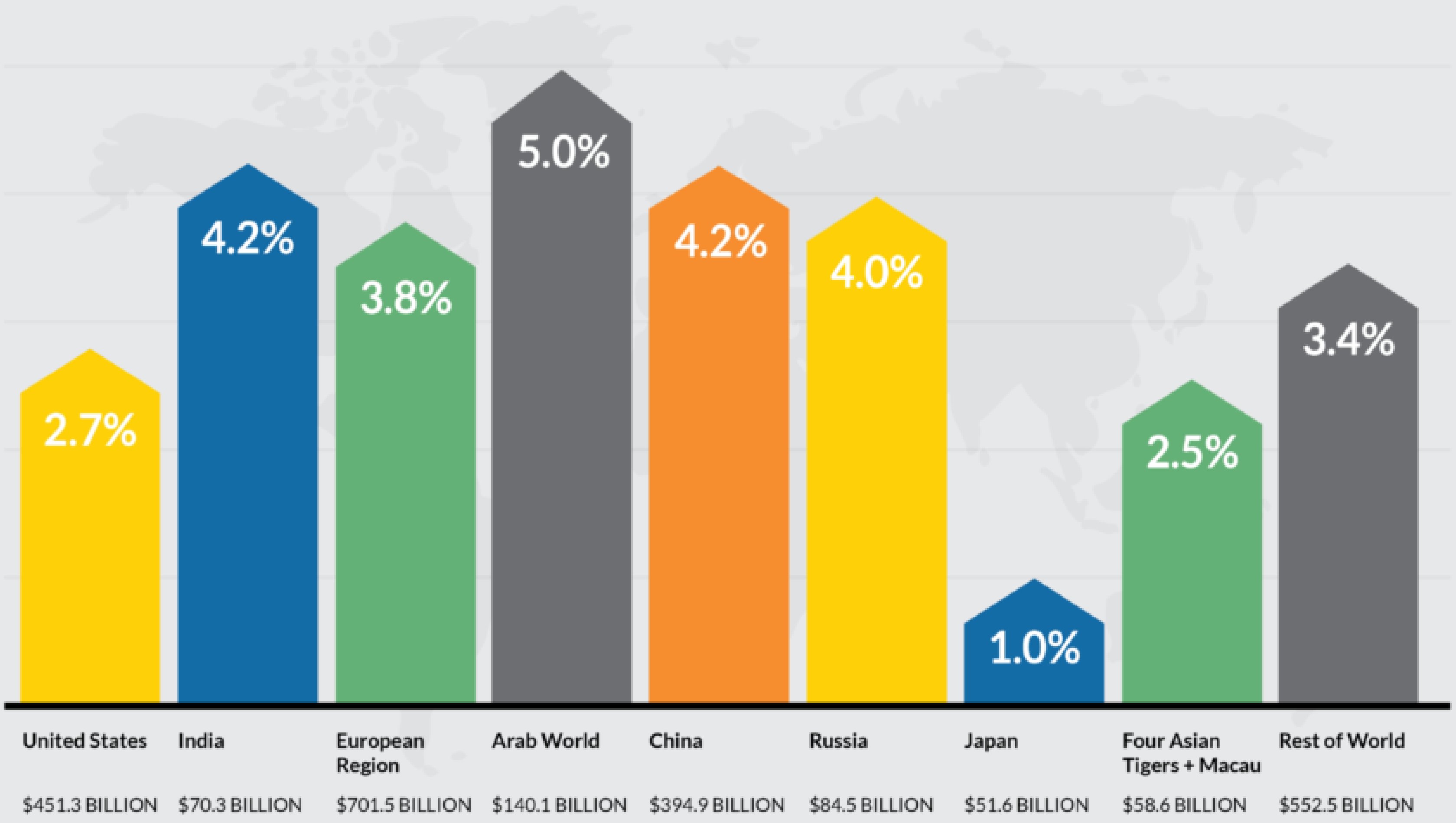
CORROSION

By Sonaali Borkar

Combined Cost of Corrosion Represents 3.4% of Global GDP (2013)



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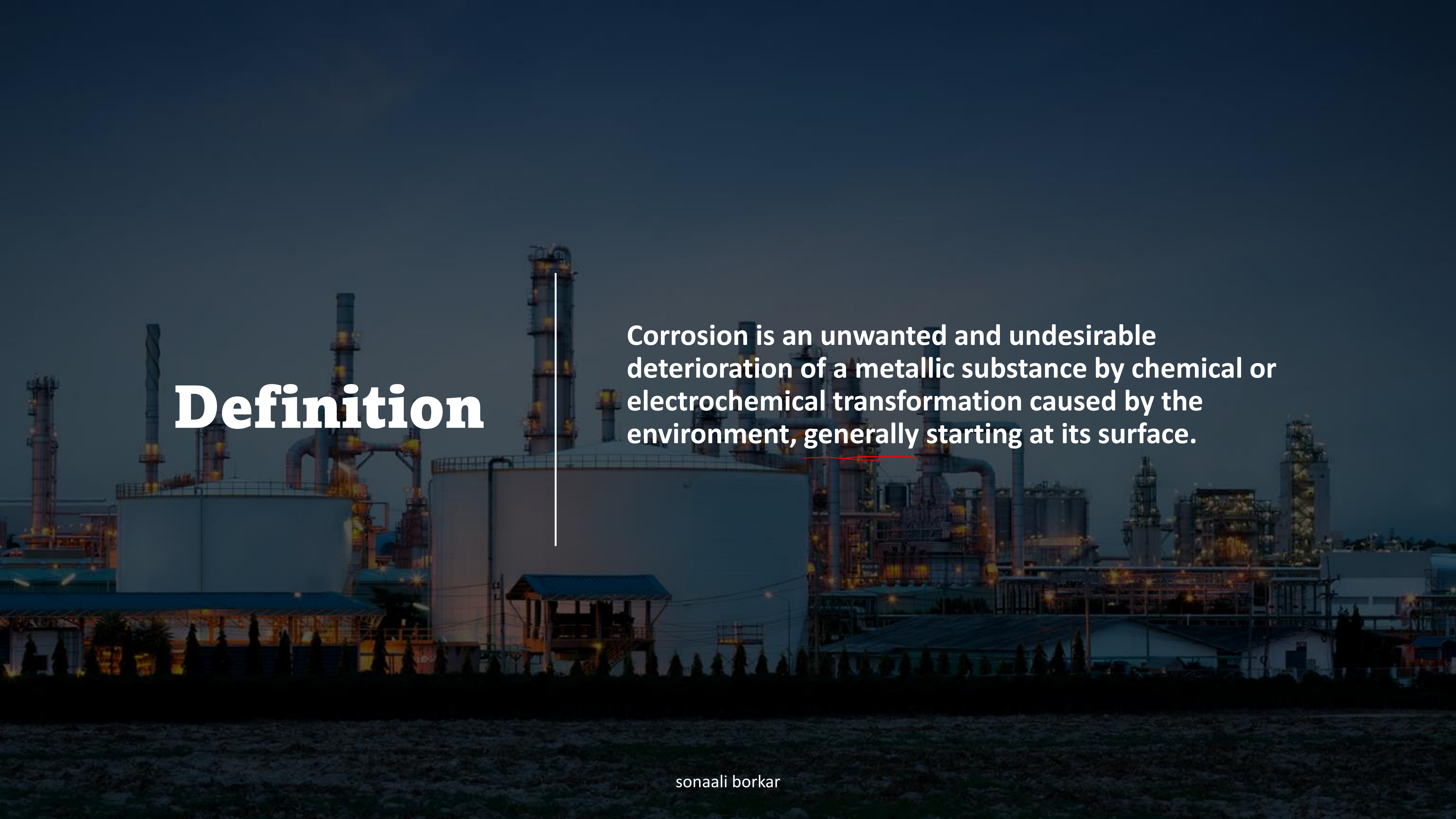
CORROSION means ???



Definition

Corrosion is an unwanted and undesirable deterioration of a metallic substance by chemical or electrochemical transformation caused by the environment, generally starting at its surface.

Types of corrosion

Atmospheric corrosion <u>or</u> Dry corrosion <u>or</u> Chemical corrosion

Electrochemical corrosion <u>or</u> Wet corrosion or Immersed corrosion.

DRY Corrosion	WET Corrosion
Absence of electrolyte	Presence of Electrolyte
Direct attack on metals	Formation of electrochemical cell
Slow process	Fast process
Product is on site	Product is at cathode
Uniform rate of corrosion	Depends on factors like size of the anode

Dry corrosion

1. Oxidation corrosion (caused by oxygen, chlorine, sulphur dioxide, carbon dioxide etc.)
2. Hydrogen embrittlement (caused by hydrogen and hydrogen sulphide)
3. Liquid metal corrosion (caused by molten liquids)

Stable Metal Oxide Film

- Grained structure
- Volume of oxide film more than area of metal surface
- Cuts the contact of metal with oxygen
- Ex. Al, Cu, Cr etc.

Unstable Metal Oxide Film

Metal oxide film unstable

Oxide film is decomposed to metal and oxygen

Ex. Noble metals like Au, Pt etc.

Porous Metal Oxide Film

Volume of the oxide film is less than the area of the metal surface

Pores are formed

Ex. Na. Be, K, Li etc.

Volatile Metal Oxide Film

- The oxide film is volatile
- Evaporates as soon as formed
- Highly destructive
- Ex. MoO3

Hydrogen Embrittlement

$$H + H \longrightarrow H_2 (g)$$

$$C + 4H \longrightarrow CH_4 \quad (g)$$

$$H_2 \xrightarrow{\text{heat}} H + H$$

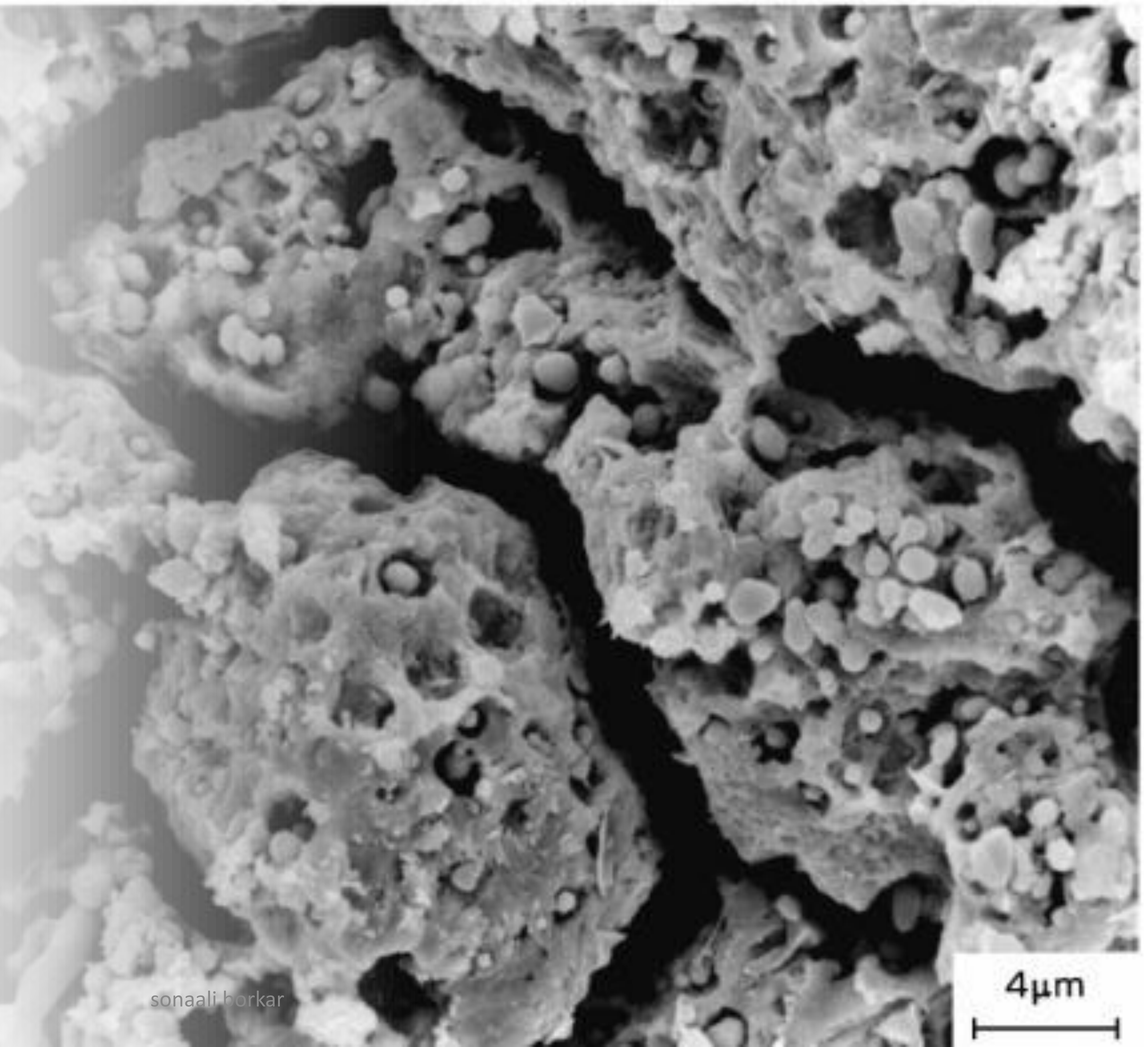
Figure 1: Cross section of a bolt showing fast fracture region and progressive hydrogen induced cracking (right) phases of hydrogen embrittlement. ©CALTRANS, 2013

Liquid Metal Corrosion

Corrosion of Solid metal by…..

- ❖ **Dissolution of solid metal into liquid metal**
- ❖ **Penetration of liquid metal into solid metal**

- ❖ **Ex . In nuclear reactor, the sodium metal is used as a coolant, and it corrodes cadmium**



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Electrochemical corrosion

What is Electrochemical Corrosion ?

→Corrosion of Metal

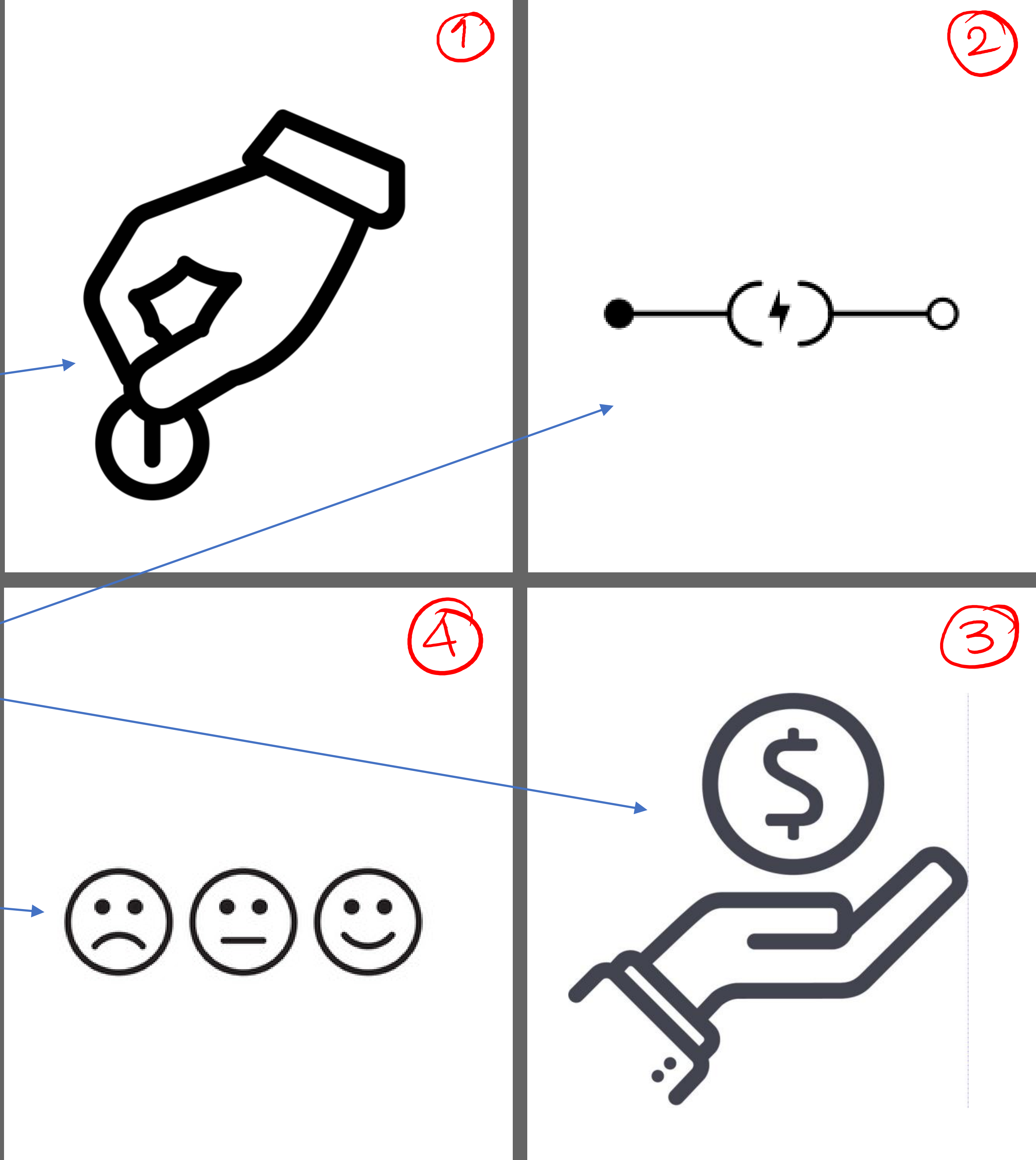
- Where a conducting liquid is in contact with metal

OR

- When two dissimilar metals or alloys are either immersed or dipped partially in a solution

Requirement for an electrochemical corrosion

- Anode
- Cathode
- Presence of an electrolyte
- Nature of an electrolyte



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Mechanism of Electrochemical corrosion

- Evolution of Hydrogen
- Absorption of Oxygen

Electrochemical series

Standard Reduction Potential Table (at 25^{o}C, 101kPa, 1M)

Half-Reaction	volts
$Li^{+} + e^{-} \rightarrow Li$	- 3.04
$Al^{+3} + 3e^{-} \rightarrow Al$	- 1.68
$Zn^{+2} + 2e^{-} \rightarrow Zn$	- 0.76
$Fe^{+2} + 2e^{-} \rightarrow Fe$	- 0.44
$2H_2O + 2e^{-} \rightarrow H_2 + 2OH^{-}$	- 0.41
$Ni^{+2} + 2e^{-} \rightarrow Ni$	- 0.26
$Pb^{+2} + 2e^{-} \rightarrow Pb$	- 0.13
$2H^{+} + 2e^{-} \rightarrow H_2$	0.00
$Cu^{+2} + 2e^{-} \rightarrow Cu$	0.34
$Cu^{+} + e^{-} \rightarrow Cu$	0.52
$Fe^{+3} + e^{-} \rightarrow Fe^{+2}$	0.77
$Ag^{+} + e^{-} \rightarrow Ag$	0.80
$O_2 + 4H^{+2} + 4e^{-} \rightarrow 2H_2O$	0.82
$Br_2 + 2e^{-} \rightarrow 2Br^{-}$	1.07
$Cl_2 + 2e^{-} \rightarrow 2Cl^{-}$	1.36
$Au^{+3} + 3e^{-} \rightarrow Au$	1.52

Weak Oxidizing Agents / Strong Reducing Agents ↑

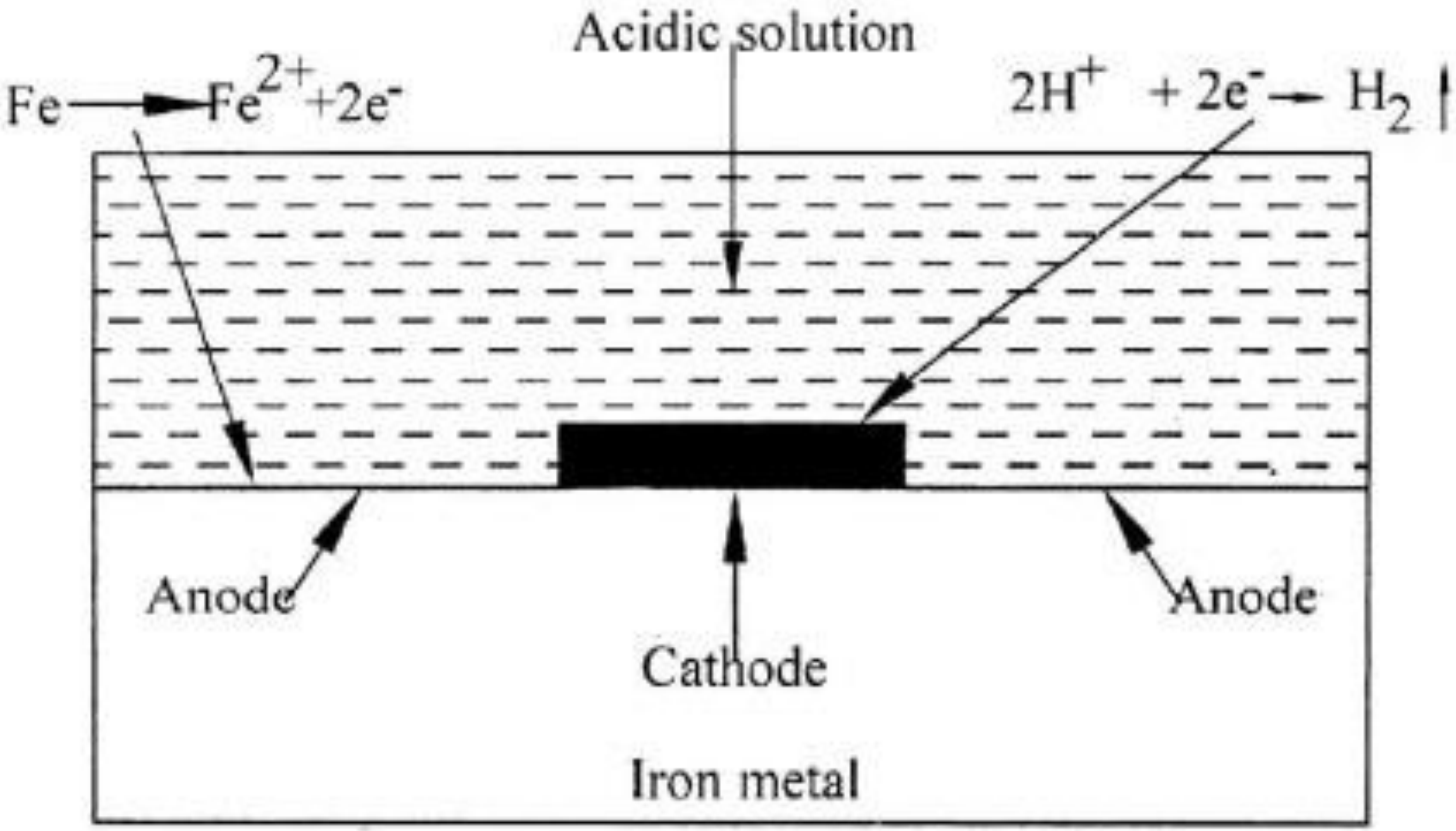
Strong Oxidizing Agents / Weak Reducing Agents ↓

Galvanic Series

Table 1- The Galvanic Series of Metals

Cathodic	Least Active High Potential	Platinum
		Gold
		Carbon (graphite)
		Titanium
		Type 316 or 304 stainless steel (passive)
		Monel metal (70% nickel, 30% copper)
		Silver
		Nickel
		Lead
		Bronze, Copper, Brass
		Tin
		Lead/Tin solder
		Type 316 or 304 stainless steel (active)
		Cast Iron/Mild Steel
		Cadmium
		Aluminium
		Zinc
Anodic	Most Active Low Potential	Magnesium

Hydrogen evolution



Dissimilar Metals and corrosion

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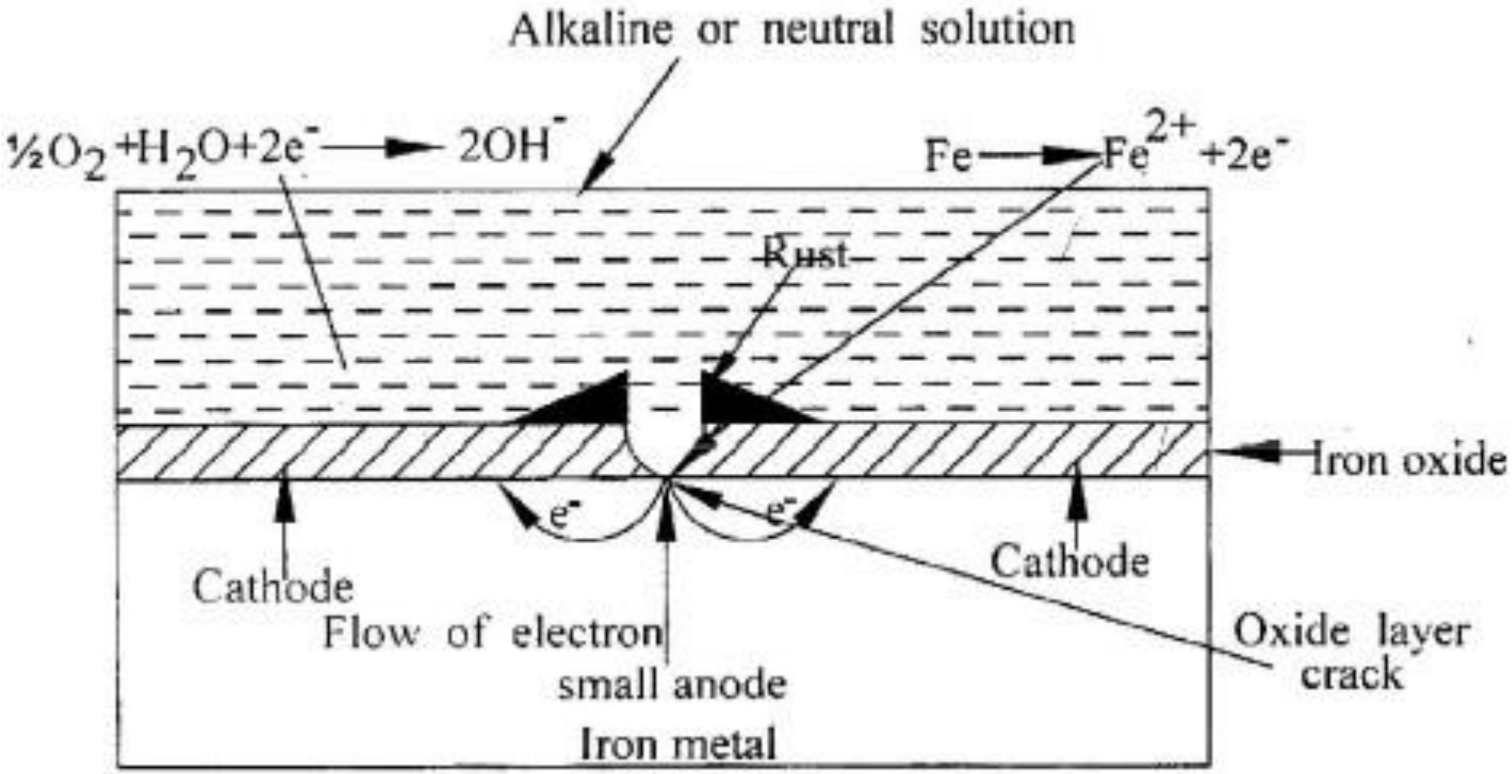
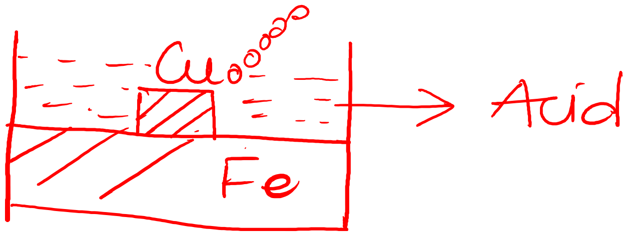
Oxygen absorption



H_2 evolution Mechanism

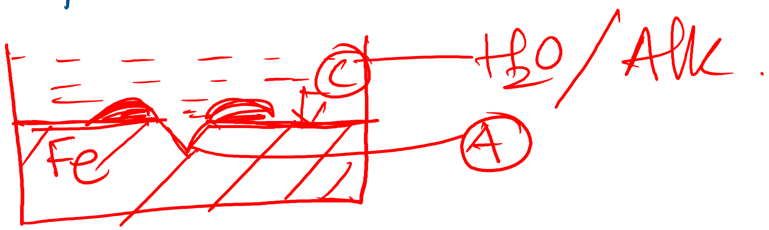
1. $Fe \to Fe^{2+} + 2e^-$



2. Acidic Electrolyte
3. Metal → dissimilar
4. Cathode → $2H^+ + 2e^- \to H_2 \uparrow$
5. No corrosion Product
6. Rate of corrosion w.r.t. electrolyte → ↑
7. Rate of corrosion wrt Area of A & C → ↓
8. A → (b) → (C) – (S)

O_2 Absorption Mechanism

1. $Fe \to Fe^{2+} + 2e^-$

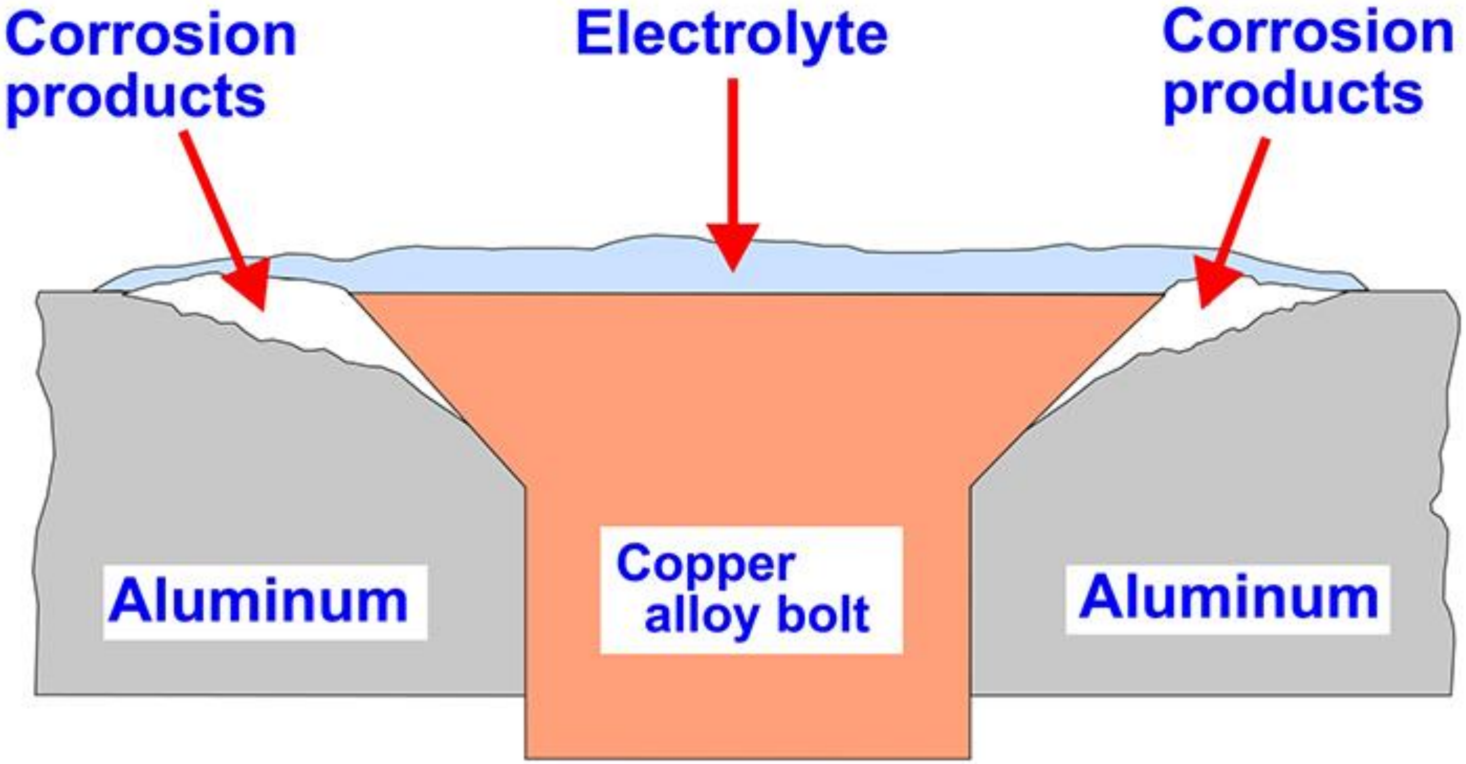


2. Alkaline / neutral.
3. Same Metal.
4. $\frac{1}{2} O_2 + 2e^- + H_2O \longrightarrow 2OH^-$
5. Corrosion product — $Fe(OH)_3 \downarrow$, $Fe_3O_4 \downarrow$
6. Rate of corrosion w.r.t. electro → ↓
7. Rate of corrosion wrt Area of Anode & Cathode → ↑
8. A – (s) & C – (b)

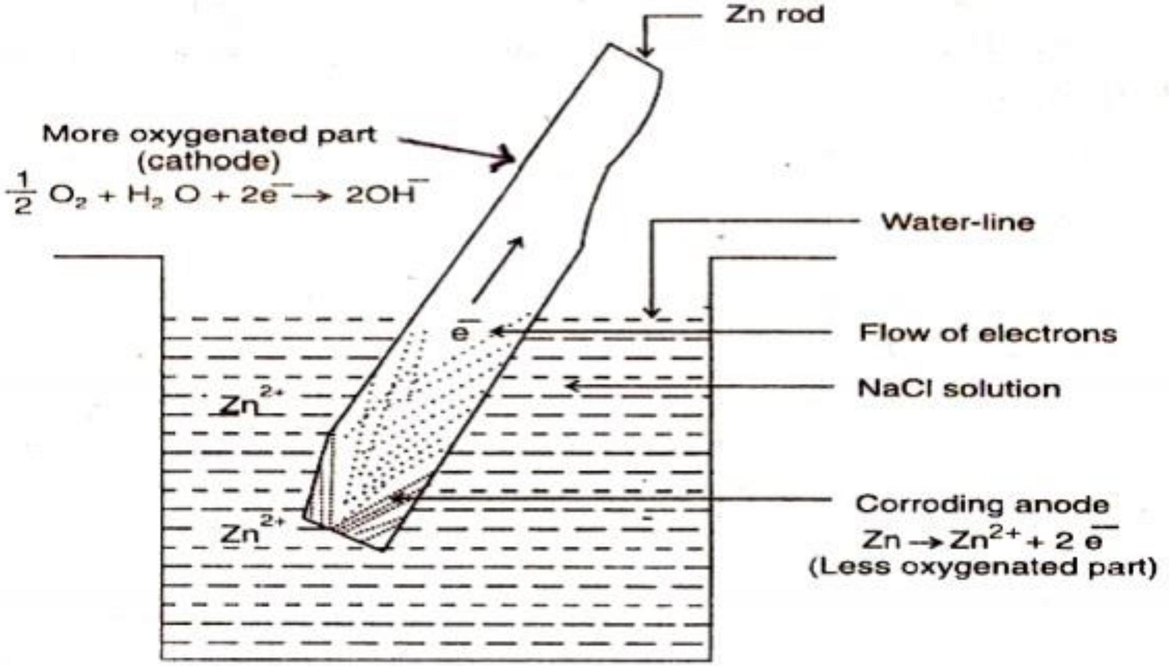
Types of Corrosion

- Galvanic Corrosion
- Differential Aeration Corrosion
- Pitting Corrosion
- Intergranular Corrosion
- Stress Corrosion

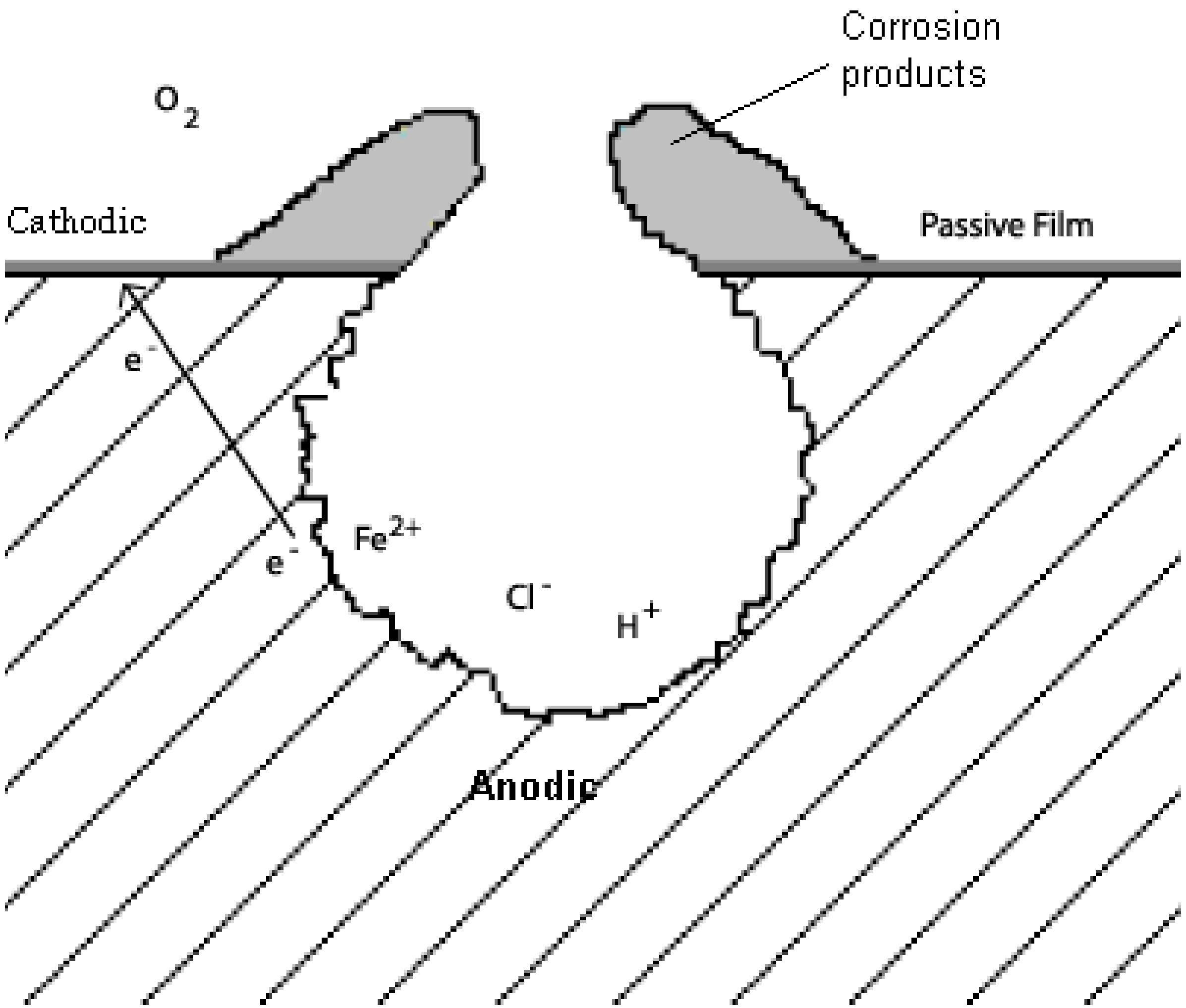
Galvanic Corrosion



Differential Aeration Corrosion



Pitting corrosion Mechanism



Pitting Corrosion

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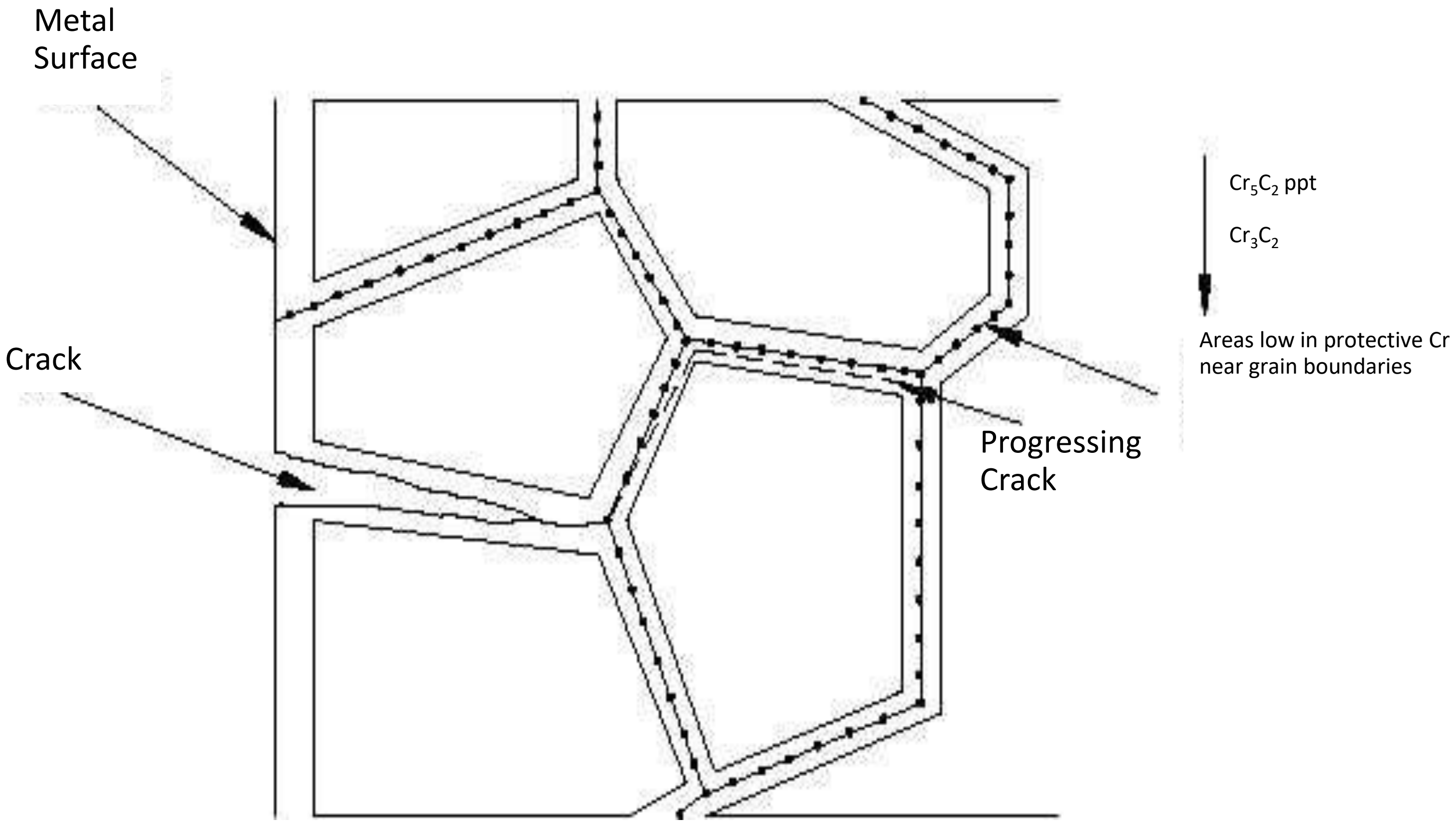
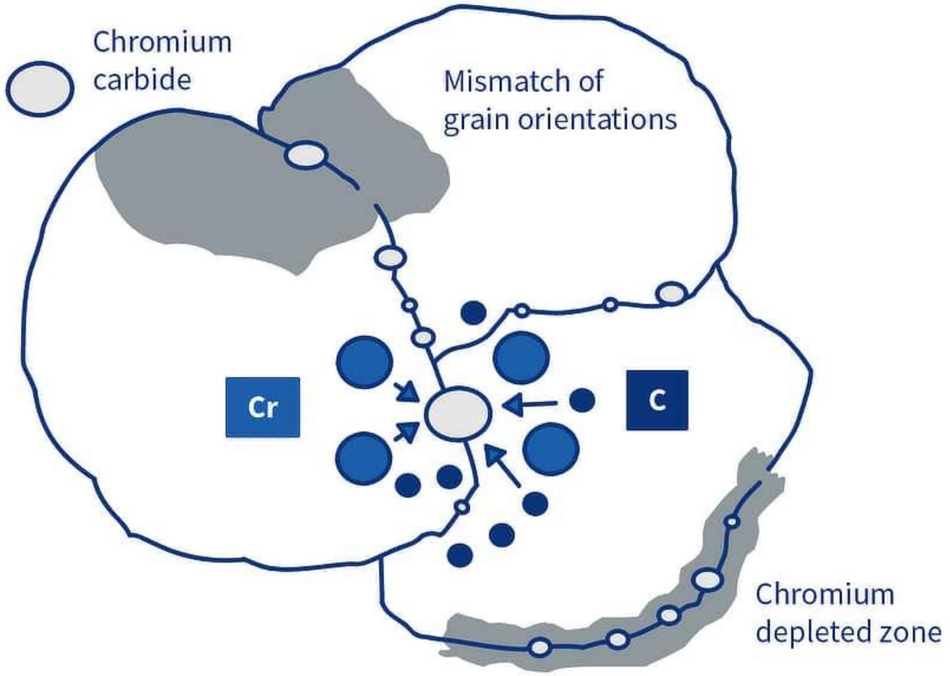
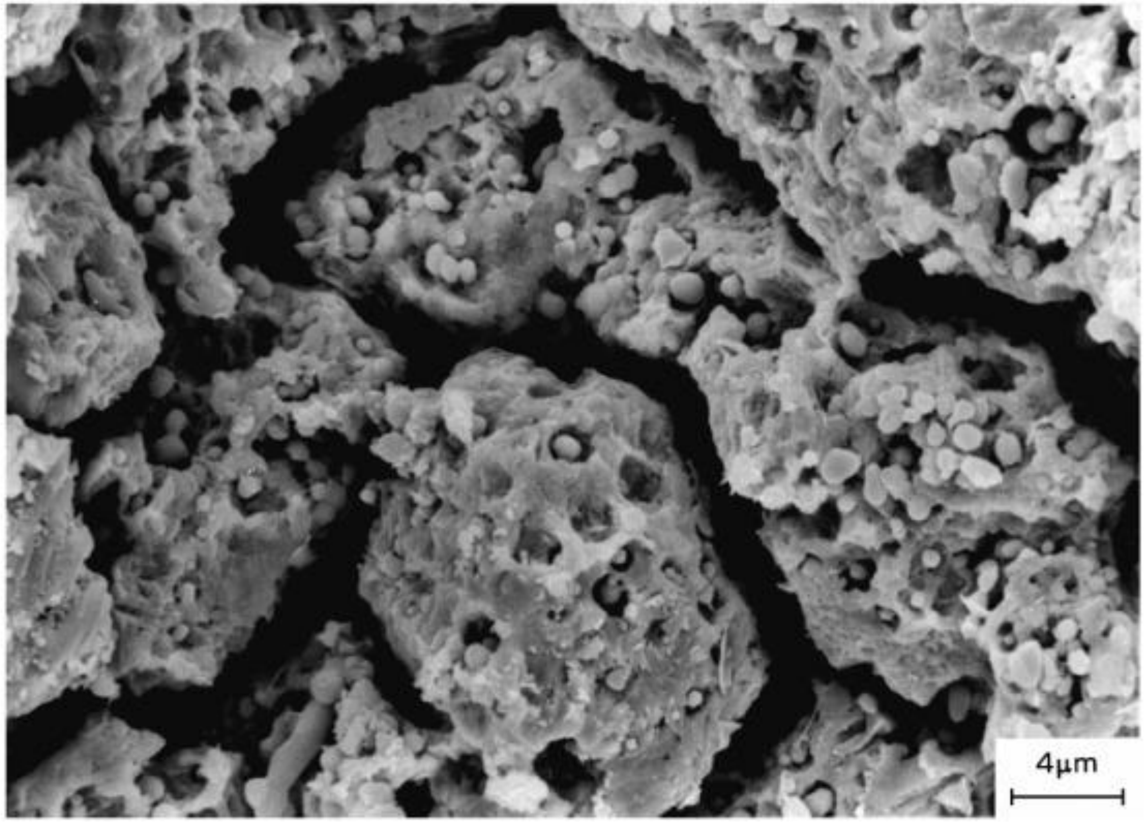
Intergranular corrosion Mechanism

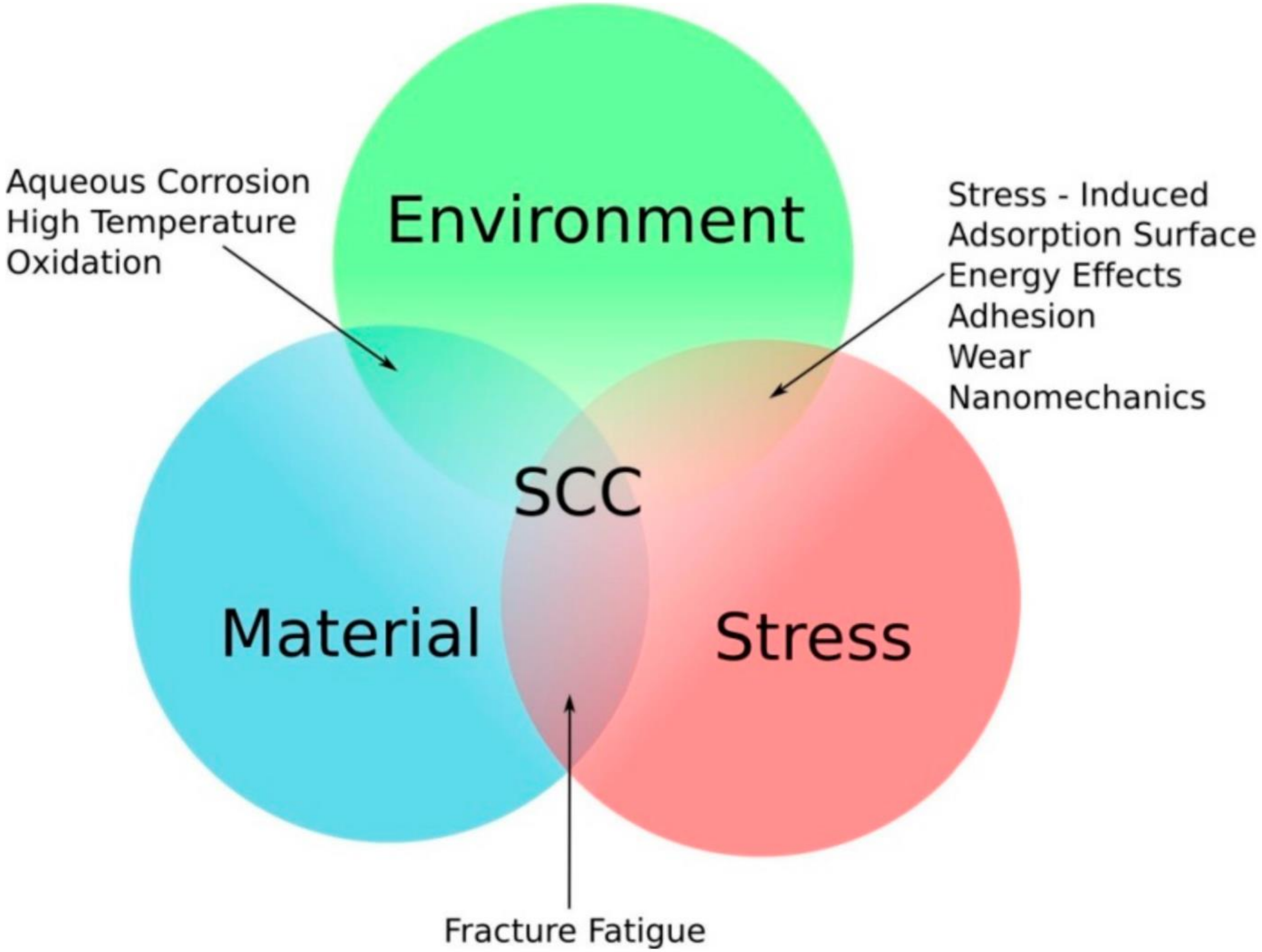


Intergranular Corrosion





Stress corrosion




Stress Season Cracking


Caustic Embrittlement

Factors affecting rate of corrosion

Rate of Corrosion depends upon..

1. Nature of metal
2. Nature of environment

Nature of Metal

1. Position of metal in electrochemical series
2. H_2 Over voltage
3. Nature of surface film
4. Solubility of corrosion products
5. Volatility of corrosion products
6. Relative areas of anode and cathode
7. Purity of metal
8. Physical state of metal
9. Passive character of metal

① Position of M in EC series

Rate of corr

① M - higher — A — Fe

M - lower — C — Cu

② Diff betn M → More → ROC ↑

→ less → ↓

② H_2 overvoltage — Cu 0.34 — Zn -0.76V

Diff betn T & P value

ROC ∝ 1/ H_2 overvoltage

↓ H_2 overpot → ↑ ROC

③ Nature of Surf. film

Stable → less ROC

MtO2 Unstable → No corr

Porous → more corr

Volatile → more corr

④ Solubility of corr. product

Soluble → ROC → ↑

Insoluble → ROC → ↓

⑤ volatility of corr pdt

$M + O_2 \rightarrow MO_2$

MoO_3

* specific
* volatile → ROC ↑

⑥ Rel. Areas of A & C

Area of Anode → More → ↓ ROC

Area of Cathode → More ↑

(* Ref Demand & Supply)

⑦ Purity of Metal

Pure → ROC ↓

Impure → Fe (Cu, Sn, Pb...) ROC ↑

Purity

Zn → 99.999% → 1

99.99% → 2650

99.95% → 5000

⑧ Phy. state of Metal

* Pure & Impure
* Grain size
* Orientation of crystals

ROC will vary.

⑨ Passive character of Metal. (Cr, Al, Fe, W, Ti)

Metal → Active-Passive behaviour.

Al | Fe

A C

Cr

Nature of Environment

1. Temperature
2. Presence of moisture
3. Presence of impurities in atmosphere
4. Presence of suspended particles in atmosphere
5. Influence of pH
6. Nature of ions present
7. Conductance of corroding medium
8. Formation of oxygen concentration cell

① Temperature

Temp ↑ → ↑ ROC
Generally

Possibility

	Temp	ROC
① Microbial	↑ →	↓
② Stress →	↓ —	↓↑

② Pr. of moisture

	ROC
dry →	
moisture —	↑

(electrolyte)
Electrochem Corr

③ Pr. of impurities
* Chem Industry
* near sea shore

Salts, acids, gases
ROC ↑es

→ Impurities give electrolyte → nature
Acidic Ne All

④ Suspended p'tcles

Salt ptcles, Metals.
nanoptcles - Activity
ROC ↑.

C p'tcles → Absorb
impurities ROC ↓

⑤ Influence of pH

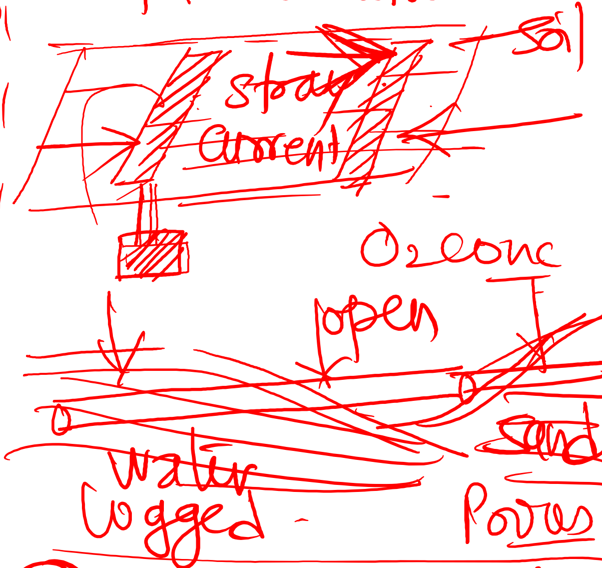
Acid → chain Reac
→ ROC ↑
neutral — ↓ ?
Alkaline — ↓
But O_2 is more
$\boxed{\text{ROC} \uparrow}$

⑥ Nature of ions

SO_4, NH_4
ROC → ↑.

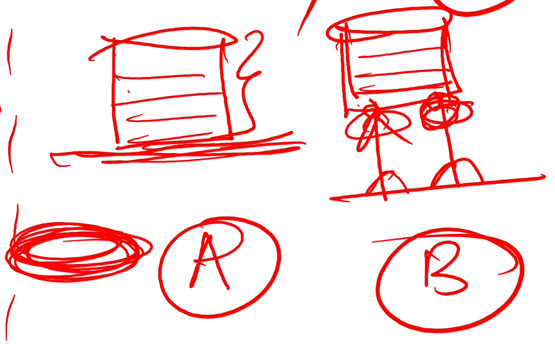
Silica → Silicates
ROC ↓.

⑦ Conductance of Medium



⑧ O_2 conc. cell

less oxy - A
more oxy - C

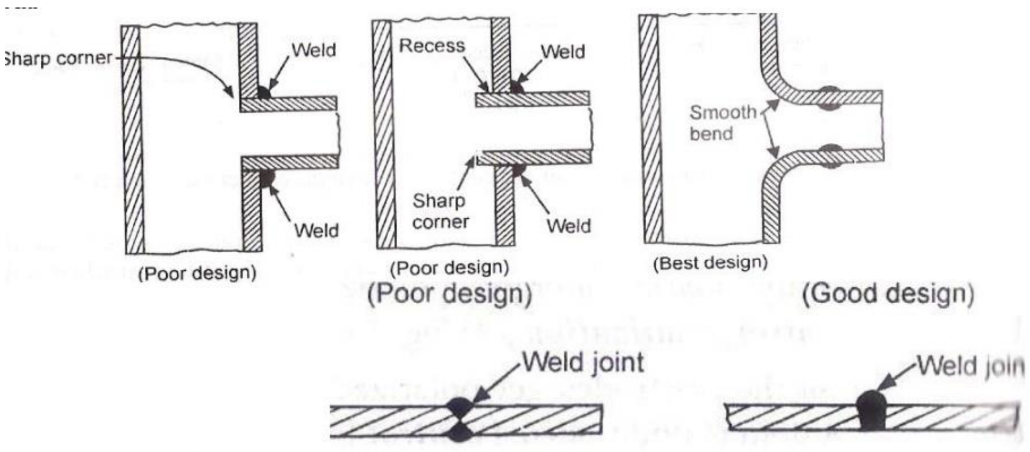


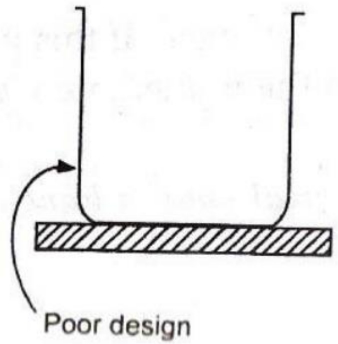
Prevention of Corrosion

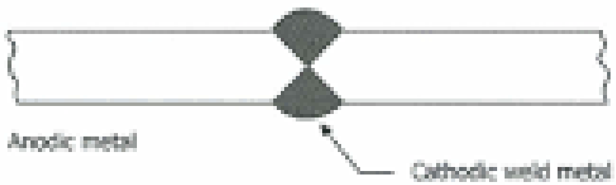
Categories to Prevent

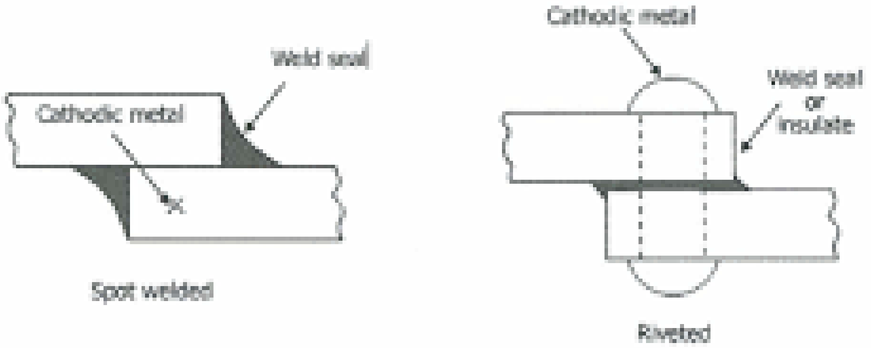
- **Improvement Of Design**
- **Proper Selection Of Materials**
- **Cathodic Protection**
    - Sacrificial Anodic Protection
    - Impressed Current Cathodic Protection
- **Anodic Protection Method**
- **Use Of Protective Coatings**

Design and Materials





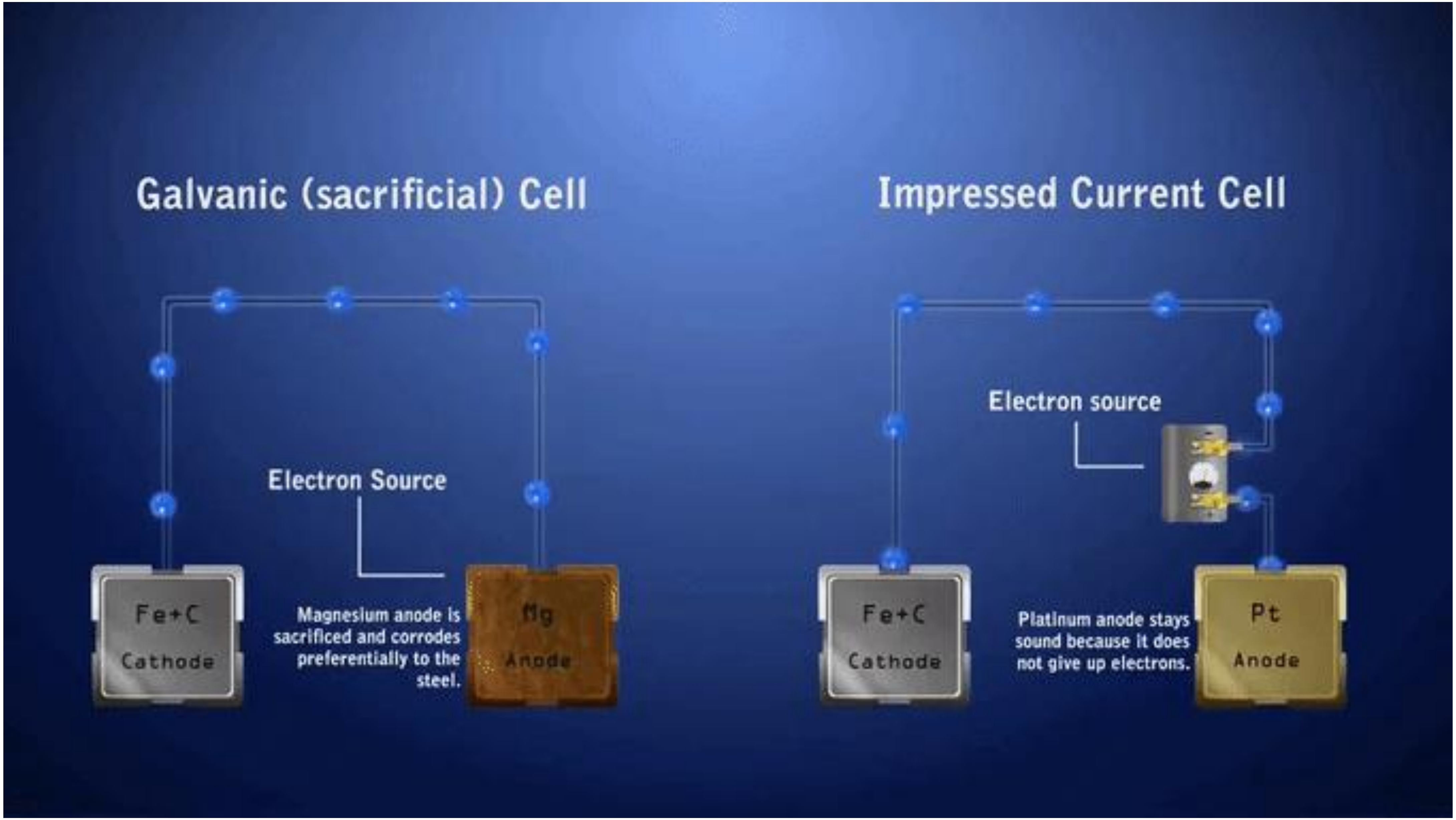




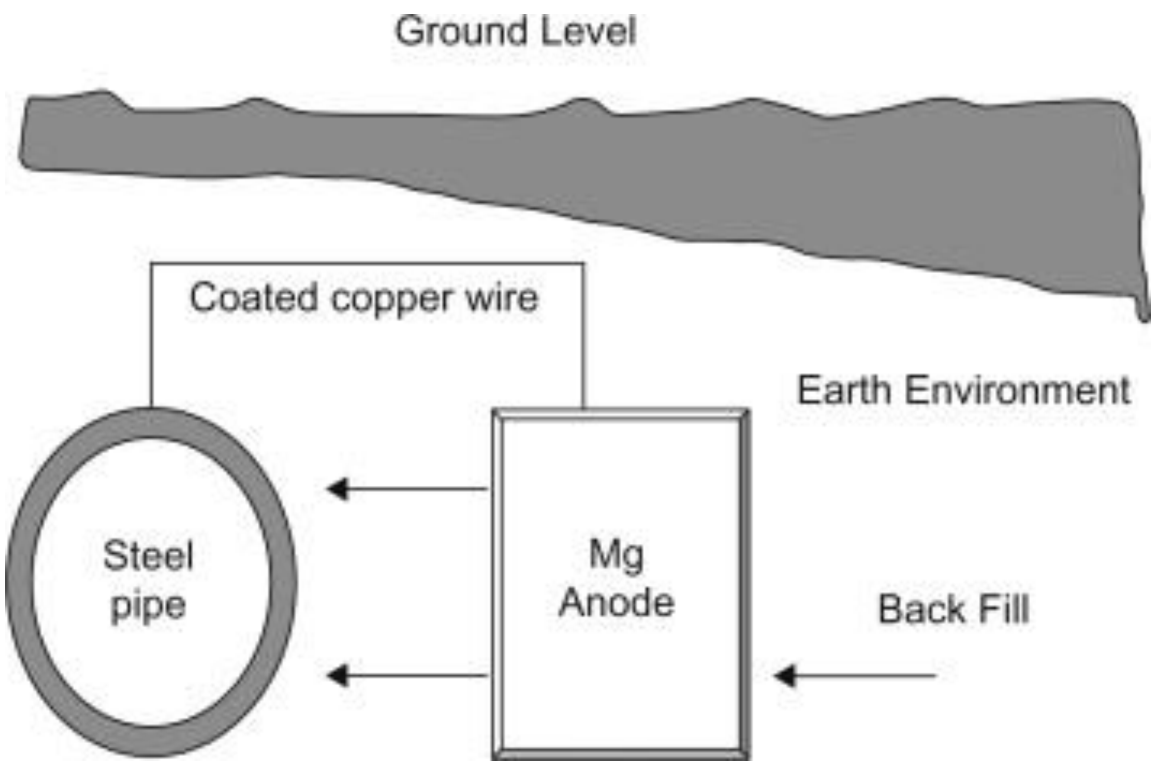
Cathodic protection

Sacrificial anode

Impressed current

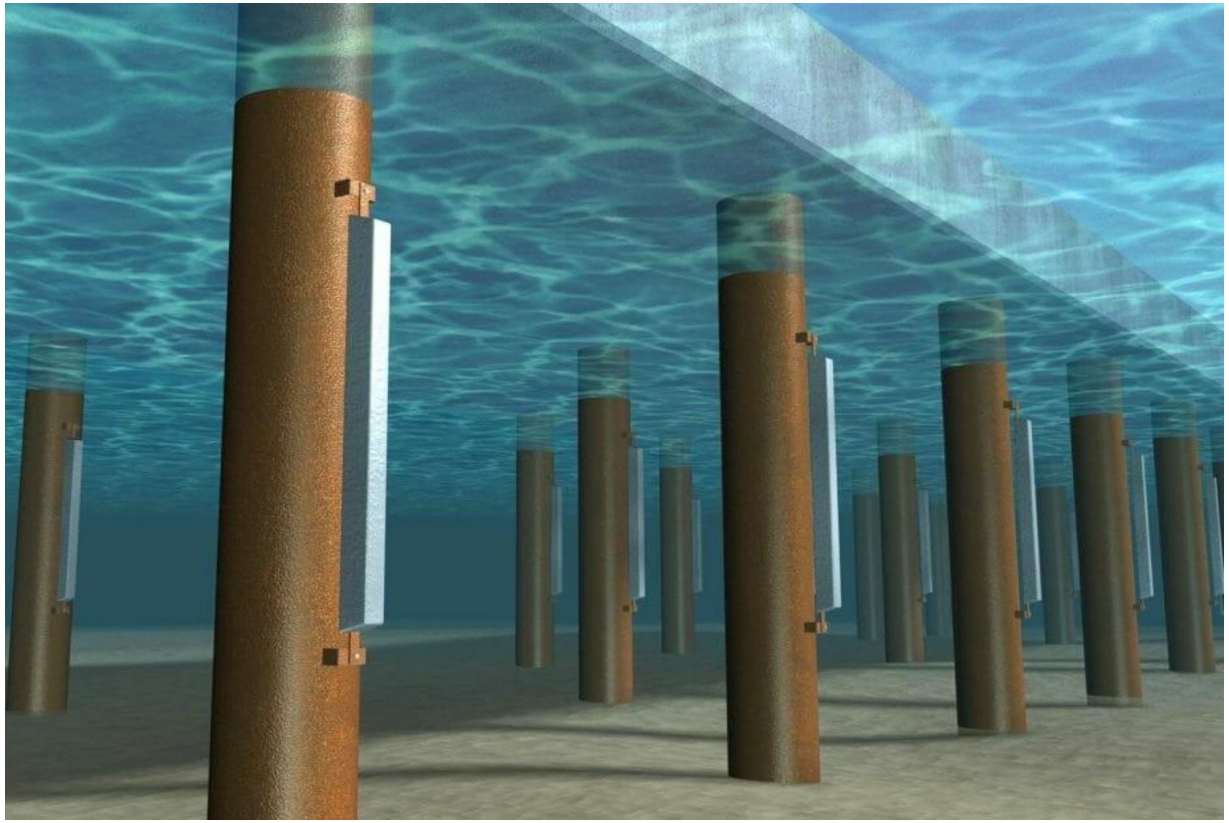

Galvanic (sacrificial) Cell
Electron Source
Fe+C
Cathode
Magnesium anode is sacrificed and corrodes preferentially to the steel.
Mg
Anode
Impressed Current Cell
Electron source
Fe+C
Cathode
Platinum anode stays sound because it does not give up electrons.
Pt
Anode

Sacrificial anode protection

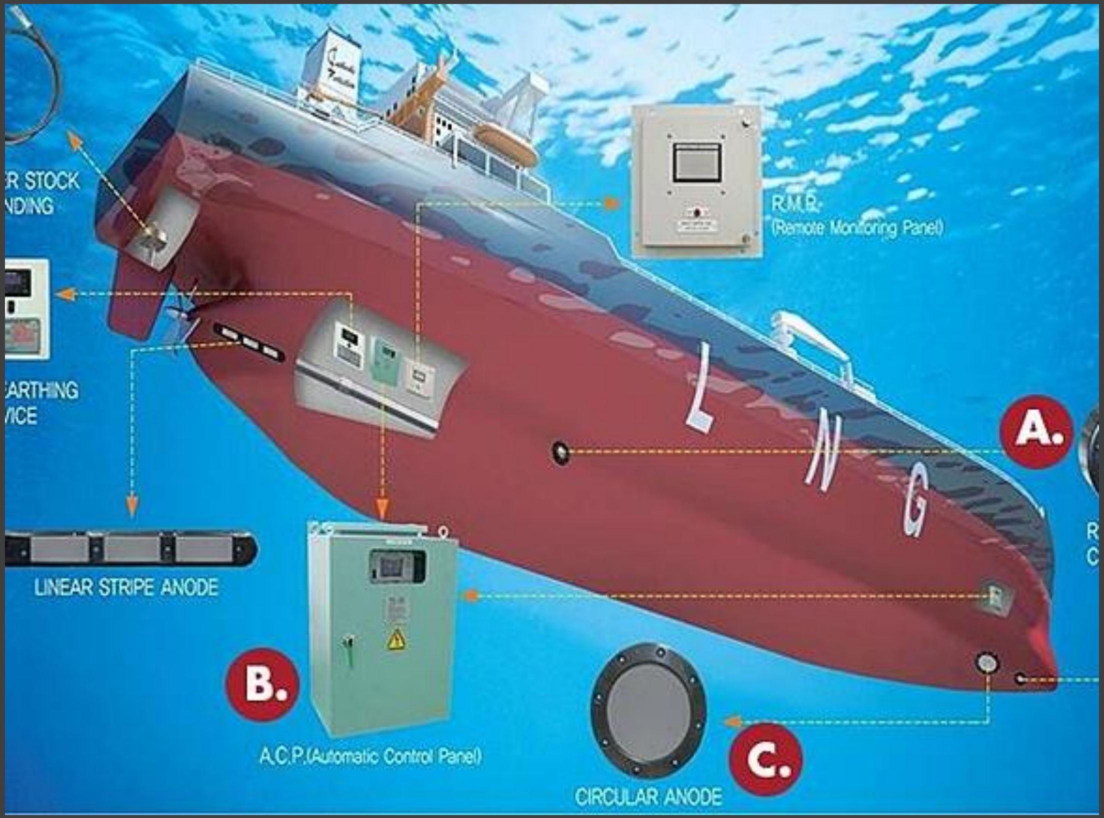


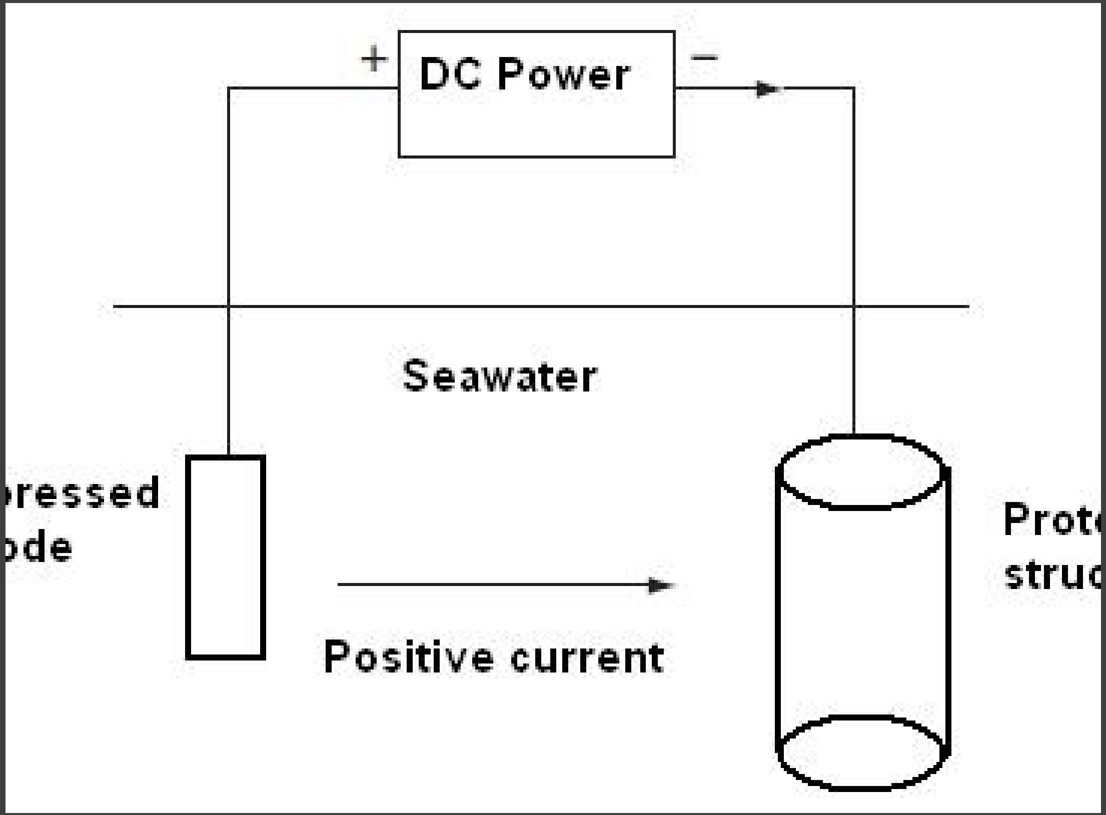
Applications of Sacrificial Anode Method

- Protection of buried pipelines
- Underground cables
- Marine structures
- Ship hulls
- Water tanks
- Pipes



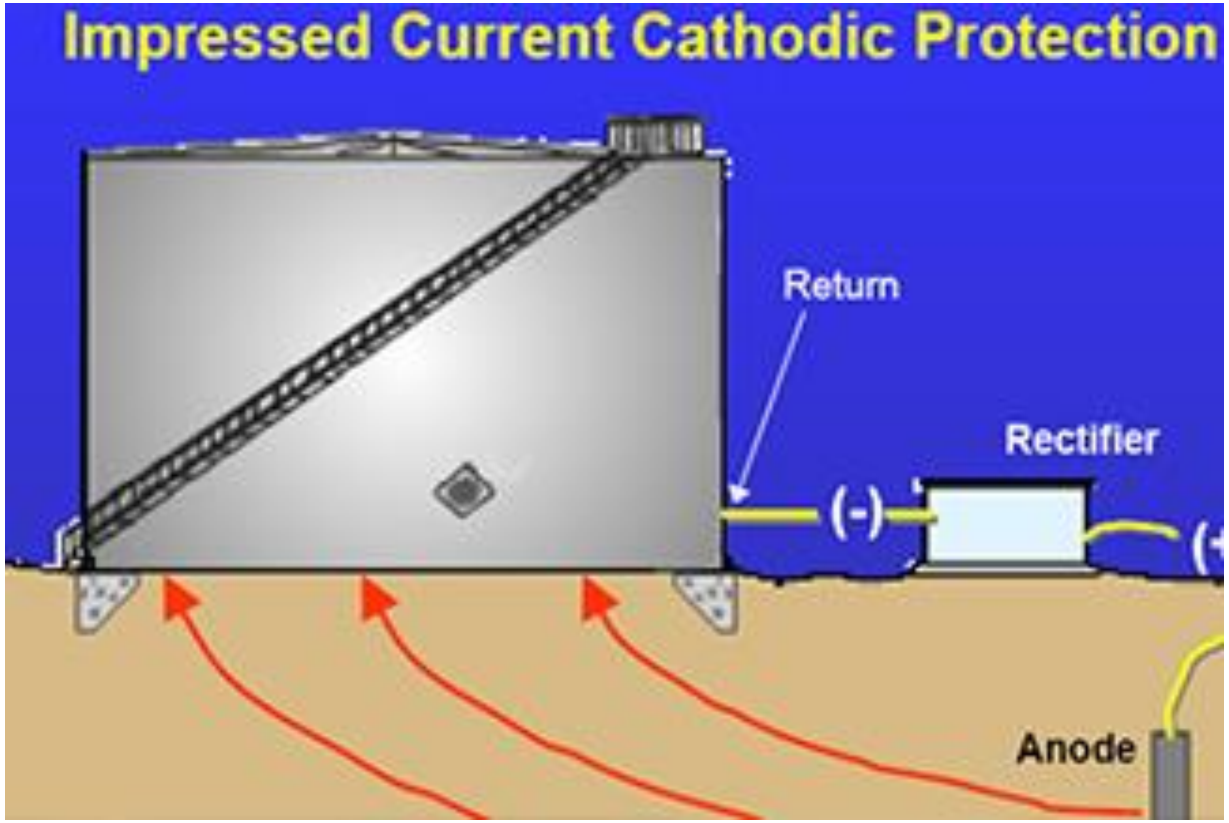
Impressed Current Cathodic Protection





Applications of Impressed Current method

- It is useful for large structures
- Applied to open water box coolers
- Water tanks
- Buried water and oil pipelines
- Condensers
- Transmission line towers

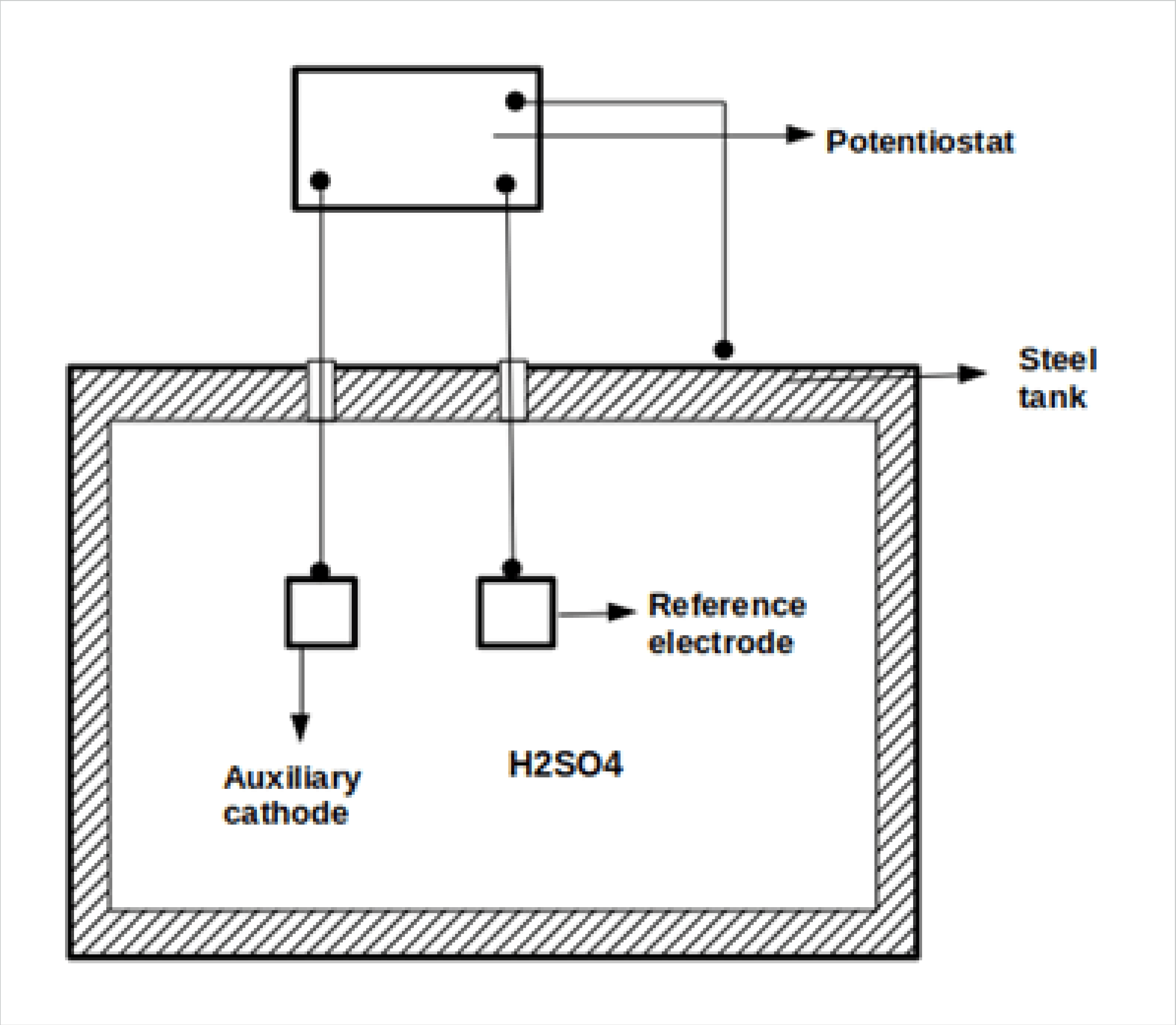


Impressed Current Cathodic Protection
Return
Rectifier
(-)
Anode

Sl. No.	Sacrificial Anode method	Impressed Current method
1/	External power supply is not required.	External power supply is required.
2/	The cost of investment is low.	The cost of investment is high.
3/	This requires periodic replacement of sacrificial anode.	Replacement is not required as anodes are stable.
4/	Soil and microbiological corrosion effects are not considered.	Soil and microbiological corrosion effects are taken into account.
5/	This is the most economical method especially when short term protection is required.	This is well suited for large structures and long term operations.
6/	This is a suitable method when the current requirement and the resisitivity of the electrolytes are relatively low.	This is a suitable method even when the current requirement and the resistivity of the electrolytes are high.

Anodic Protection

- Metals showing active passive behaviour
- Fe, Ni, Cr, Ti and their alloys
- Potentiostat is used which maintains a constant potential at anode
- Low current density
- Fe is passivated at pH =7 at 0.1 V.

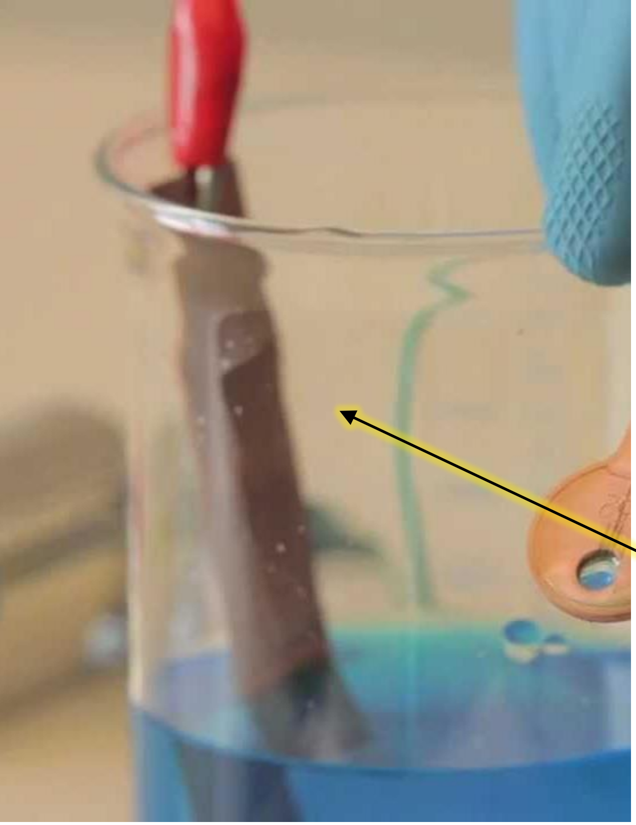


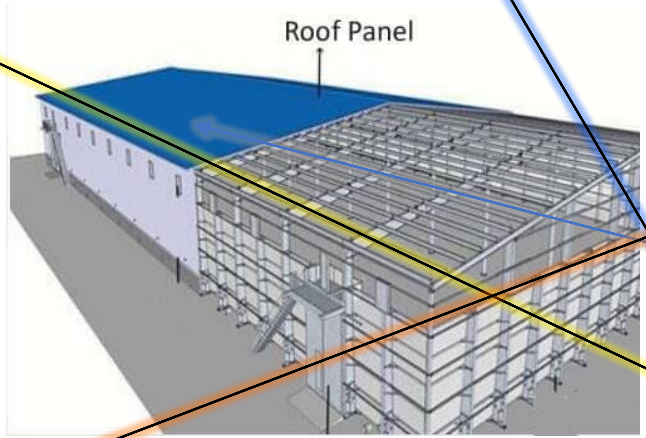
Applications of Anodic Protection

- Applicable in extremely corrosive environments
- Equipment made up of passive metals and Low current requirement
- Acid coolers in dilute sulphuric acid plants
- Storage tanks for sulphuric acid
- Chromium in contact with hydrofluoric acid

Cathodic Protection	Anodic Protection
1. Applicable to all metals	1. Metals which show active passive behavior
2. Can be used without electricity	2. Needs electricity
3. Low installation cost, High maintenance cost	3. High installation cost, low maintenance cost
4. Simple and standard	4. Wide range of complex structures
5. Corrosion rate can't be measured	5. Can be Measured

Metallic Coatings



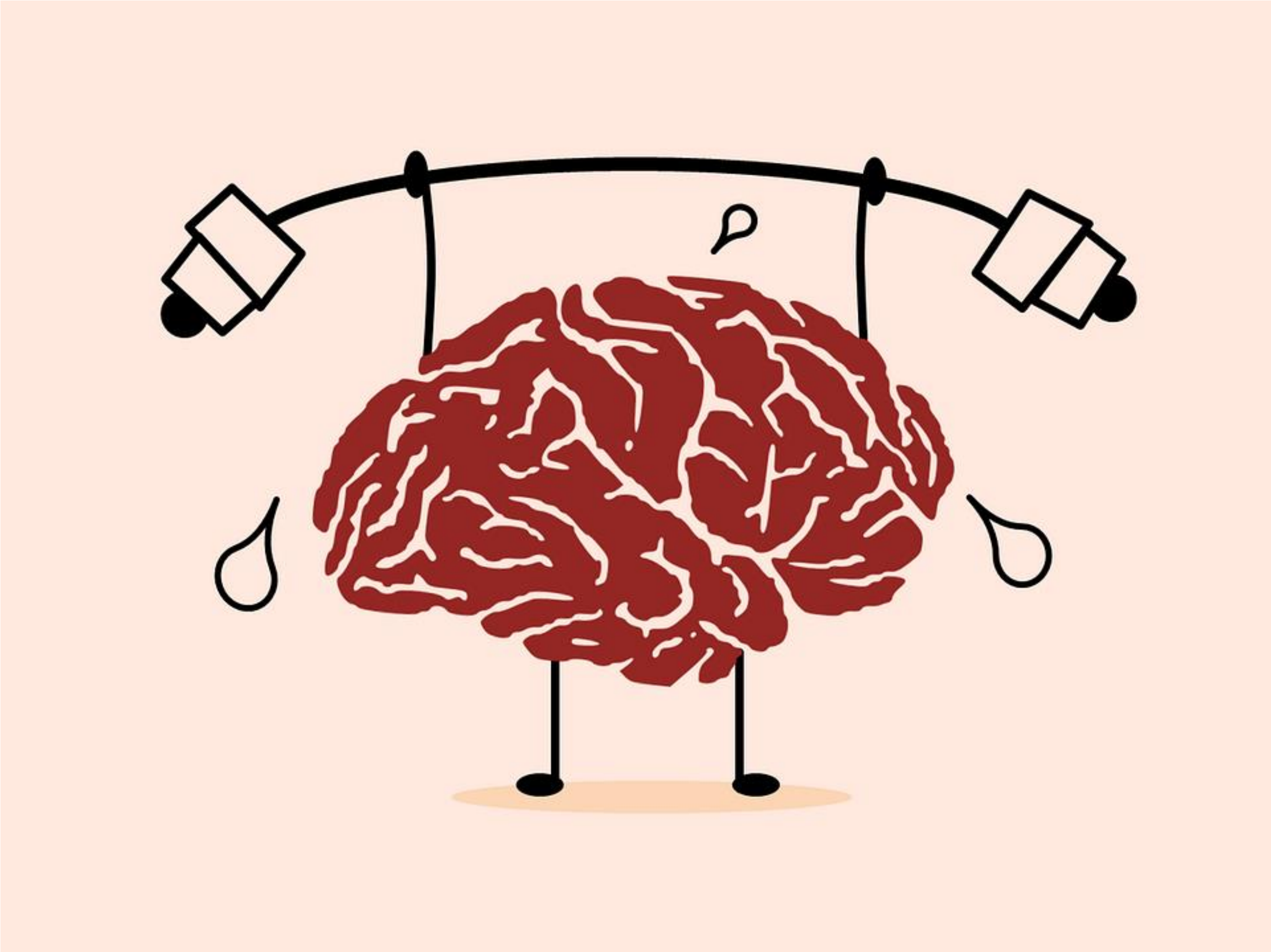


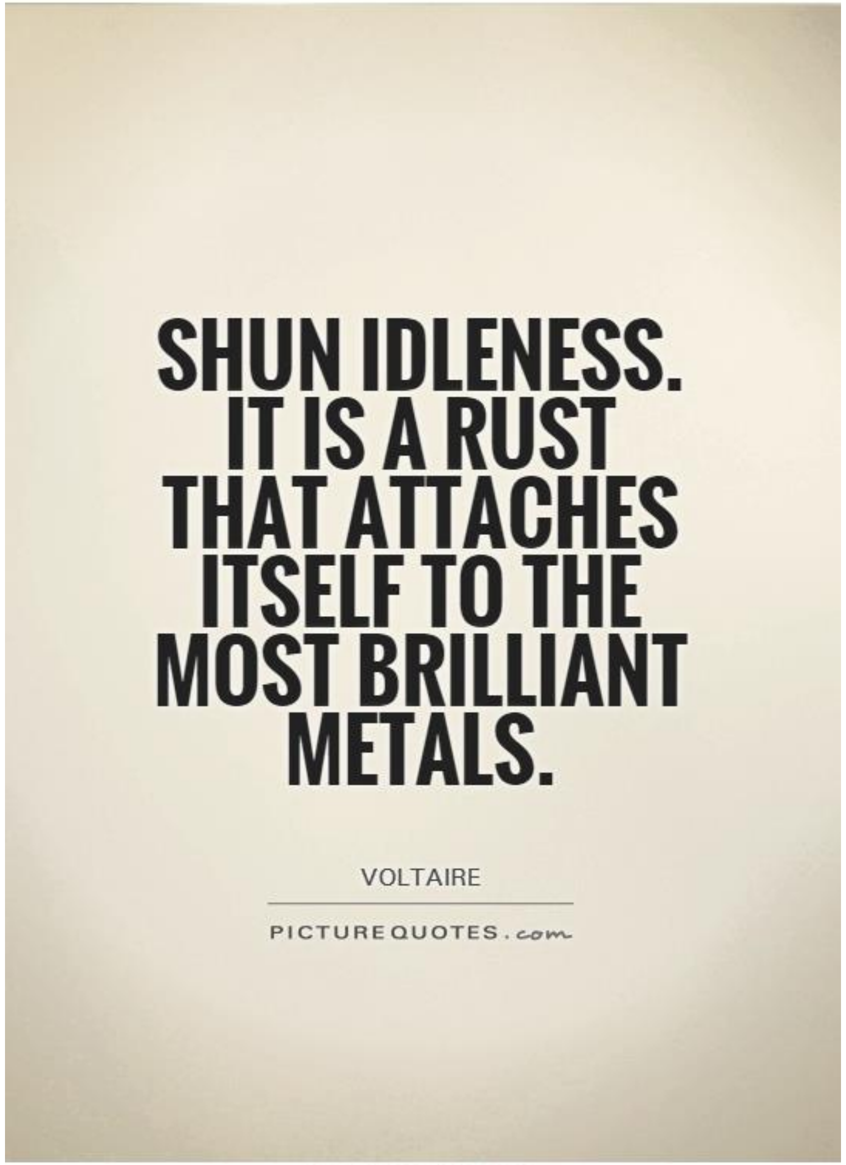
- Hot dipping
  - Galvanizing
  - Tinning
- Metal cladding
- Electroplating
- Metal spraying
- Cementation

Galvanizing (Anodic Coating)

Tinning (Cathodic Coating)

	Galvanizing	Tinning
	Galvanizing	**Tinning**
1	Process of covering iron or steel, with a thin coat of ZINC to prevent it from rusting.	Process of coating steel with a thin coat of TIN to prevent it, from corrosion
2	Zinc protects iron sacrificially.,Since it is more electro-positive,than iron and does not permit iron to pass into the solution.	Tin protects the base metal iron, from corrosion due to its noble, nature and higher corrosion resistance.
3	In galvanized articles, zinc continues to protect the underlying iron by galvanic cell action, even if the coating of zinc,is broken at any place	Tin protects underlying iron till the coat is intact. Any break in coating causes rapid corrosion of iron.
4	Galvanized containers cannot be used for storing acidic foodstuffs as zinc reacts with food acid forming poisonous compounds	Tin coated containers and utensils can be used for storing any food stuff as tin is non-toxic and protects metal from corrosion
5	Anodic Coating	Cathodic Coating
6	Ex, galvanizing rooftops	Ex. Storing food stuffs cans

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