation of polymers

- As other engineering materials, polymers also deteriorated during their service. However, in contrast to electrochemical nature of metal corrosion, polymer degradation is of physiochemical in nature.
- As polymer structures are complex, so are the mechanisms involved in their deterioration.
- Many factors involved in degradation of polymers, like – temperature, radiation, environment, moisture, bacteria or external loads/stress.
- Polymers degrade mainly in three forms – swelling and dissolution, bond rupture, and weathering.

1 SWELLING & DISSOLUTION

- When exposed to humid environment or liquids, polymers gets swelling due to diffused and absorbed moisture.

- It may also involve dissolution of polymers, hence swelling is considered as partial dissolution. Dissolution involves complete solution of polymer in solvent.



2 BOND RUPTURE

- ✓ Bond rupture, also known as scission, may occur due to effects like radiation, heat energy, or chemical reactions.

- ✓ When polymers are exposed to certain types of radiation, which may result in broken bonds and rearrangement of atoms leads to degradation of polymers.

- ✓ At elevated temperatures, bonds in polymers may get weakened, leading to deterioration of polymers. Some chemical elements like oxygen, ozone can alter the chain scission rate as a result of chemical reactions.

PP degradation

3 WEATHERING

- When exposed to outdoor weather for long periods of time, polymer may get decoloured, distort from their original shape.
- This may be due to many actions including radiation of the sun, oxidation, etc.

Figure 1.1: Weathered and unweathered samples of painted steel. Note the colour change.

Figure 1.2: Diagram showing paint pigments in a resin matrix. It can be seen that weathering only removes the smaller pigments, resulting in the colour change