



Corrosion in Materials

Thapar Institute of Engineering & Technology
(Deemed to be University)
Bhadson Road, Patiala, Punjab, Pin-147004
Contact No. : +91-175-2393201
Email : info@thapar.edu

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THAPAR INSTITUTE
OF ENGINEERING & TECHNOLOGY
(Deemed to be University)

Syllabus

Corrosion process: Corrosion, Cause of corrosion, Types of corrosion, Protection against corrosion.

CLO: Propose a solution to prevent corrosion.

Corrosion

Corrosion is the deterioration and loss of metal, or material by chemical or electrochemical reactions with its environments.

- It is a very natural process.
- Most of metallic elements (except noble metals) present in the most stable state having low energy, normally oxides (as metallic ores)

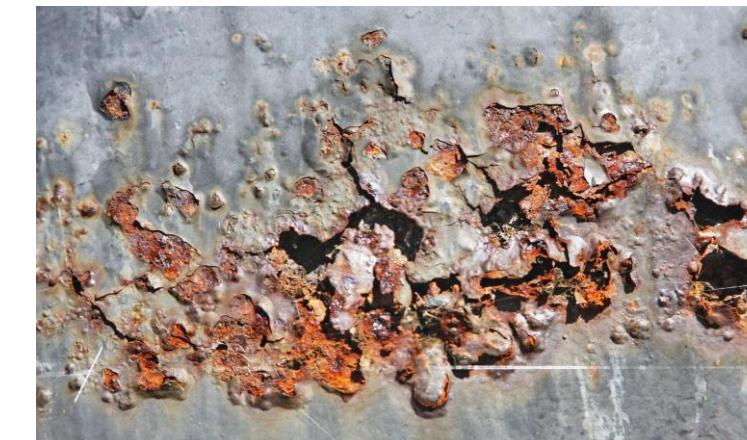
Reason for corrosion

The tendency to decrease the energy of the system as a result of the corrosion reactions.

- Metals get oxidized
- Polymers react with oxygen and degrade
- Ceramic refractories may dissolved in contact with molten materials

Corrosion

Example: Formation of rust on the surface of iron, formation of green film on the surface of copper



The responsible factors for the corrosion of a metal are the **metal** itself, the **environmental chemicals**, **temperature** and the **design**.

Electro-Chemical Corrosion

Electro-chemical reaction: most common mechanism by which corrosion occur at or near room temperature as a result of a chemical reaction metals with water, o aqueous solutions of salts, acids or bases. It is named electro-chemical corrosion as a chemical reaction accompanied the passage of **electric-current takes place.**

Metal atoms characteristically lose or give up electrons in what is called an **oxidation** reaction.



The electrons generated from each metal atom that is oxidized are transferred to and become a part of another chemical species. This is a **reduction** reaction.

Electro-Chemical Corrosion

Examples



Reduction of hydrogen ions in an acid solution



Reduction reaction in an acid solution containing dissolved oxygen



Reduction reaction in a neutral or basic solution containing dissolved oxygen

Electrode potential

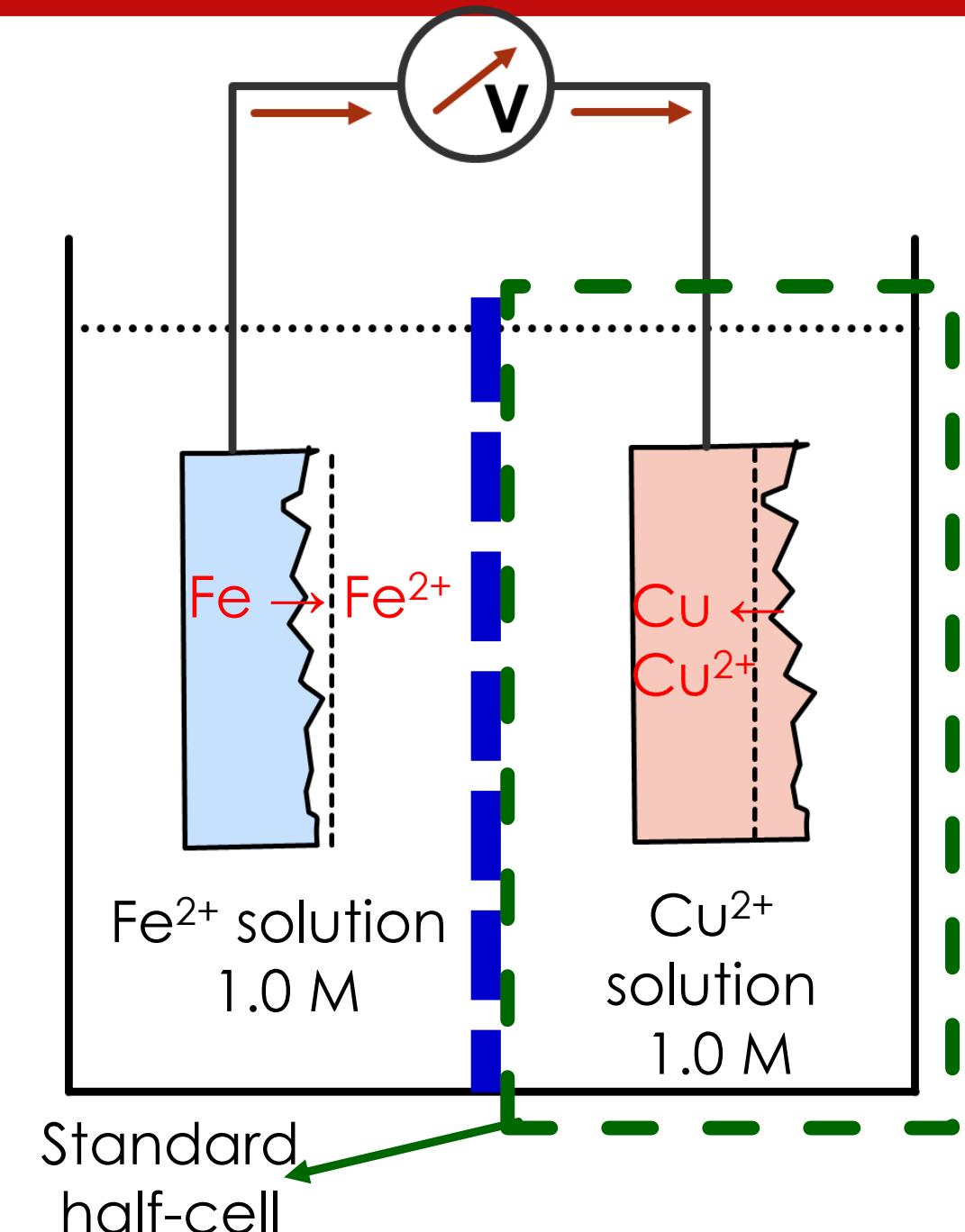
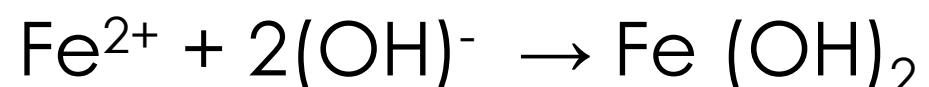
- When an electrode (e.g. Zn) is immersed in an aqueous solvent containing its own ions. Some of Zn^{2+} metal ions leave the electrode by giving their valence electrons to the metal electrode and go into the solvent. **The negative charge builds up in the electrode.**
- The **solvent becomes +ve** and the opposing electrical layers leads to a **dynamic equilibrium** wherein there is no further (net) dissolution of the electrode.
- If the metal-in concentration in the solution is kept fixed, normally one mole of ions per litre (having unit activity) at a constant temperature ($25^{\circ}C$) the electric potential of the metal now becomes the property of the metal. **It gives the tendency of a metal to go into solution i.e. to corrode, or to get plated.**
- The electrode potential is measured with the electrode in contact with a solution containing an unit concentration of ions of the same metal with the **standard hydrogen electrode** as the counter electrode (whose potential is taken to be zero).

Galvanic Cell

Liberated electrons move from anode to the higher potential area the cathode (copper side), where they consumed in the cathodic reaction:



The cations Fe^{2+} migrate through the electrolyte towards the cathode and the anions (OH^-) migrate towards the anode. Both combine and produce an insoluble compound by the reaction:



Simple Galvanic Cell

Standard electrode potential of metals

Standard potential at 25°C

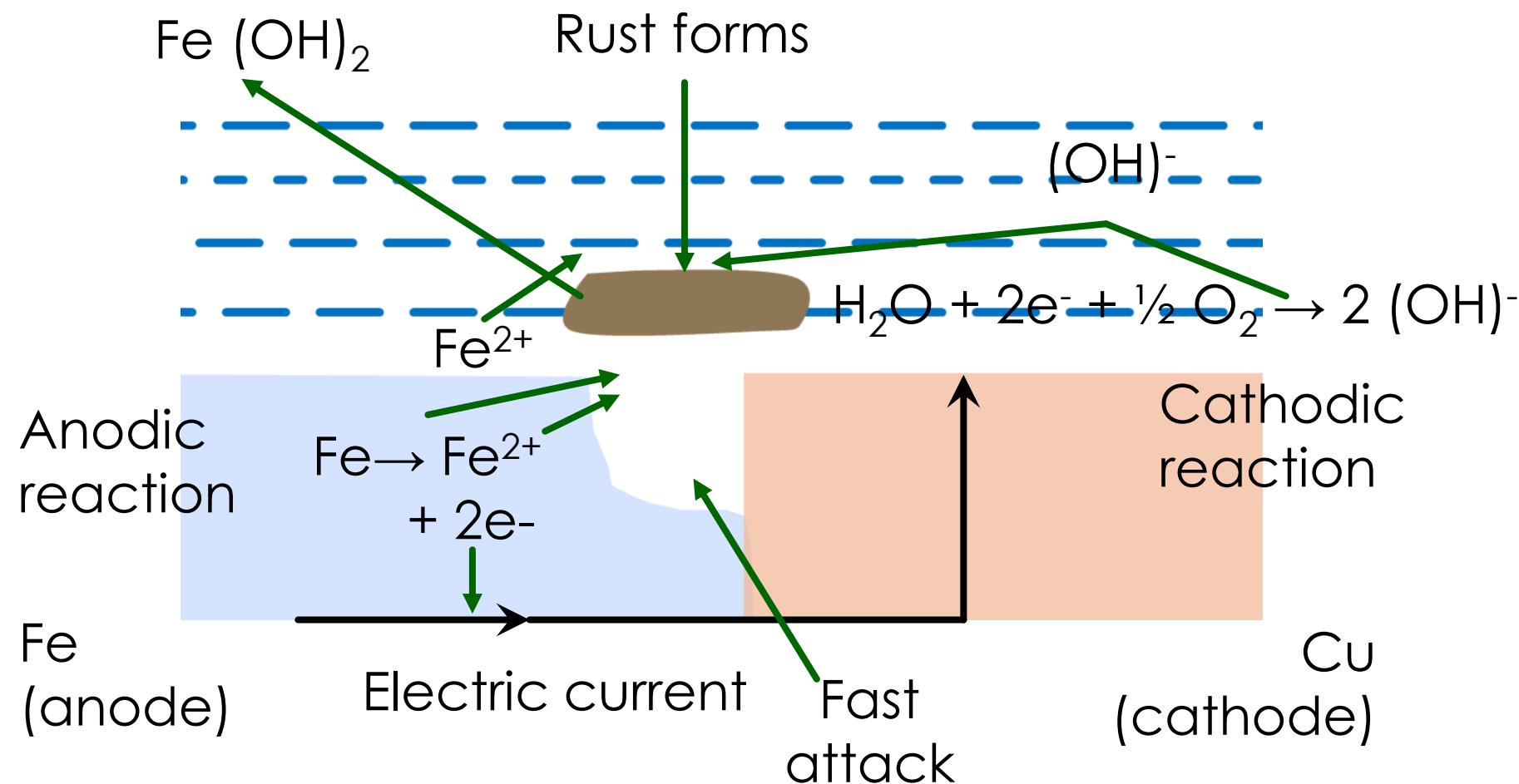
	System	Potential in V
<i>Noble end</i>	Au / Au ³⁺	+1.5
	Ag / Ag ⁺	+0.80
	Cu / Cu ²⁺	+0.34
	H ₂ / H ⁺	0.0
	Pb / Pb ²⁺	-0.13
	Ni / Ni ²⁺	-0.25
	Fe / Fe ²⁺	-0.44
	Cr / Cr ³⁺	-0.74
	Zn / Zn ²⁺	-0.76
	Al / Al ³⁺	- 1.66
<i>Active end</i>	Li / Li ⁺	-3.05

Increasing propensity to dissolve

Anode and cathode

Not all metallic materials oxidize to form ions with same degree of ease.

Two dissimilar metals Fe and Cu are placed in electrical contact in the presence of an electrolyte (e.g. salt solution having dissolved oxygen). The potential of each metal is related to its relative tendency to dissolve .



Anode and cathode

Two dissimilar metals Fe and Cu are placed in electrical contact in the presence of an electrolyte (e.g. salt solution having dissolved oxygen). The potential of each metal is related to its relative tendency to dissolve .

Fe has lower potential acts as anode and dissolved (i.e. corrode) by reaction,



Anodic reactions are oxidation reaction.

Cathodic reaction, $\text{H}_2\text{O} + 2\text{e}^- + \frac{1}{2}\text{O}_2$ (dissolved oxygen) $\rightarrow 2(\text{OH})^-$
Cathodic reactions are reduction reactions.

More anodic metal corrodes.

Galvanic Cell

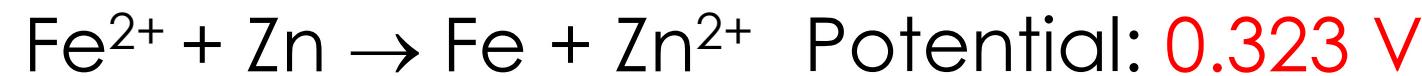
When externally connected, electrons generated from the oxidation of iron flow to the copper cell in order that Cu^{2+} be reduced.

In addition, there will be some net ion motion from each cell to the other across the membrane.

This is called a *galvanic couple* - two metals electrically connected in a liquid **electrolyte** wherein one metal becomes an anode and corrodes, while the other acts as a cathode.

An electric potential or voltage will exist between the two cell halves.

For example:



Various electrode pairs have different voltages !

Galvanic Cell

Galvanic series: This represents the relative reactivity of a number of metals and commercial alloys 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
- Copper
- Brasses (Cu-Zn alloys)
- Inconel (active)
- Nickel (active)
- Tin
- Lead
- 316 Stainless steel (active)
- 304 Stainless steel (active)
- Cast iron
- Iron and steel
- Aluminium alloys
- Cadmium
- Commercially pure aluminium
- Zinc
- Magnesium and magnesium alloys

Corrosion penetration rate

The corrosion rate, or the rate of material removal as a consequence of the chemical action, is an important corrosion parameter.
It is the thickness loss of material per unit of time.

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

where W = weight loss after exposure time t ; ρ = density, and A = exposed specimen area, K is a constant.

There is an electric current associated with electrochemical corrosion reactions.

$$r = \frac{i}{nF}$$

where

i = current density (the current per unit surface area of material corroding)

n = number of electrons associated with the ionization of each metal atom

$F = 96,500 \text{ C/mol.}$

Galvanic Cell : Passivation

- Some normally active metals and alloys, under particular environmental conditions, lose their chemical reactivity and become extremely inert. E.g., chromium, iron, nickel, titanium, and many of their alloys.
- This passive behaviour results from the formation of a highly adherent and very thin oxide film on the metal surface, which serves as a protective barrier to further corrosion.
- e.g. Ashoka Pillar, Delhi



Summary

1. Corrosion is a loss due to electrochemical reactions in the environment.
2. Electrochemical reaction between two different metals gives rise to corrosion.
3. The corrosion in galvanic series is more when the potential difference is more.
4. Passivation is loss of chemical reactivity of the material.