Unit 3: Corrosion

Engineering Chemistry — DI01000071

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Unit 3 Syllabus Overview

Topics Covered

#	Topic
1	Definition & Significance of Corrosion
2	Types: Dry (Chemical) Corrosion
3	Types: Wet (Electrochemical) Corrosion
4	Mechanism of Rusting of Iron
5	Factors Affecting Corrosion
6	Prevention: Coatings (metallic, non-metallic)
7	Prevention: Galvanizing & Tinning
8	Prevention: Cathodic Protection
9	Prevention: Corrosion Inhibitors

Weightage: ≈12% of paper **PYQ:** 7-mark asked every exam

Definition & Significance of Corrosion

Definition

Corrosion is the gradual deterioration or destruction of metals by chemical or electrochemical reaction with the surrounding environment (atmosphere, moisture, or chemicals).

Examples

- Rusting of iron ($Fe_2O_3 \cdot xH_2O$)
- Tarnishing of silver (Ag_2S)
- Green patina on copper ($CuCO_3 \cdot Cu(OH)_2$)
- Dissolution of Zn in acid

Economic Significance

- Billions lost annually worldwide
- Structural failures (bridges, pipelines)
- Shortened equipment life
- India: $\approx$\$14 billion/year loss

Dry Corrosion

(Chemical Corrosion)

Dry (Chemical) Corrosion

Definition

Corrosion caused by the **direct chemical reaction** of metals with dry gases (O_2, CO_2, SO_2, halogens) — no moisture required; occurs at high temperatures.

Type	Agent	Product
Oxidation by O_2	Oxygen	Metal oxide
Oxidation by halogens	Cl_2, Br_2	Metal halide
Oxidation by SO_2	Sulphur dioxide	Metal sulphate
H_2 embrittlement	H_2	Metal hydride

Example Reactions

$4Fe + 3O_2 \rightarrow 2Fe_2O_3$ (iron oxide at high temp.)
$Cu + Cl_2 \rightarrow CuCl_2$
$2Ag + H_2S \rightarrow Ag_2S + H_2$ (tarnishing)

Pilling-Bedworth (P-B) Ratio

Definition

$$P\text{-}B \text{ Ratio} = \frac{\text{Volume of metal oxide formed}}{\text{Volume of metal consumed}}$$

P-B < 1 (porous oxide)

Oxide layer **porous** $\Rightarrow$ does not protect.
Corrosion continues.
Example: Alkali metals (Na, K, Mg)

P-B ≈ 1 (protective)

Oxide layer **compact & adherent** $\Rightarrow$ protects.
Corrosion stops (passivation).
Example: Al (Al_2O_3), Cr, Ni

P-B > 2: Oxide flakes/cracks (not protective either) — e.g., Fe_2O_3 (scale at high temp.)

Wet Corrosion

(Electrochemical Corrosion)

Wet (Electrochemical) Corrosion

Definition

Corrosion occurring in presence of **moisture/electrolyte** by electrochemical mechanism. Metal acts as galvanic cell — different regions act as anode and cathode.

Requirements

1. Two dissimilar metals (or regions)
2. Electrolyte (moisture)
3. Electrical contact between them
4. Oxygen or H^+ (cathodic agent)

Anodic vs Cathodic

Anode (active metal):
$M \rightarrow M^{n+} + ne^-$ (oxidation)

Cathode (noble region):
$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$
or $2H^+ + 2e^- \rightarrow H_2 \uparrow$

Mechanism of Rusting of Iron (PYQ W'23, Su'24)

Step-by-Step Mechanism

Anodic reaction ($Fe \rightarrow Fe^{2+}$):

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

Cathodic reaction (O_2 reduction):

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$$

Formation of $Fe(OH)_2$:

$$Fe^{2+} + 2OH^- \rightarrow Fe(OH)_2$$

Oxidation to $Fe(OH)_3$ and dehydration:

$$4Fe(OH)_2 + O_2 + 2H_2O \rightarrow 4Fe(OH)_3$$

$$2Fe(OH)_3 \rightarrow Fe_2O_3 \cdot 3H_2O \textbf{ (Rust)}$$

Rust colour: Reddish-brown; loose, porous structure; no protection

Differential Aeration Corrosion

Principle

When different parts of the same metal are exposed to **different oxygen concentrations**, the part with **less O_2** becomes the anode and corrodes.

Mechanism

Less O_2 region (anode):

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

More O_2 region (cathode):

$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$

Practical Example

Iron pipe partially buried in soil:

Underground (less O_2) $\rightarrow$ anode $\rightarrow$ corrodes

Above ground (more O_2) $\rightarrow$ cathode $\rightarrow$ protected

Also: Iron under rust pits vs open surface

Galvanic Corrosion

Principle

When two **dissimilar metals** are in electrical contact in an electrolyte, a galvanic cell forms. The **more active metal** (lower E°) acts as anode and corrodes faster.

Examples

Couple	Anode	Result
Fe–Cu	Fe (-0.44 V)	Fe corrodes near Cu joint
Zn–Fe	Zn (-0.76 V)	Zn corrodes, Fe protected
Al–Cu	Al (-1.66 V)	Al corrodes rapidly

Rule: Greater the potential difference between metals, faster the galvanic corrosion.

Waterline (Concentration Cell) Corrosion

Definition

Corrosion occurring at the **water–air interface** (waterline) due to **differential oxygen concentration** above vs below the waterline.

Mechanism

Below waterline: Less O_2 $\rightarrow$ anode $\rightarrow$ corrodes (pitting)

At/above waterline: More O_2 $\rightarrow$ cathode $\rightarrow$ rust deposits appear here

Observed in

- Ship hulls
- Water storage tanks
- Marine structures
- Bridge pillars in rivers

Note: Rust is deposited where O_2 is high; actual metal loss is below the waterline!

Factors Affecting Corrosion (PYQ Su'23, W'24)

Factor	Effect on Corrosion
Nature of metal	Active metals (high O.N., low E°) corrode faster
Purity of metal	Impure metals corrode faster (galvanic cells formed)
Physical state	Fine powder $>$ bulk; stressed metal corrodes faster at stress
Position in e-chem series	More active $=$ more corrosion tendency
pH of medium	Acidic medium accelerates corrosion
O_2 concentration	More $O_2 \rightarrow$ faster cathodic reaction
Temperature	Higher temp. accelerates rate
Humidity	More moisture $\rightarrow$ more electrolyte $\rightarrow$ faster wet corrosion
Presence of CO_2/SO_2	Makes water acidic; accelerates corrosion

Passivation

Definition

Passivation is the formation of a thin, adherent, compact, and impervious oxide film on a metal surface that **prevents further corrosion**.

Passive Metals

Metal	**Passive Film**
Aluminium	Al_2O_3
Chromium	Cr_2O_3
Nickel	NiO
Stainless steel	Cr_2O_3 layer
Titanium	TiO_2

Characteristics of Passive Film

- Thin (nanometres thick)
- Adherent — does not peel
- Impervious to gases/liquids
- Self-repairing (heals if scratched)
- P-B ratio ≈ 1

Corrosion Prevention — Overview

Methods of Corrosion Prevention

Category	Methods
Proper design	Avoid dissimilar metal contact; minimize crevices
Metallic coatings	Galvanizing, tinning, chromium plating, anodizing, electroplating
Non-metallic coatings	Painting, plastic/rubber lining, ceramic/enamel coating
Cathodic protection	Sacrificial anode, impressed current method
Inhibitors	Anodic, cathodic, mixed inhibitors (add to corrosive medium)
Alloying	Stainless steel (Fe+Cr+Ni), Monel metal (Ni+Cu)

Key principle: Break any one link of the corrosion chain (electrolyte, anode, cathode, or electrical contact).

Metallic Coatings (PYQ W'25, Su'24)

Types of Metallic Coatings

Method	Metal Used	Base Metal/Use
Galvanizing	Zinc	Iron/steel; roofing, pipes
Tinning	Tin	Iron (food cans, cookware)
Chrome plating	Chromium	Auto parts, tools
Nickel plating	Nickel	Base under chrome; sanitary
Copper plating	Copper	Printed circuits, decorative
Silvering	Silver	Cutlery, mirrors
Anodizing	Al_2O_3	Aluminium articles

Application Methods

Electroplating | **Hot-dip** | **Spraying** | **Cementation** | **Cladding**

Galvanizing (PYQ W'23, Su'24)

Definition

Coating of **zinc** on iron/steel to prevent rusting. Zinc is more active than iron ($E^\circ_{Zn} < E^\circ_{Fe}$), so zinc acts as sacrificial anode even if coating is scratched.

Process (Hot-Dip)

1. Clean iron: remove rust/scale with dilute H_2SO_4 (pickling)
2. Rinse with water; flux ($ZnCl_2$) treatment
3. Dip in molten zinc at 450 °C
4. Withdraw and cool; zinc–iron alloy interlayer forms

Uses: Roofing sheets, water pipes, buckets, nails, wire fence, corrugated iron sheets.

Tinning

Definition

Coating of **tin** on iron/steel. Tin ($E^\circ = +0.14$ V) is **less active** than iron (-0.44 V), so tin protects by **barrier action** only — if scratched, iron underneath corrodes faster.

Process

1. Clean iron (pickle with H_2SO_4)
2. Flux treatment ($ZnCl_2$)
3. Dip in molten tin (240 °C)
4. Squeeze through rollers for uniform coat

Applications & Comparison

Uses: Food cans, milk containers, kitchen utensils.

Tin is non-toxic and food-safe, hence preferred over Zn for food contact.

Galvanizing vs Tinning

Feature	Galvanizing	Tinning
Coating metal	Zinc (Zn)	Tin (Sn)
Position vs Fe	More active	Less active
Protection type	Sacrificial + barrier	Barrier only
If scratched	Zn corrodes, Fe safe	Fe corrodes faster
Food safe?	No (Zn toxic)	Yes (Sn non-toxic)
Application	Outdoor structures	Food containers
Process temp	$\approx 450\,^{\circ}\mathrm{C}$	$\approx 240\,^{\circ}\mathrm{C}$
Thickness	Thicker coat needed	Thinner coat sufficient

Key exam point: Galvanizing protects sacrificially; tinning only by barrier — if tinning is broken, corrosion is accelerated.

Non-Metallic Coatings

Organic Coatings

Type	Examples
Paints	Lead-based, oxide paints
Varnish	Alkyd, polyurethane
Lacquers	Nitrocellulose lacquer
Bituminous	Tar, asphalt (pipelines)
Plastic	PVC, polyethylene lining
Rubber	Vulcanized rubber lining

Inorganic Coatings

Type	Examples/Use
Enamel	Cookware, bath fittings
Ceramic	Furnaces, tiles
Cement	Underground pipes
Phosphating	Steel pre-treatment

Mechanism: Barrier between metal and environment; no electrochemical protection

Cathodic Protection

(Sacrificial Anode & Impressed Current)

Cathodic Protection (PYQ W'24, Su'25)

Principle

Make the metal to be protected the **cathode** of the electrochemical cell — cathode does not corrode (only oxidation/anode corrodes). Achieved by two methods:

1. Sacrificial Anode Method
2. Impressed Current Method (ICCP)

Where Used

- Underground pipelines (oil, gas, water)
- Ship hulls
- Marine structures (jetties, offshore platforms)
- Water storage tanks
- Concrete-embedded steel reinforcement

Sacrificial Anode Method (PYQ W'24, Su'24)

Principle

A more **active metal** (sacrificial anode) is electrically connected to the structure to be protected. The active metal corrodes preferentially, making the structure the cathode.

Anode Materials

Applied to	**Anode Used**
Iron structure	Zinc or Magnesium
Ship hull	Zinc blocks
Oil pipelines	Mg-alloy

Features

- No external power needed
- Simple installation
- Anodes must be replaced periodically
- Economical for small structures

Impressed Current Cathodic Protection (ICCP)

Principle

An **external DC source** is connected with its **negative terminal to the structure** (making it cathode) and positive to an **inert anode** (scrap iron, graphite, platinum) buried nearby.

Advantages

- External current can be adjusted
- Inert anode lasts longer
- Economical for large structures (pipelines >100 km)
- Effective in any soil/water

Setup

DC Source (+ve) $\rightarrow$ inert anode (in ground)
DC Source (−ve) $\rightarrow$ pipeline/structure
Current flows; structure becomes cathode; no corrosion.

Sacrificial Anode vs ICCP

Feature	Sacrificial Anode	ICCP
External power	Not required	Required (DC source)
Anode material	Active metal (Zn/Mg)	Inert (graphite/Pt)
Cost	Low initial cost	Higher initial cost
Maintenance	Replace anodes periodically	Monitor current levels
Scale of use	Small structures	Large pipelines, ships
Current control	None	Adjustable
Risk of overprotection	No	Yes (H embrittlement)

Both methods make the metal the cathode — this is the unifying principle.

Corrosion Inhibitors (PYQ W'23, W'25)

Definition

Substances added in **small amounts** to the corrosive medium that **significantly reduce the corrosion rate** without changing the properties of the medium.

Type	Mechanism	Examples
Anodic inhibitor	Forms oxide passive film on anode	Na_2CrO_4, $NaNO_2$, NaOH
Cathodic inhibitor	Precipitates on cathode; blocks O_2 reduction	$ZnSO_4$, $CaCO_3$, $MgSO_4$
Mixed inhibitor	Acts on both electrodes	Phosphates, silicates, amines
Organic inhibitor	Adsorbs on metal surface; forms protective film	Amines, mercaptans, thiourea

Application: Cooling water systems, acid pickling baths, oil/gas pipelines

Alloying for Corrosion Resistance

Why Alloying Helps

Adding **alloying elements** that form a stable, adherent oxide layer on the metal surface provides corrosion resistance by passivation.

Alloy	Composition	Property
Stainless steel (304)	Fe + 18% Cr + 8% Ni	Cr_2O_3 passive layer
Stainless steel (316)	+ 2% Mo	Resistant to Cl^-
Aluminium alloys	Al + Mg/Cu/Si	Al_2O_3 passive layer
Monel metal	67% Ni + 33% Cu	Seawater resistant
Inconel	Ni + Cr + Fe	High-temp. resistance
Cupronickel	Cu + Ni	Marine applications

Minimum 12% Cr needed in stainless steel for effective passivation (Cr_2O_3 layer)

Corrosion in Specific Environments

Atmospheric Corrosion

Humidity	>60% RH accelerates
SO_2	Forms H_2SO_4; attacks
CO_2	Mild acidification
NaCl (marine)	Electrolyte; aggressive

Soil Corrosion

Factors: moisture, pH, aeration, salt content, SRB bacteria (anaerobic)

Marine Corrosion

Seawater: high NaCl + dissolved O_2 = aggressive electrolyte.

Splash zone: Most aggressive (O_2 high, wet)
Tidal zone: Differential aeration
Underwater: Biological fouling

Used: Cathodic protection + anti-corrosion paints (epoxy-zinc primer) for ships

PYQ 7-Mark Questions — Corrosion (Unit 3)

Frequently Asked Long Questions

Question	Papers
Explain mechanism of rusting of iron	W'23, Su'24
Explain sacrificial anode method with diagram	W'24, Su'24
Describe cathodic protection (impressed current)	Su'25, W'25
What is galvanizing? Explain process and uses	W'23, Su'24
Compare galvanizing and tinning	Su'23, W'24
What are corrosion inhibitors? Types and examples	W'23, W'25
Explain electrochemical (wet) corrosion mechanism	Su'24, W'25

Strategy

Every 7-mark corrosion answer needs: definition + mechanism (reactions) + diagram + examples + comparison or application

Unit 3 Mid-Point Summary

Topic	Key Points
Definition	Deterioration by chemical/electrochemical reaction
Dry corrosion	Direct reaction with gases; P-B ratio; passivation
Wet corrosion	Electrolyte needed; anode corrodes; OIL RIG
Rusting	4-step: $Fe^{2+} \rightarrow Fe(OH)_2 \rightarrow Fe(OH)_3 \rightarrow$ rust
Galvanic corrosion	Dissimilar metals; active one corrodes
Diff. aeration	Less O_2 = anode; more O_2 = cathode
Prevention	Coatings | Galvanizing | Tinning | Inhibitors | CP
Cathodic protection	Sacrificial anode or impressed current (ICCP)

Stress Corrosion Cracking (SCC)

Definition

Cracking caused by the **combined action of tensile stress** (residual or applied) and a **specific corrosive environment**. Metal fails at stress much lower than yield strength.

Examples

Metal	**Environment**
Brass	NH_3 (season cracking)
Stainless steel	Cl^- ions (seawater)
Al alloys	$NaCl + H_2O$
Steel	NaOH (caustic SCC)

Prevention

- Stress relief annealing
- Reduce Cl^- concentration
- Use SCC-resistant alloys
- Cathodic protection
- Shot peening (compressive stress)

Pitting Corrosion

Definition

Localized corrosion that produces small pits or holes on the metal surface. Very dangerous — deep pits cause structural failure with little visible surface damage.

Mechanism

1. Passive film breaks at a point (scratch or Cl^- attack)
2. Small exposed area becomes **anode** (concentrated corrosion)
3. Large passive area = **cathode** (small anode:cathode ratio)
4. Pit deepens rapidly; autocatalytic process

Critical factor: Chloride ions (Cl^-) break passive films on stainless steel, Al, Ti. Marine environments are high risk.

Crevice Corrosion

Definition

Corrosion occurring in **narrow gaps** (crevices) between metal surfaces or between metal and non-metal — bolts, gaskets, riveted joints, lap joints.

Mechanism

Inside crevice: O_2 depleted $\rightarrow$ anode
Outside: O_2 rich $\rightarrow$ cathode
Self-accelerating — pH drops inside crevice (Cl^- accumulates)

Prevention

- Seal crevices with weld/sealant
- Use non-absorbent gaskets
- Design to allow drainage
- Use Cl^--resistant alloys (316 SS)

Hydrogen Embrittlement

Definition

The absorption of atomic hydrogen into metals during corrosion or electroplating, making them **brittle and prone to cracking** under stress.

How It Occurs

- Atomic H (not H_2) enters metal lattice
- H accumulates at defects/grain boundaries
- Internal pressure builds $\rightarrow$ cracks
- Most common in high-strength steels

Prevention

- Bake after electroplating (200 °C, 12 hr)
- Use low-hydrogen welding electrodes
- Apply hydrogen barrier coatings
- Avoid overprotection in cathodic protection (ICCP risk)

Painting as Corrosion Prevention

Principle

Paint forms a **physical barrier** between metal and corrosive environment. Effective only when paint film is **intact and adherent**.

Paint System Layers

Layer	Purpose
1. Surface preparation	Sand-blast / phosphate treatment
2. Primer	Adhesion + anti-corrosion (zinc-rich, red oxide)
3. Undercoat	Build film thickness
4. Topcoat	Weather/UV resistance; decorative

Zinc-rich primers have Zn particles that provide sacrificial protection even under the paint film.

Phosphating & Chromating (Surface Treatments)

Phosphating

Steel is treated with **phosphoric acid solution** $\rightarrow$ forms insoluble zinc/iron phosphate layer on surface.

Type	Zinc phosphate, Iron phosphate
Basis	Adherent, porous layer
Use	Pre-treatment before painting; i

Chromating (Passivation)

Metal treated with chromic acid/chromate salts $\rightarrow$ forms Cr(III) oxide passive film.

Used on	Al, Zn, Mg alloys
Result	Adherent Cr_2O_3 film
Use	Aerospace, auto industry

Note: Hexavalent Cr (Cr^{6+}) is toxic; Cr^{3+}-based alternatives used.

Corrosion Resistance of Common Metals

Metal	Why Resistant	Environment	Weak vs.
Aluminium	Al_2O_3 passive layer	Air, weak acid	HCl, NaOH
Chromium	Cr_2O_3 film	Air, oxidizing acid	HCl, H_2SO_4
Nickel	NiO film	Many environments	Oxidizing acids
Titanium	TiO_2 film (very stable)	Seawater, acids	HF
Stainless steel	Cr_2O_3 (12%+ Cr)	Air, water, mild acids	Cl^-, HCl
Gold/Platinum	Noble (high E°)	Almost all	Aqua regia
Zinc	$ZnO/Zn(OH)_2$ (slight)	Air, neutral water	Acids, alkalis

Biocorrosion (Microbiologically Influenced Corrosion)

Definition

Corrosion caused or accelerated by microorganisms (bacteria, fungi) in the surrounding environment. Common in soils, marine environments, and water systems.

Organisms

SRB: Sulfate-reducing bacteria
$SO_4^{2-} \rightarrow H_2S$ (attacks iron)

IOB: Iron oxidizing bacteria
Oxidize $Fe^{2+} \rightarrow Fe^{3+}$ (pitting)

Prevention

- Biocides in water systems
- Protective coatings
- Cathodic protection
- Pipe pigging (physical cleaning)
- Sterile soil backfill

Unit 3 PYQ Pattern Analysis

Topic	Su'23	W'23	Su'24	W'24	Su'25/W'25
Rusting mechanism	2	7	7	2	2
Cathodic protection	2	2	2	7	7
Galvanizing	7	7	7	2	2
Tinning	2	2	2	2	2
Galvanizing vs Tinning	7	2	2	7	2
Corrosion inhibitors	2	7	2	2	7
Wet corrosion	2	2	7	2	7
Dry corrosion / P-B ratio	2	2	2	2	2
Factors affecting	2	2	2	7	2

High probability 7-mark: Rusting mechanism + Cathodic protection + Galvanizing

Corrosion Numerical — Weight Loss Calculation

Corrosion Rate Expressed as

mpy (mils per year): $\text{mpy} = \dfrac{534 \times W}{D \times A \times T}$

Where: W = weight loss (mg), D = density (g/cm^3), A = area (in^2), T = time (hr)

Or simply: **corrosion rate** $= \dfrac{\text{mass loss}}{\text{area} \times \text{time}}$ $\quad (\text{mg cm}^{-2}\ \text{hr}^{-1})$

Example

Iron plate (area $= 10\,\text{cm}^2$) loses $0.5\,\text{mg}$ in 2 hours.

Corrosion rate $= \dfrac{0.5}{10 \times 2} = \mathbf{0.025}\,\text{mg cm}^{-2}\text{h}^{-1}$

PYQ Short-Answer Practice — Unit 3 (2 Marks)

Common 2-Mark Questions

#	Question
1	Define corrosion. Give two examples.
2	What is dry corrosion? Give one example with reaction.
3	Define Pilling-Bedworth ratio. What does P-B < 1 indicate?
4	What is passivation? Name two passive metals.
5	Distinguish between galvanizing and tinning.
6	What is a sacrificial anode? Name two metals used.
7	Define differential aeration corrosion. Give one example.
8	What is pitting corrosion? Why is it dangerous?
9	Name two types of corrosion inhibitors with examples.
10	What is stress corrosion cracking?

Exam Tips — Unit 3 Corrosion

Do's

- Write all 4 steps of rusting mechanism with chemical equations
- Clearly label anode/cathode in cathodic protection diagram
- State P-B ratio with all three cases
- Distinguish galvanizing vs tinning in a table
- Mention that inhibitors are added in small amounts

Don'ts

- Don't say tinning protects sacrificially (it doesn't!)
- Don't skip the oxidation reaction in wet corrosion
- Don't mix cathodic protection with cathodic inhibitors
- Don't forget that ICCP uses a DC source
- Don't confuse galvanizing (Zn) with chromium plating

Unit 3 Revision Flash Points

Must Know Facts

- Rusting: Fe $\rightarrow$ rust (4 reactions)
- P-B ratio: <1 = porous; ≈ 1 = protective
- Galvanizing temp: $\approx 450\,^{\circ}\text{C}$ (hot-dip Zn)
- Tinning temp: $\approx 240\,^{\circ}\text{C}$ (hot-dip Sn)
- Sacrificial anodes: Zn, Mg (for Fe structures)
- Stainless steel: min 12% Cr for corrosion resistance
- ICCP: negative terminal to structure

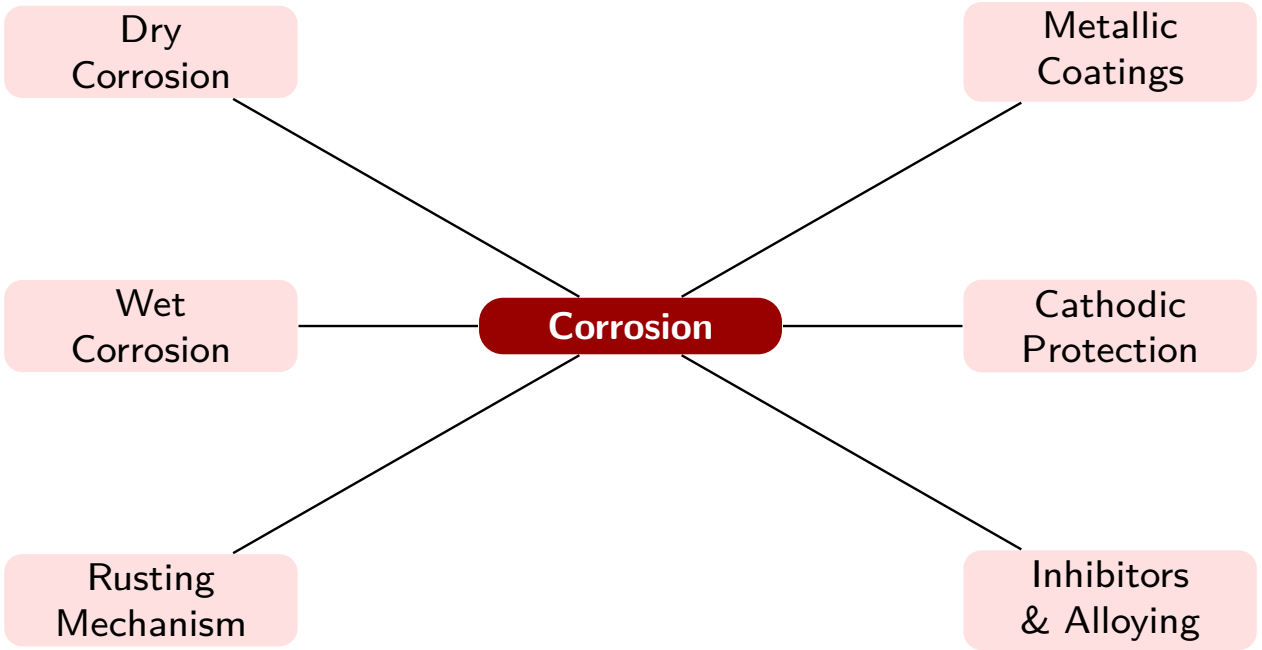
Quick Comparison

Anode	Corrodes (oxidation)
Cathode	Protected (reduction)
Zn on Fe	Sacrificial (active E°)
Sn on Fe	Barrier only (noble E°)
Dry corrosion	No moisture
Wet corrosion	Electrochemical

Unit 3 Key Summary Table

Topic	Core Content
Dry corrosion	Direct rxn with O_2/halogens/SO_2; P-B ratio
Wet corrosion	Electrochemical; anode oxidizes; cathode protected
Rusting	$Fe \rightarrow Fe^{2+} \rightarrow Fe(OH)_2 \rightarrow Fe(OH)_3 \rightarrow$ rust
Galvanic corrosion	Dissimilar metals + electrolyte; active metal = anode
Diff. aeration	Less O_2 = anode; more O_2 = cathode
Galvanizing	Zn on Fe; sacrificial; 450°C hot-dip
Tinning	Sn on Fe; barrier only; 240°C; food-safe
Cathodic protection	Sacrificial anode (Zn/Mg) or ICCP (DC supply)
Inhibitors	Anodic (chromate) / Cathodic ($ZnSO_4$) / Mixed
Passivation	Adherent P-B≈1 oxide film (Al_2O_3, Cr_2O_3)

Unit 3 — Corrosion Mind Map



P-B ratio | OIL RIG | Galvanizing | Tinning | Sacrificial anode | ICCP

High-Temperature (Elevated Temp.) Corrosion

Definition

Corrosion of metals at **elevated temperatures** ($>300^{\circ}C$) by direct reaction with gases (O_2, SO_2, steam, fuel combustion products). Also called **oxidation corrosion** or **scaling**.

Reactions

$4Fe + 3O_2 \rightarrow 2Fe_2O_3$ (scale)
$Ni + SO_2 \rightarrow NiO + S$
$2Cu + O_2 \rightarrow 2CuO$ (black scale)

Prevention

- Use high Cr/Ni alloys (Inconel, stainless)
- Protective coatings (aluminizing, chromizing)
- Ceramic coatings for furnace parts
- Control furnace atmosphere (reducing or inert)

Effect of pH on Corrosion

pH vs Corrosion Rate

pH	Effect on Iron Corrosion
< 4 (acidic)	Dissolution: $Fe + H_2SO_4 \rightarrow FeSO_4 + H_2$ (very fast; protective film dissolves)
4–10 (near neutral)	Moderate; $Fe(OH)_2$ forms; rate depends on O_2 access
> 10 (alkaline)	Passivation (stable Fe_2O_3 film); corrosion slows
Highly alkaline (>14)	Fe dissolves as $HFeO_2^-$ (amphoteric); corrosion again

Practical note: Concrete (pH $\approx$12) protects embedded steel by making it passive — but carbonation (CO_2 lowers pH) can cause depassivation and rebar corrosion.

Corrosion of Steel in Concrete (RCC)

Why Steel is Protected in Fresh Concrete

Fresh concrete is alkaline (pH ≈12–13). This causes steel reinforcement to form a **passive oxide film** that prevents corrosion.

Why Corrosion Starts in RCC

Carbonation: $CO_2 + H_2O \rightarrow H_2CO_3$ lowers pH below 9 $\Rightarrow$ passive film destroyed

Chloride ingress: Cl^- (from seawater or deicing salts) breaks passive film locally $\Rightarrow$ pitting corrosion

Prevention: Dense concrete (low w/c ratio) | Epoxy-coated rebars | Cathodic protection | Stainless steel rebars

Corrosion in Chemical Industry

Environment	Corrosive Agent	Material Used
Sulfuric acid	Conc. H_2SO_4	Lead, SS 316, glass-lined
Hydrochloric acid	HCl (dilute)	Rubber/plastic lining, Hastalloy
Alkali services	NaOH	Nickel, SS 304
Seawater	NaCl + O_2	Cupronickel, Ti, SS 316
Oxidizing acids	HNO_3	Stainless steel (passive)
High-temp gas	O_2, SO_2	Inconel, Incoloy
H_2S environment	Wet H_2S	Hard but ductile grades

Key principle: Match material to environment — no single metal resists all corrosive conditions.

Design Considerations for Corrosion Control

Engineering Design Rules

- **Avoid galvanic couples:** Use metals close in series, or insulate joints
- **Eliminate crevices:** Seal joints; use butt welds instead of lap welds
- **Allow drainage:** No pockets where water collects; incline surfaces
- **Minimize stress concentrations:** Smooth surfaces; avoid sharp corners
- **Accessibility:** Design for inspection, maintenance, and coating replacement
- **Material selection:** Use corrosion-resistant alloys in aggressive zones

Electrochemical Basis of Corrosion Control

Evans Diagram (Qualitative)

The corrosion potential and current are set by the intersection of anodic (oxidation) and cathodic (reduction) polarization curves. Methods to reduce corrosion current:

Method	Effect on Evans Diagram
Anodic inhibitor	Shifts anodic curve to lower current (passivates anode)
Cathodic protection	Shifts cathode potential below corrosion potential
Coatings	Remove electrode from electrolyte (no circuit)
Sacrificial anode	Provides anodic current from the anode (Zn/Mg), not the structure
ICCP	Applies cathodic current equal to corrosion current

Notable Corrosion Failures (Real Engineering Cases)

Why Study Corrosion Failures?

Corrosion failures cause loss of life, environmental damage, and economic losses. Understanding them guides prevention.

Case	Corrosion Type	Lesson
Aloha Airlines (1988)	Fatigue + pitting (Cl^-)	Inspect aging aircraft
Corroded Pt. Pleasant Bridge (1967)	SCC in wires	Avoid high-stress + hostile env.
Alaskan oil pipeline	Differential aeration	Cathodic protection + coatings
Statue of Liberty copper	Galvanic (Cu-Fe frame)	Isolation between metals
Petrobras P-36 (2001)	Crevice corrosion	Regular inspection of welds

Corrosion Monitoring Techniques

Electrochemical Methods

Method	**Principle**
LPR	Linear polarization r
EIS	Electrochemical imp
Potentiodynamic	Polarization scan
ZRA	Zero resistance amme

Non-Electrochemical Methods

Coupon test	Weight loss measur
UT	Ultrasonic thickness
RT/XT	X-ray/neutron testi
Acoustic emission	Crack detection

Simplest lab method: Coupon (test) specimens of known area immersed in corrosive solution for fixed time; weigh before/after.

Economic Impact of Corrosion

Global and National Statistics

Global annual cost	≈\$2.5 trillion (3.4% of global GDP)
USA	≈\$270 billion/year
India	≈\$14–20 billion/year
Industries affected	Oil/gas, infrastructure, aerospace, marine

Preventable Costs?

Studies suggest **25–40%** of corrosion costs are preventable with existing knowledge and technology — problem is implementation and maintenance.

Prevention Value

Every \$1 spent on corrosion prevention saves \$7–\$10 in repair/replacement costs.

Corrosion Behaviour: Aluminium vs Iron

Feature	Aluminium	Iron
Thermodynamic tendency	More reactive ($E^\circ = -1.66$ V)	Less reactive ($E^\circ = -0.44$ V)
Actual corrosion rate	Very slow (passive)	Moderate to fast
Oxide formed	Al_2O_3 (compact, P-B$\approx$1.3)	Fe_2O_3 (flaky, P-B$>$2)
Oxide property	Adherent, impervious, self-sealing	Loose (rust), porous
Net protection	Very good	Poor (rusts through)
Use in corrosive env.	Aircraft, marine, cookware	Needs coatings/protection

Key insight: Thermodynamic reactivity $\neq$ corrosion rate; kinetics (passive film) can override thermodynamics.

Corrosion and Environmental Pollution

Acid Rain and Corrosion

$SO_2 + H_2O \rightarrow H_2SO_3 \rightarrow H_2SO_4$ (acid rain, pH 4–5)
$NO_x + H_2O \rightarrow HNO_3$

Acid rain attacks: metals, limestone buildings, marble monuments, concrete

Tarnishing of Monuments

Material	**Effect**
Limestone/Marble	$CaCO_3 + H_2SO_4 \rightarrow CaSO_4 + H_2O + CO_2$
Bronze (Cu-Sn)	Green patina: $Cu_2(OH)_2CO_3$
Iron structures	Rust, pitting, loss of cross-section

Electroplating vs Galvanizing vs Tinning

Feature	Electroplating	Galvanizing	Tinning
Method	Electrolytic	Hot-dip (or electro)	Hot-dip
Coating metal	Any metal	Zinc	Tin
Thickness control	Very precise	Variable	Variable
Adhesion	Excellent	Good	Good
Alloy layer formed?	No	Yes (Zn-Fe)	Yes (Sn-Fe)
Sacrificial?	Depends on metal	Yes (Zn is active)	No (Sn is noble)
Food safe?	Depends	No	Yes
Cost	Higher per unit	Low (bulk)	Low (bulk)

Selecting the Right Corrosion Prevention Method

Decision Framework

Situation	Recommended Method
Outdoor structural steel	Galvanizing + epoxy primer
Food processing equipment	Stainless steel (316) or tinning
Underground pipeline	ICCP + polyethylene wrapping
Ship hull	Cathodic protection + anti-fouling paint
Electrical components	Nickel/gold electroplating
Boilers/pipes (water)	Anodic inhibitors (chromate, nitrite)
High-temp furnace parts	Ceramic/aluminide coating

Unit 3 — Formula & Data Summary

Key Formulas and Values

Formula/Value	Note
P-B Ratio $= V_{\text{oxide}}/V_{\text{metal}}$	< 1 porous; ≈ 1 protective
Corrosion rate = mass loss / (area $\times$ time)	$\text{mg/cm}^2\text{/hr}$
Rusting: $\text{Fe} \rightarrow \text{Fe}^{2+} + 2e^-$	Anodic reaction
$\text{O}_2 + 2\text{H}_2\text{O} + 4e^- \rightarrow 4\text{OH}^-$	Cathodic (neutral)
$2\text{H}^+ + 2e^- \rightarrow \text{H}_2$	Cathodic (acidic)
Galvanizing temp	$\approx 450\,^\circ\text{C}$
Tinning temp	$\approx 240\,^\circ\text{C}$
Stainless steel Cr content	Min 12% for passivation

Unit 3 Complete — Bridge to Unit 4: Fuels

Unit 3 Summary

Topic	Core Outcome
Dry corrosion	Gases attack directly; P-B ratio; passivation
Wet corrosion	Electrochemical; 4 types of corrosion cells
Rusting	4-step mechanism; anode(Fe) + cathode(O_2)
Galvanizing	Zn sacrificial coating; hot-dip 450°C
Tinning	Sn barrier coating; 240°C; food-safe
Cathodic protection	Sacrificial anode (Zn/Mg) or ICCP
Inhibitors	Anodic / cathodic / mixed / organic

Coming Next — Unit 4: Fuels

Unit 4 covers **classification of fuels**, calorific values, Dulong's formula, solid/liquid/gaseous fuels, and combustion analysis.