Applied Chemistry

Corrosion of Metals — Mechanism and Prevention

1. Introduction to Corrosion of Metals

Corrosion is defined as the gradual destruction or deterioration of a metal, due to chemical or electrochemical reaction with substances present in its surrounding environment, such as atmospheric gases, moisture, or other chemical agents. Corrosion converts the metal, over time, into a more chemically stable compound, such as an oxide, hydroxide, sulphide, or carbonate, essentially reversing the metallurgical process by which the metal was originally extracted from its ore.

Corrosion is a matter of great engineering and economic significance, since it causes the gradual weakening, disfigurement, and eventual failure of metal structures, machinery, and components, resulting in substantial economic losses worldwide each year, in terms of material replacement, structural failures, and maintenance costs.

2. Types of Corrosion

Corrosion is broadly classified into two types, based on the mechanism by which it occurs:

Type of Corrosion	Mechanism	Example
Chemical (Dry) Corrosion	Direct chemical reaction between a metal surface and dry gases (such as oxygen, sulphur dioxide, or chlorine) in the surrounding atmosphere, without the involvement of any moisture or electrolyte; typically forms a thin oxide (or other compound) film directly on the metal surface	Formation of a black oxide layer on iron when heated in dry air; tarnishing of silver in the presence of sulphur-containing gases
Electrochemical (Wet) Corrosion	Occurs in the presence of moisture (an electrolyte) on the metal surface, through the setting up of tiny electrochemical (galvanic) cells on the metal surface, involving anodic and cathodic regions, with current flow between them through the moisture layer	Rusting of iron exposed to moist air; corrosion of metal structures in humid or marine environments

Of these two types, electrochemical (wet) corrosion is by far the more common and significant form of corrosion encountered in practical engineering situations, since most

metal structures and components are exposed to atmospheric moisture or humid conditions during their service life.

3. Mechanism of Electrochemical Corrosion — Hydrogen Evolution and Oxygen Absorption

Electrochemical corrosion occurs through the formation of tiny galvanic (electrochemical) cells on the surface of a metal, wherever slight differences in composition, stress, or exposure create regions that behave, respectively, as anodic (more reactive) and cathodic (less reactive) areas on the same metal surface. At the anodic region, the metal itself undergoes oxidation and dissolves into the moisture layer as metal ions, releasing electrons: $M \rightarrow M^{n+} + n\,e^-$. These released electrons then flow through the metal to the nearby cathodic region, where they are consumed in one of two possible reduction mechanisms, depending on the nature of the surrounding environment.

Mechanism	Description	Typical Condition
Hydrogen (H_2) Evolution Mechanism	Occurs mainly in acidic, oxygen-free environments; at the anodic region, the metal loses electrons and dissolves as metal ions ($M \rightarrow M^{n+} + ne^-$), while at the cathodic region, hydrogen ions from the acidic medium gain these electrons and are reduced, evolving hydrogen gas ($2H^+ + 2e^- \rightarrow H_2\uparrow$)	Corrosion of metals such as iron in acidic solutions, in the absence of dissolved oxygen
Oxygen (O_2) Absorption Mechanism	Occurs mainly in neutral or slightly alkaline environments in the presence of dissolved oxygen; at the anodic region, the metal loses electrons and dissolves as metal ions ($M \rightarrow M^{n+} + ne^-$), while at the cathodic region, dissolved oxygen, together with water, is reduced by absorbing these electrons, forming hydroxide ions ($O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$), which then combine with the metal ions to form the corrosion product (such as rust)	Rusting of iron exposed to moist, aerated (oxygen-containing) air — the most common form of atmospheric corrosion

In practice, the oxygen absorption mechanism accounts for the great majority of atmospheric corrosion observed in everyday engineering situations, such as the familiar rusting of iron and steel structures exposed to humid air, since most natural environments contain both moisture and dissolved atmospheric oxygen.

4. Factors Affecting the Rate of Corrosion

The rate at which corrosion proceeds on a given metal surface is influenced by a number of factors, related both to the nature of the metal itself and to the surrounding environment. The most important of these factors are summarised below:

Factor	Effect on Rate of Corrosion
Nature of the Metal	Highly reactive metals (with a strong tendency to lose electrons) generally corrode more readily than less reactive, noble metals; the position of the metal in the electrochemical (reactivity) series is a good general indicator of its susceptibility to corrosion.
Presence of Impurities in the Metal	Impurities present in a metal can set up tiny local galvanic cells on the metal surface (with the impurity and the base metal acting as electrodes of differing reactivity), significantly accelerating the rate of corrosion at these localised points.
Nature of the Corrosion Product Formed	If the oxide (or other corrosion product) layer formed is continuous, adherent, and impervious, it can protect the underlying metal from further attack, slowing corrosion; if the layer formed is porous, loose, or flaky (as with ordinary rust on iron), it fails to protect the metal, and corrosion continues progressively.
Presence of Moisture, Humidity, and Electrolytes	Higher atmospheric humidity and the presence of dissolved salts or acidic/alkaline pollutants in moisture on the metal surface increase the electrical conductivity of the surface film, promoting electrochemical corrosion and increasing its rate.
Temperature	An increase in temperature generally increases the rate of the electrochemical reactions responsible for corrosion, and can also increase the rate of diffusion of reactants and products, thereby generally accelerating the rate of corrosion.
pH of the Environment	Strongly acidic or, in certain cases, strongly alkaline environments generally accelerate corrosion, since they provide a more electrochemically active medium and, in acidic conditions particularly, promote the hydrogen evolution mechanism of corrosion.
Presence of Atmospheric Pollutants	Pollutant gases such as sulphur dioxide and industrial fumes can dissolve in atmospheric moisture to form acidic solutions on metal surfaces, significantly increasing the rate of corrosion in polluted or industrial environments.

5. Internal Corrosion Preventive Measures

Internal corrosion prevention methods involve modifying the composition or internal condition of the metal itself, in order to reduce its inherent susceptibility to corrosion.

5.1 Purification

Since impurities present within a metal often set up localised galvanic cells that accelerate corrosion, purifying the metal to reduce the level of such impurities is an effective method

of reducing its overall susceptibility to corrosion, since a purer metal presents a more uniform surface with fewer sites for localised electrochemical attack.

5.2 Alloying

Alloying involves deliberately combining a base metal with other selected elements to form an alloy with improved corrosion resistance, compared to the pure base metal. A well-known example is the addition of chromium (and nickel) to iron to produce stainless steel, in which the chromium forms a thin, tough, and continuously self-repairing protective oxide film on the surface of the alloy, significantly improving its resistance to corrosion compared to ordinary iron or mild steel.

5.3 Heat Treatment

Heat treatment processes, such as annealing, can be used to relieve internal stresses that develop within a metal during manufacturing processes such as casting, forging, welding, or cold working. Since regions of internal stress within a metal often behave as more anodic (reactive) sites and can promote localised corrosion, relieving these stresses through appropriate heat treatment can significantly reduce the tendency of the metal towards such localised corrosive attack.

6. External Corrosion Preventive Measures

6.1 Metal Coatings — Anodic and Cathodic Coatings

One of the most widely used external methods of corrosion prevention is to apply a protective coating of a different metal over the surface of the base metal to be protected. Depending on the relative reactivity of the coating metal compared to the base metal, such coatings are classified as anodic or cathodic coatings:

Type of Metal Coating	Description	Example
Anodic Coating	A coating of a more reactive (more anodic) metal applied over the base metal to be protected; the coating metal, being more reactive, preferentially corrodes (sacrifices itself) in place of the base metal, even if the coating layer becomes scratched or damaged, continuing to protect the exposed base metal	Galvanising — coating iron or steel with a layer of zinc, which corrodes preferentially, protecting the underlying iron even where the zinc layer is scratched
Cathodic Coating	A coating of a less reactive (more cathodic, more noble) metal applied over the base metal; the coating metal itself resists corrosion effectively and protects the base	Tinning — coating steel (as in tin cans) with a layer of tin, which resists corrosion effectively, but once

	metal only as long as the coating remains continuous and undamaged, but corrosion of the exposed base metal is often accelerated at any point where the coating is scratched or broken	scratched, the exposed steel corrodes more rapidly than if left uncoated

Because of this important difference, anodic coatings (such as galvanising) are generally preferred for protecting structural components that may be susceptible to scratches or minor surface damage during service, since they continue to provide effective protection even when locally damaged, unlike cathodic coatings, which can actually accelerate localised corrosion once breached.

6.2 Organic Inhibitors

Organic inhibitors are chemical substances which, when added in small quantities to a corrosive environment (such as an acidic pickling solution, or as a component of a protective paint or coating), adsorb onto the surface of a metal and form a thin, protective barrier film. This adsorbed film suppresses the rate of the anodic or cathodic reactions responsible for corrosion (or both), thereby significantly reducing the overall rate of corrosion of the metal in contact with the treated environment.

Organic inhibitors are commonly used in applications such as acid pickling of metals (to remove scale without excessively attacking the underlying metal), in cooling water systems, in oil and gas pipelines, and as additives incorporated into protective paints and coatings applied to metal structures.

7. Multiple Choice Questions (MCQs)

Answer the following questions by selecting the most appropriate option.

1. Corrosion is best defined as:

A) The intentional coating of a metal for decoration
B) The gradual destruction (deterioration) of a metal due to chemical or electrochemical reaction with its environment
C) The mechanical wear of a metal due to friction
D) The melting of a metal at high temperature

2. Chemical (dry) corrosion occurs mainly through:

A) Direct reaction of a metal with dry gases in the atmosphere, without moisture
B) Formation of galvanic cells in the presence of moisture
C) Mechanical abrasion of the metal surface
D) Reaction with liquid water only

3. Electrochemical (wet) corrosion occurs mainly through:

A) Direct reaction with dry gases only

B) The setting up of tiny galvanic cells on a metal surface in the presence of moisture

C) Complete absence of any electrolyte

D) Mechanical stress alone

4. The hydrogen evolution mechanism of electrochemical corrosion typically occurs in:

A) Neutral, oxygenated environments

B) Acidic, oxygen-free environments

C) Strongly basic environments only

D) Completely dry environments

5. In the hydrogen evolution mechanism, hydrogen gas is liberated at the:

A) Anodic region

B) Cathodic region

C) Neither electrode

D) Only in the electrolyte, away from both electrodes

6. The oxygen absorption mechanism of electrochemical corrosion is the most common cause of:

A) Corrosion of metals in strongly acidic, oxygen-free solutions

B) Rusting of iron exposed to moist, aerated air

C) Dry oxidation of metals at very high temperatures only

D) Corrosion in a complete vacuum

7. In the oxygen absorption mechanism, hydroxide ions are formed at the:

A) Anodic region

B) Cathodic region

C) Neither electrode

D) Only outside the metal surface

8. Which of the following factors generally increases the rate of corrosion of a metal?

A) Formation of a continuous, protective oxide film

B) Presence of impurities that set up local galvanic cells

C) Complete absence of moisture

D) Very low humidity

9. Purification of a metal, as an internal corrosion prevention measure, helps mainly by:

A) Increasing the number of impurities present

B) Reducing impurities that would otherwise form local galvanic cells and accelerate corrosion

C) Making the metal more reactive

D) Increasing the moisture content of the metal

10. Alloying, as an internal corrosion prevention measure, helps mainly by:

A) Increasing the reactivity of the base metal

B) Improving corrosion resistance, as seen in the addition of chromium to make stainless steel

C) Removing all metal atoms from the surface

D) Making the metal magnetic

11. Heat treatment, as an internal corrosion prevention measure, helps mainly by:

A) Relieving internal stresses in the metal that would otherwise promote localised corrosion

B) Increasing the porosity of the metal

C) Introducing more impurities into the metal

D) Reducing the strength of the metal only

12. Galvanising, the coating of iron with zinc, is an example of:

A) A cathodic coating

B) An anodic coating

C) An organic inhibitor

D) Alloying

13. In an anodic coating, if the coating layer becomes scratched, the underlying base metal is:

A) Corroded more rapidly than before

B) Still protected, since the more reactive coating metal continues to corrode preferentially

C) Immediately destroyed

D) Unaffected by the coating at all

14. Tinning, the coating of steel with tin (as in tin cans), is an example of:

A) An anodic coating

B) A cathodic coating

C) An organic inhibitor

D) Heat treatment

15. In a cathodic coating, if the coating layer becomes scratched, corrosion of the exposed base metal is generally:

A) Completely prevented

B) Accelerated, since a galvanic cell is set up with the more noble coating metal

C) Reduced to zero

D) Unaffected

16. Organic inhibitors used to prevent corrosion generally work by:

A) Increasing the rate of the anodic or cathodic reaction

B) Adsorbing onto the metal surface and forming a protective barrier film that suppresses the corrosion reaction

C) Dissolving the metal surface completely

D) Increasing the humidity around the metal

Answer Key

1. B) The gradual destruction (deterioration) of a metal due to chemical or electrochemical reaction with its environment | 2. A) Direct reaction of a metal with dry gases in the atmosphere, without moisture | 3. B) The setting up of tiny galvanic cells on a metal surface in the presence of moisture | 4. B) Acidic, oxygen-free environments | 5. B) Cathodic region | 6. B) Rusting of iron exposed to moist, aerated air | 7. B) Cathodic region | 8. B) Presence of impurities that set up local galvanic cells | 9. B) Reducing impurities that would otherwise form local galvanic cells and accelerate corrosion | 10. B) Improving corrosion resistance, as seen in the addition of chromium to make stainless steel | 11. A) Relieving internal stresses in the metal that would otherwise promote localised corrosion | 12. B) An anodic coating | 13. B) Still protected, since the more reactive coating metal continues to corrode preferentially | 14. B) A cathodic coating | 15. B) Accelerated, since a galvanic cell is set up with the more noble coating metal | 16. B) Adsorbing onto the metal surface and forming a protective barrier film that suppresses the corrosion reaction

8. Broad / Long Answer Questions

1. Define corrosion, and explain briefly why it is considered an economically significant problem in engineering.

2. Distinguish between chemical (dry) corrosion and electrochemical (wet) corrosion, giving one example of each.

3. Explain the hydrogen evolution mechanism of electrochemical corrosion, giving the relevant anodic and cathodic reactions.

4. Explain the oxygen absorption mechanism of electrochemical corrosion, giving the relevant anodic and cathodic reactions, and explain why this mechanism is responsible for the common rusting of iron.

5. Discuss any five factors that affect the rate of corrosion of a metal.

6. Explain purification, alloying, and heat treatment as internal methods of preventing (or reducing) the corrosion of a metal.

7. Explain the concept of metallic coatings as an external method of corrosion prevention, distinguishing between anodic and cathodic coatings.

8. Explain, with the example of galvanised iron, why an anodic coating continues to protect the base metal even after the coating is scratched or damaged.

9. Explain, with the example of tin-coated steel, why a cathodic coating can accelerate corrosion of the base metal once the coating is scratched or damaged.

10. Explain the use of organic inhibitors as an external method of corrosion prevention, describing briefly how they function to reduce the rate of corrosion.