ا لجمهورية الجزائرية الديمقراطية الشعبية

Democracy and Popular Power in Algeria

وزارة التعليم العالي والبحث العلمي

The Ministry of Higher Education and Scientific Research

جامعة الشادلي بن جديد الطارف

The Chadli Bendjedid El-Tarf University

كلية العلوم والتكنولوجيا

School of Technology and the Sciences

Process Engineering Department

Course organization and planning CORROSION

«For the sake of the students "LICENCE PROCESS ENGINEERING»

Course presented by:

Dr. HERBADJI ABDELMADJID

Academic Year 2025–2026

Planning for Corrosion

Executed within the framework of professional license training: Process engineering

Dr. HERBADJI Abdelmadjid

1. Details about the course

- *The establishment*
  - ✓ Chadli Bendjedid el Tarf University
  - ✓ Department of Process Engineering

- *Course Title: Corrosion*
  - ✓ Public target: third year Génie des Procédés, License
  - ✓ Credit : 01
  - ✓ The Coefficient : 01
- ✓ The teaching unit: Discovery
  - ✓ Duration: 15 weeks
  - ✓ Hourly: Sunday Class: 9:30–11:00
  - ✓ Classroom : 01

- *Lecturer*
  - ✓ Dr. HERBADJI Abdelmadjid
  - ✓ E–mail : a.herbadji@univ-eltarf.dz

- Availability at the Faculty Office:
  - ✓ Sunday: 11h00 - 14h00.
  - ✓ Tuesday : 10h00 - 14h00
  - ✓ Wednesday: 11h00 - 14h00.
  - ✓ *Response on the Moodle Forum:* Any question related to the course must be asked on the forum (Moodle) for the general benefit of your classmates. Response time: 24 to 48 hours.
  - ✓ *Response by Email*: No questions related to the course are allowed by email. You are only permitted to send the assignments/projects I have requested, or if you need advice and support on a personal or professional level. Response time: 24 to 48 hours.

2. Course Presentation

This course aims to develop solid skills in the field of metallic materials corrosion, with a focus on electrochemical mechanisms, types of corrosion, as well as various methods of prevention and protection. It prepares students to diagnose corrosion-related problems in various industrial environments and to propose effective solutions for the durability of installations.

This course is intended for 3rd year students in Process Engineering.

It enables them to :

- Understand the fundamental principles of corrosion
- Identify the forms of corrosion (uniform, localized, galvanic, stress corrosion cracking, etc.
- Master the use of Pourbaix diagrams and electrochemical tools for corrosion analysis,
- Recommend appropriate protection solutions: coatings, inhibitors, cathodic protection, selection of suitable materials
- Detect the causes of metallic degradation in specific environments such as industrial, marine, or acidic waters,

  Apply monitoring and preventive maintenance strategies.

The course also addresses the different contexts of corrosion applications (petrochemical industry, water treatment, construction, medical equipment, etc.) and the methods of adapting solutions according to the type of material, environment, and mechanical stress.

3. Course Content

The course is structured into three learning units, each addressing a fundamental aspect of corrosion. Each unit is developed through progressive teaching sequences, enabling students to assimilate key concepts and reinforce them through practical activities, case studies, and formative assessments.

Chapter I. Introduction to Metal Corrosion

This unit is dedicated to a general presentation of the corrosion phenomenon, emphasizing its industrial, economic, and environmental implications. It introduces the fundamental principles of electrochemistry applied to corrosion, including redox reactions and the role of the surrounding environment.

The unit then presents the necessary conditions for the initiation of corrosion, as well as the initial diagnostic tools used to detect its presence. Finally, a comparison between different types of corrosion (dry, wet, electrochemical) is provided to familiarize students with the diversity of mechanisms and contexts in which it may occur

Chapter II. Potential–pH Diagrams (Pourbaix Diagrams)

This unit is dedicated to a detailed presentation of potential–pH diagrams, also known as Pourbaix diagrams, which make it possible to predict the thermodynamic stability of metals in different environments.

The unit introduces the principles of constructing these diagrams, the regions of corrosion, immunity, and passivation, as well as their interpretation in the context of aqueous corrosion analysis. It is followed by a presentation of the most common metals (iron, aluminum, copper, zinc, etc.) with their characteristic diagrams and their behavior in acidic, neutral, or basic environments.

The unit concludes with a study of the limitations of using Pourbaix diagrams and their complementarity with kinetic data for a comprehensive assessment of corrosion risk

Chapter III. Methods of Protection against Corrosion

Corrosion protection is a strategic field that requires a thorough understanding of material degradation mechanisms. This unit is designed to train engineers capable of identifying and applying the most appropriate protection methods, depending on the type of corrosion, the material involved, and the exposure environment.

It presents the most common protection principles and techniques, including: protective coatings (organic, inorganic, metallic), corrosion inhibitors, cathodic and anodic protection, as well as the design and selection of resistant materials.

The unit also highlights strategies for adapting protection methods to specific industrial situations, whether for buried structures, marine environments, or closed systems subjected to high stresses.

4. Prerequisites

It is recommended that learners have basic knowledge in the following areas:

- General Chemistry and Electrochemistry
- Materials Science
- Chemical Thermodynamics
- These concepts are essential for understanding the electrochemical mechanisms underlying corrosion, the interpretation of Pourbaix diagrams, as well as the phenomena of material degradation.

To assess the students' level, review questions on these prerequisites will be asked at the beginning of the course or integrated into certain sessions in order to identify any gaps and adjust the pedagogical support according.

Targeted learning outcome

At the end of the course, the learner will be able to:

- **In terms of knowledge:**:

Understand the fundamental principles of electrochemical corrosion.

Identify the different types of corrosion (uniform, localized, galvanic, etc.).

Interpret a Pourbaix diagram to predict the regions of stability, immunity, and corrosion.

Know the appropriate protection methods according to the type of corrosion and the material.

Analyze the factors influencing corrosion in a given environment

- **In terms of skills:**

Use electrochemical tools to diagnose a case of corrosion.

Propose a prevention or treatment solution for corrosion in a real-world context.

Select an appropriate coating or protection technique.

- **In terms of attitudes and interpersonal skills :**

Adopt a rigorous approach to analysis and prevention.

Work in a multidisciplinary team to solve a corrosion-related problem.

Demonstrate critical thinking when evaluating techno-economic protection choices.

5. Assessment methods for learning outcomes

Within the framework of this introductory module, assessment is based solely on a final exam, which accounts for 100% of the final grade. No continuous assessment or practical work is planned.

Final Exam (100% of the grade):

The final exam covers all the concepts addressed during the course sessions. Its purpose is to evaluate the understanding of corrosion phenomena, the ability to interpret diagrams and concepts, as well as the aptitude to propose technical protection solutions.

It consists of two parts:

- **Case analysis (13 points)**
- The candidate will be required to solve a problem based on a real corrosion case. This involves identifying the type of corrosion, analyzing the influencing factors, and proposing an appropriate protection strategy.
- **Summary questions (7 points)**

  This section includes MCQs (Multiple Choice Questions) and SCQs (Single Choice Questions) designed to test theoretical knowledge of the key course concepts (types of corrosion, Pourbaix diagrams, protection methods, etc.).

6. Operational Procedures

The course is organized solely as theoretical sessions, aiming to provide students with essential knowledge related to the corrosion of metals, its mechanisms, types, and various protection methods.

The sessions are structured to allow a logical progression in learning, moving from basic concepts to more applied notions.

The course is conducted in person and can be complemented by educational resources available online through the distance learning platform. This platform allows students to:

- Access downloadable course materials.
- Review the concepts covered in class at their own pace.
- Ask questions or request clarifications through discussion forums.
- Reinforce their learning through optional supplementary activities provided by the instructor.

The training is therefore designed to promote autonomy, guided self-learning, and continuous contact with the instructor, even outside of class hours.

Course
PRESENTATION
Corrosion

Realized within the framework of professional license training: process engineering

Dr. HERBADJI Abdelmadjid

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CHAPTER I

This chapter provides several definitions and fundamental concepts aimed at giving the student a preliminary understanding of the classes and types, from a morphological perspective, of metal corrosion as well as its economic implications.

I. CHAPTER I: INTRODUCTION TO THE CORROSION

I.1 Introduction

Corrosion is a natural phenomenon known since Antiquity, but its scientific understanding has gradually developed over the centuries. As early as the Roman era, the deterioration of metals exposed to water and air, particularly iron and copper, was observed. However, the explanations of that time were rudimentary and often attributed to mysterious or divine forces.

The scientific study of corrosion truly began with the rise of chemistry and electrochemistry in the 18th and 19th centuries. One of the first to identify the electrochemical mechanisms of corrosion was Humphry Davy (1778–1829), who highlighted the role of electricity in the degradation of metals. He developed cathodic protection, which is still used today to protect ships and pipelines.

Later, Michael Faraday (1791–1867) further advanced this work by demonstrating the relationship between corrosion and electrochemical reactions. He established the foundations of the laws of electrolysis, which are essential for understanding metallic corrosion.

In the 20th century, with the development of industry and metallurgy, research on corrosion took on a more applied dimension. Scientists identified different types of corrosion (uniform, galvanic, pitting, and stress-related, etc.) and developed prevention methods, such as protective coatings and resistant alloys.

Today, corrosion is a crucial field of study in engineering, chemistry, and materials science, as it has major economic and safety impacts, particularly in the oil, aerospace, and maritime industries.

In recent decades, the field of corrosion has undergone significant technological progress thanks to the emergence of advanced characterization techniques. Tools such as scanning electron microscopy (SEM), atomic force microscopy (AFM), and electrochemical impedance spectroscopy (EIS) have enabled researchers to observe corrosion processes at the microscopic and even nanometric scale. These methods have improved the understanding of localized corrosion phenomena and facilitated the development of innovative protective materials, including smart coatings capable of self-healing. As a result, corrosion science has transitioned from a primarily empirical discipline to a highly sophisticated field integrating materials science, surface engineering, and nanotechnology.

Beyond scientific and technological aspects, corrosion has also become a major economic and strategic concern worldwide. Studies estimate that corrosion-related damage represents between 3% and 4% of the global GDP each year, due to maintenance operations, material replacement, and industrial shutdowns. This economic burden has pushed governments and international organizations to establish strict standards for corrosion prevention and inspection, especially in critical sectors such as energy production, transportation, construction, and water treatment. As a result, corrosion management has evolved into a multidisciplinary practice that integrates material selection, design optimization, predictive modeling, and environmental control to ensure long-term safety and sustainability of infrastructures.

In recent years, environmental factors and climate change have increasingly influenced corrosion processes, making the phenomenon more complex and difficult to predict. Rising temperatures, increased humidity, higher CO_2 concentrations, and more frequent extreme weather events accelerate many types of corrosion, especially atmospheric and marine corrosion. Industrial emissions and pollutants such as sulfur oxides and nitrogen oxides further intensify metal degradation by forming acidic environments. As a response, researchers are developing predictive models that incorporate climatic data to anticipate corrosion rates in different regions, allowing industries and governments to adopt more effective long-term strategies for infrastructure durability.

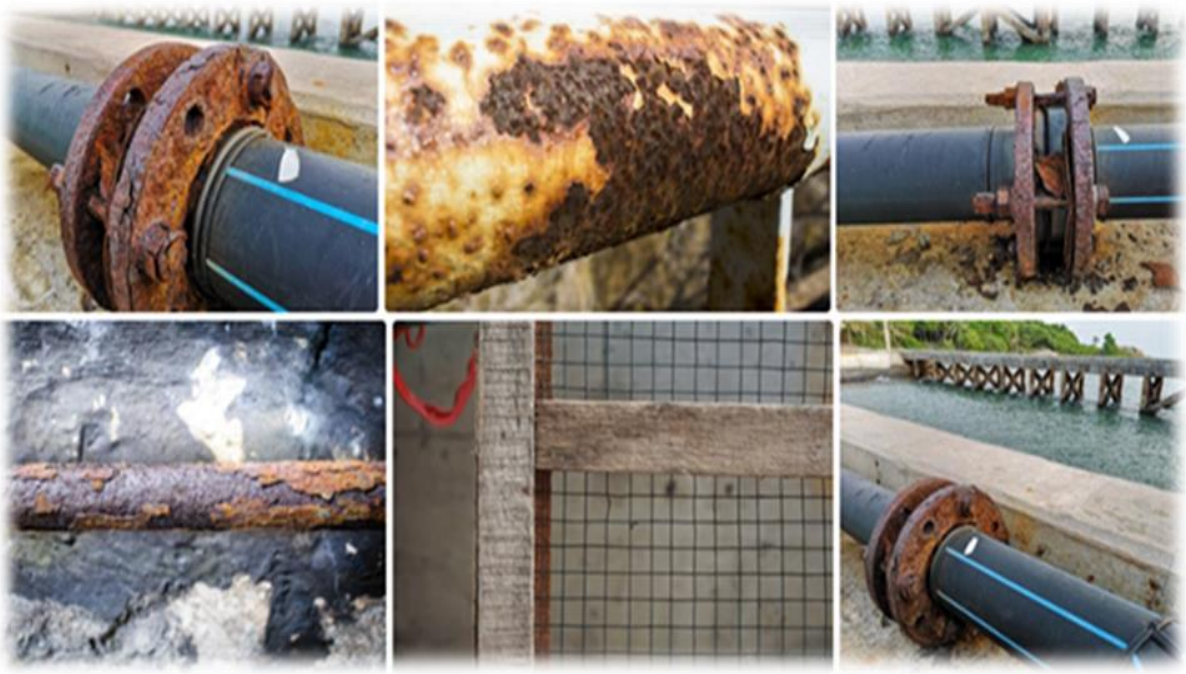


Figure I.1 : General Diagram of Corrosion

I.2 Importance of corrosion

The study of corrosion makes it possible to extend the service life of industrial equipment, improve the safety of infrastructures, and reduce costs related to material failures. It plays an essential role in fields as diverse as automotive, construction, aerospace, and medicine, where material resistance is a crucial issue.

Moreover, understanding corrosion mechanisms enables engineers to design more durable and efficient systems by selecting appropriate materials, optimizing surface treatments, and implementing advanced protection strategies such as cathodic protection or smart coatings. This proactive approach not only enhances reliability and performance but also supports sustainable development by minimizing waste, reducing the need for resource-intensive replacements, and preventing catastrophic failures that could threaten human life and the environment. As industries continue to evolve toward higher technological complexity, the importance of corrosion science becomes increasingly central to innovation and long-term infrastructure resilience.

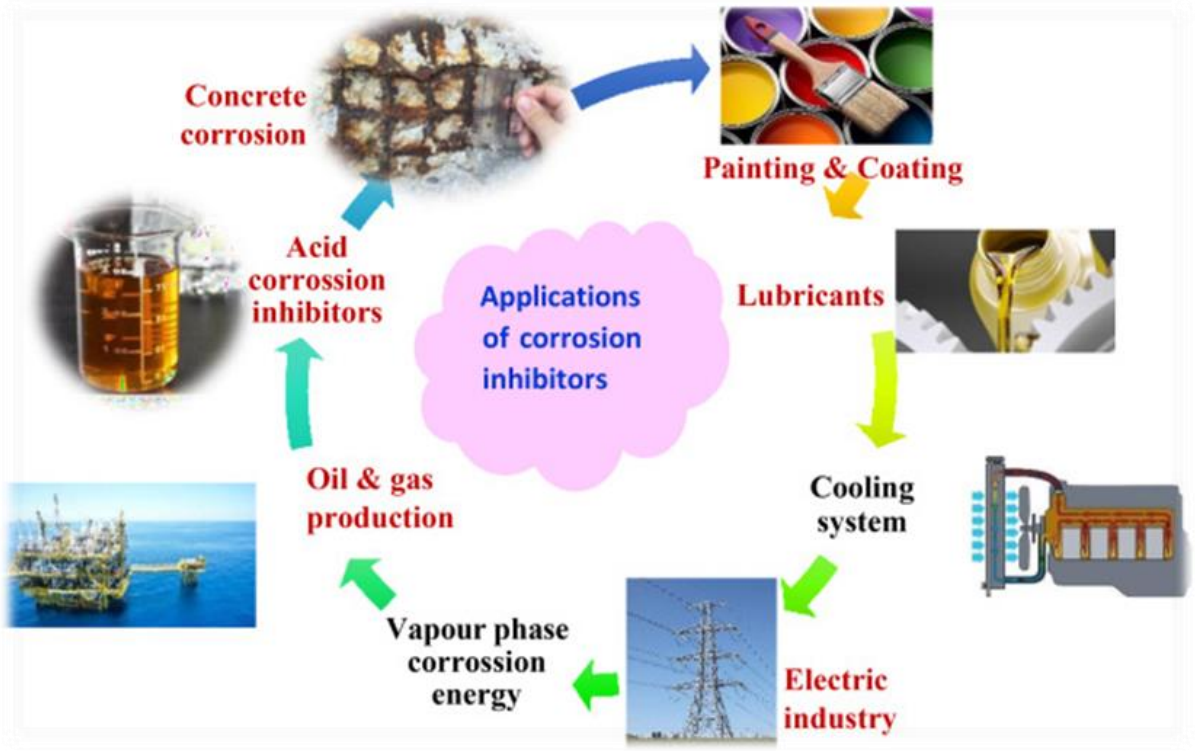


Figure I.2 : The importance of studying corrosion, its industrial impact, and prevention methods.

I.3 Definition of corrosion

Corrosion is a process of material degradation, mainly of metals, caused by chemical or electrochemical reactions with their environment. It leads to the formation of compounds such as oxides, hydroxides, or salts, thereby reducing the strength and durability of metallic structures.

Common metals tend to return to their initial energy state, and this occurs with the help of the surrounding environment.

Corrosion refers to the process by which metals and alloys naturally tend to return to more stable chemical forms such as oxides, sulfides, carbonates, or various other salts depending on the surrounding environmental conditions. This phenomenon reflects the thermodynamic tendency of metallic materials to move toward a lower-energy state, often similar to that of their original mineral ores. The study of corrosion and the associated protection methods also includes degradation mechanisms resulting from the simultaneous action of chemical agents and mechanical stresses, as observed in stress-corrosion cracking or corrosion fatigue. In certain contexts, corrosion is not merely unavoidable but may even be beneficial. For instance, it contributes to the natural breakdown of abandoned metallic objects in the environment.

Many industrial processes also rely on mechanisms analogous to natural corrosion. A typical example is the anodizing of aluminum, an electrochemical treatment designed to create a controlled oxide layer that is both protective and aesthetically appealing. Similarly, chemical and electrochemical polishing exploit superficial metal dissolution to produce a smooth, homogeneous, and glossy surface finish. These examples highlight that corrosion is not solely a destructive phenomenon; it can also serve as a valuable technological tool.

Therefore, a broader definition of corrosion can be proposed: it is an irreversible reaction occurring at the interface between a material and its environment, leading either to a loss of substance or to the incorporation of an external species into the material. Such a definition includes both the potentially beneficial aspects of certain corrosion processes and the mechanisms that do not necessarily involve visible dissolution, such as hydrogen absorption in steels, which is classified as a corrosion phenomenon due to its detrimental effects on mechanical properties.

To counteract corrosion, several strategies can be implemented. These may involve modifying the material itself (through the use of corrosion-resistant alloys), acting on the material's surface (via protective coatings, passivation, or heat treatments), or controlling the surrounding environment by reducing acidity, humidity, or the concentration of corrosive agents.

The choice of protection method depends on the type of corrosion encountered, the service conditions, and the durability requirements of the application.

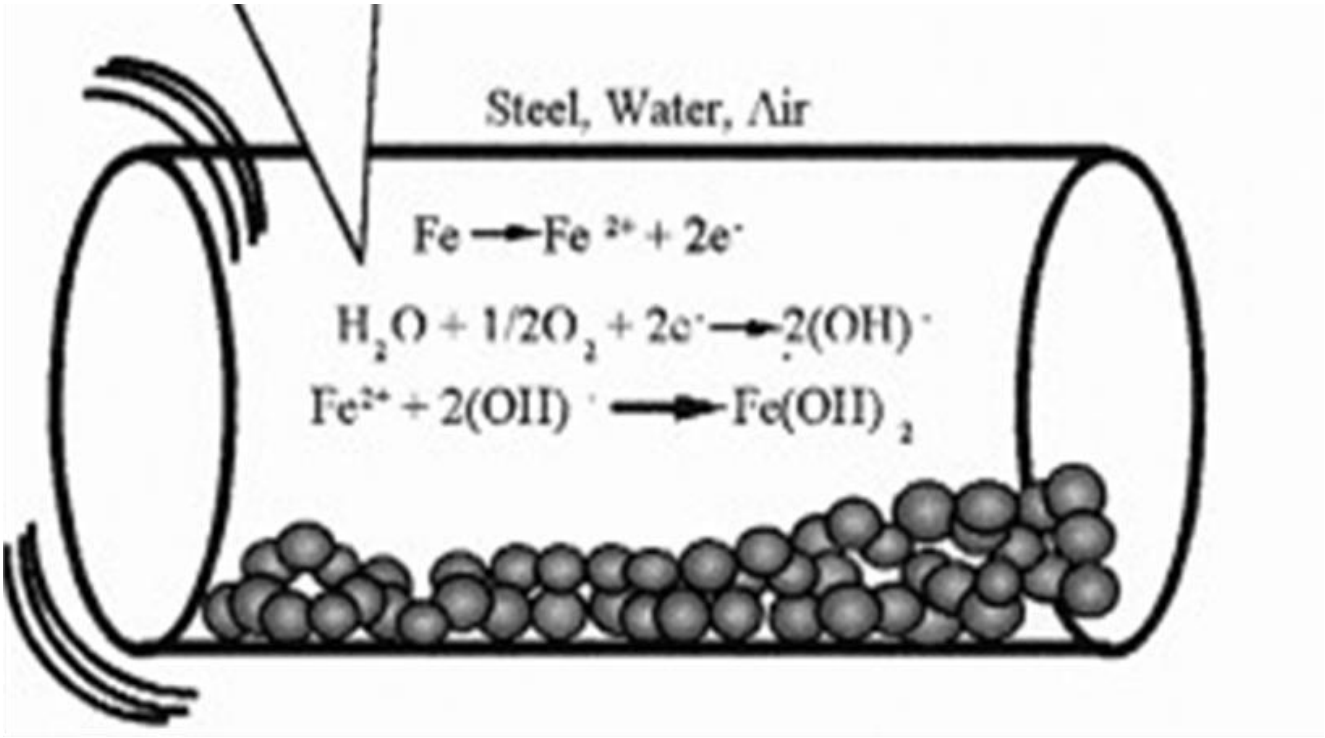


Figure I.3 : Process of Material Degradation.

I.4 The Main Causes of Corrosion:

The main causes of corrosion are:

- **Electrochemical Reactions:**

  Electrochemical reactions constitute the fundamental mechanism of metallic corrosion when a metal is exposed to an electrolyte such as water, humidity, or an ion-containing solution. In these conditions, the metal surface develops anodic and cathodic regions, creating a natural electrochemical cell. At the anodic sites, the metal undergoes oxidation by releasing electrons, leading to the formation of metal ions that dissolve into the electrolyte. Simultaneously, at the cathodic sites, these electrons are consumed by reduction reactions most commonly the reduction of dissolved oxygen in the presence of water, producing hydroxide ions. The electrolyte ensures ionic conduction between the two regions, allowing the electrochemical circuit to remain active. The presence of salts or pollutants increases conductivity and accelerates corrosion. Oxygen availability also influences the rate, as oxygen-rich areas promote faster cathodic reactions. Together, the interaction between the metal, the electrolyte, and oxygen drives the overall corrosion process and determines its intensity.

- **The existence of moisture**

  The presence of moisture is a key factor in the corrosion of metals. Water, even in small amounts such as humidity, acts as an electrolyte that facilitates the transfer of ions between anodic and cathodic sites on the metal surface. In salty or polluted environments, moisture becomes highly conductive, which accelerates the electrochemical reactions. Moisture promotes oxidation of metals, leading to the formation of oxides, hydroxides, or other corrosion products. Areas with differential moisture levels can create localized corrosion, such as pitting. In addition, water can dissolve gases like oxygen and carbon dioxide, which further contribute to the corrosion process. Controlling moisture exposure is therefore essential for minimizing metallic degradation. Protective coatings, dehumidification, and proper drainage are common strategies used to limit the impact of moisture on metals.

- **Atmospheric Pollutants:**

  Gaseous pollutants in the atmosphere significantly influence the rate of metal corrosion. Compounds such as sulfur dioxide (SO_2), nitrogen oxides (NO_x), and carbon dioxide (CO_2) dissolve in moisture to form acidic solutions on the metal surface. These acids accelerate the oxidation of metals and increase the conductivity of the electrolyte, intensifying electrochemical reactions. Pollutants can also create localized corrosion by forming concentrated acidic spots. Industrial and urban environments with high pollution levels often experience faster degradation of exposed structures. Controlling exposure to atmospheric pollutants, along with protective coatings, is crucial to limit corrosion and extend the service life of metallic materials.

- **Difference in Electric Potential:**

  A difference in electric potential between two dissimilar metals in contact can lead to galvanic corrosion. When these metals are connected through an electrolyte, the metal with the lower electric potential acts as the anode and corrodes faster, while the metal with the higher potential serves as the cathode and is protected. The rate of galvanic corrosion depends on factors such as the potential difference, the area ratio of the metals, and the conductivity of the electrolyte. This phenomenon is commonly observed in systems combining steel with copper, aluminum, or zinc. Proper material selection, insulation between metals, and the use of protective coatings can minimize the effects of galvanic corrosion and prolong the lifespan of metal structures.

- **High Temperature:**

  High temperatures accelerate the rate of chemical and electrochemical reactions on metal surfaces, increasing the likelihood of corrosion. Elevated heat promotes faster oxidation of metals, leading to the formation of oxides, scales, or other corrosion products. In addition, high temperatures can change the properties of protective films or coatings, reducing their effectiveness. Certain environments, such as industrial furnaces or engine components, are particularly susceptible to temperature-induced corrosion. Controlling operating temperatures, using heat-resistant alloys, and applying suitable surface treatments are essential strategies to limit corrosion in high-temperature conditions.

- **Mechanical Stresses:**

  Mechanical stresses can significantly influence the corrosion behavior of metals. When a material is subjected to tensile, compressive, or cyclic stresses, it becomes more susceptible to stress corrosion cracking. This phenomenon occurs when the combined effect of mechanical stress and a corrosive environment leads to the formation of cracks, which can propagate rapidly and weaken the material. Areas with pre-existing defects or surface irregularities are particularly vulnerable. Stress corrosion is common in pipelines, pressure vessels, and structural components under load. Reducing applied stresses, using stress-resistant alloys, and implementing protective coatings are effective strategies to minimize corrosion caused by mechanical stresses.

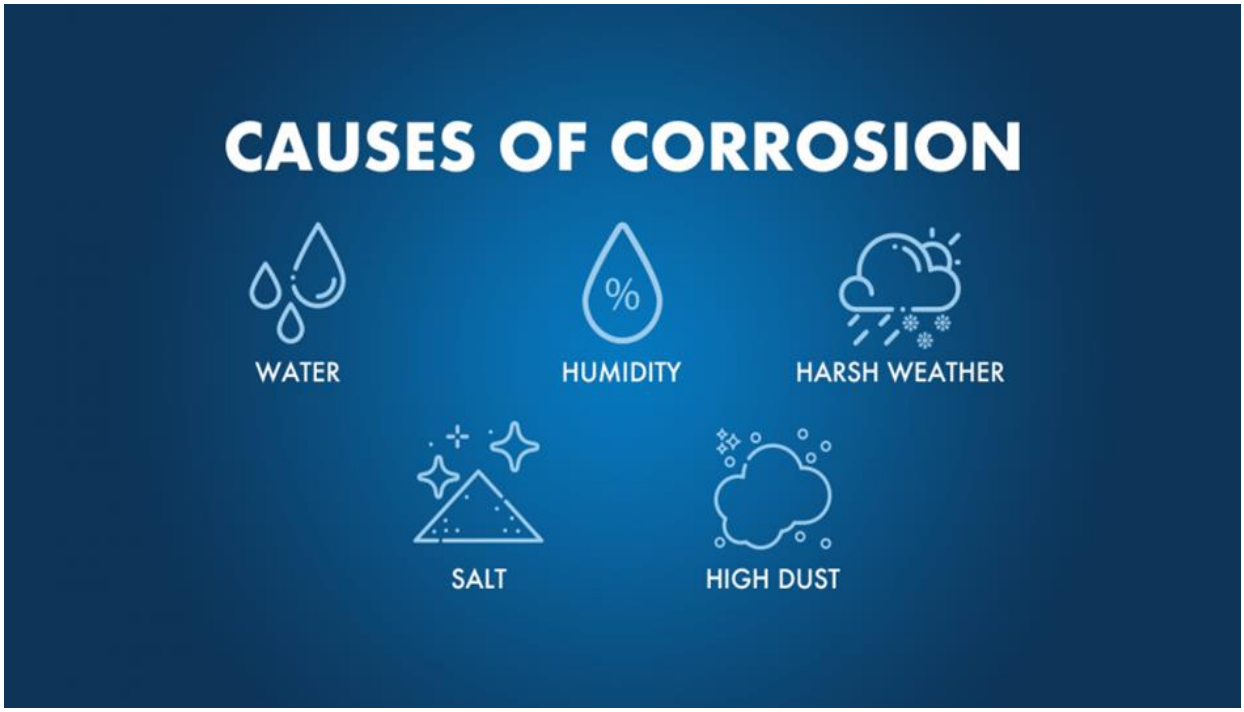


Figure I.4 : The Different Causes of Corrosion

I.5 Different Types of Corrosion

Corrosion is a natural phenomenon that affects metals and alloys, leading to their gradual degradation over time. Its occurrence and severity largely depend on the nature of the surrounding environment and the way the material interacts with it. Understanding the different types of corrosion is essential for selecting appropriate materials, designing effective protection strategies, and ensuring the durability of structures and equipment. Broadly, corrosion can be classified into three main categories:

- Electrochemical (wet) corrosion
- Chemical (dry) corrosion
- Bacterial corrosion

I.5.1 Electrochemical Corrosion

Electrochemical corrosion, also referred to as wet corrosion, is a common phenomenon of material degradation, particularly affecting metals, that occurs in the presence of an electrolyte such as water, saline solutions, or other ion-containing liquids. This type of corrosion is driven by electrochemical reactions taking place on the metal surface, where electrons are transferred between anodic and cathodic regions. The process creates a natural electrochemical cell, with distinct sites on the metal acting as anodes and cathodes.

At the anodic sites, the metal undergoes oxidation, losing electrons and forming metal ions that dissolve into the surrounding electrolyte. This reaction leads to a gradual loss of material and is often the primary cause of structural weakening. Meanwhile, at the cathodic sites, these electrons are consumed by reduction reactions, typically involving oxygen or other oxidizing agents present in the environment. The most common cathodic reaction in natural conditions is the reduction of dissolved oxygen in water, which produces hydroxide ions.

The overall corrosion rate depends on several factors, including the conductivity of the electrolyte, temperature, oxygen availability, and the presence of contaminants such as salts or acids. Electrochemical corrosion can manifest in various forms, including uniform corrosion, galvanic corrosion between dissimilar metals, crevice corrosion, and pitting corrosion, each with specific characteristics and localized effects.

Understanding these mechanisms is essential for predicting corrosion behavior, selecting resistant materials, and implementing effective protection strategies such as cathodic protection,

coatings, or inhibitors, which are widely used to prolong the service life of metallic structures in wet environments.

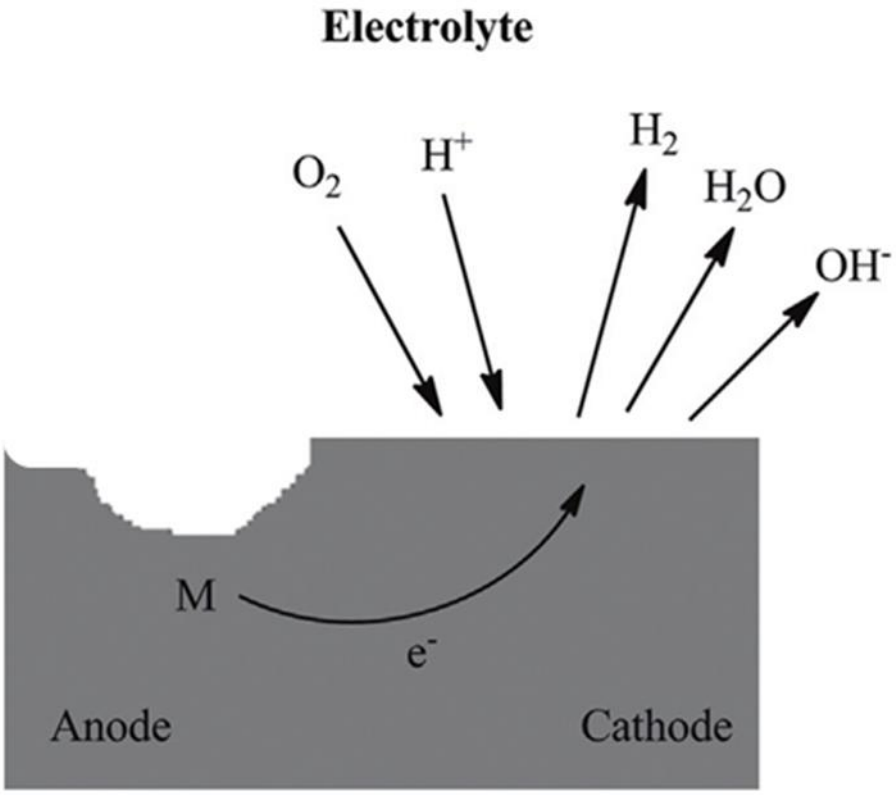


Figure I.5 : Electrochemical Corrosion

I.5.1.1 Types of Electrochemical Corrosion

Electrochemical corrosion is a natural and gradual process that damages metals through chemical and electrochemical reactions with their surrounding environment. The rate and severity of corrosion depend on many factors, including the type of metal, the presence of water or chemicals, temperature, and other environmental conditions. While some corrosion occurs slowly and uniformly across the entire surface, other forms may develop in specific areas, causing weak points that can lead to serious structural problems. Understanding how corrosion occurs and progresses is essential for predicting metal performance, planning maintenance, and applying effective protection strategies. These strategies can include protective coatings, the use of corrosion-resistant materials, or other engineering solutions designed to slow or prevent metal deterioration. By carefully studying corrosion, engineers and scientists can extend the service life of metal structures, reduce repair and replacement costs, and ensure the safety and reliability of industrial and everyday applications.

1. General (Uniform) Corrosion:

Generalized, or uniform, corrosion is a type of electrochemical corrosion that affects the entire exposed surface of a metal in a fairly homogeneous and consistent manner. Unlike localized forms of corrosion such as pitting or crevice corrosion, uniform corrosion progresses evenly across the metal surface, resulting in a gradual and predictable loss of material over time. This type of corrosion is considered one of the most common and most easily anticipated forms of metal degradation, making it particularly important for engineers and maintenance professionals to monitor and control. The rate of uniform corrosion depends on several environmental factors, including the presence and composition of electrolytes, temperature, oxygen concentration, and the chemical nature of the metal itself. Protective measures, such as applying coatings, selecting corrosion-resistant alloys, or using inhibitors in the environment, are generally effective in reducing the impact of uniform corrosion. Because it affects the whole surface consistently, uniform corrosion allows for more straightforward calculations of material loss and service life, making it possible to design preventive strategies and maintenance schedules efficiently. Despite being less dramatic than localized corrosion, generalized corrosion can still lead to significant thinning of metal components over long periods, potentially compromising structural integrity if not properly managed. Understanding this type of corrosion is fundamental for industries such as construction, maritime, pipelines, and manufacturing, where long-term durability and reliability of metallic structures are essential.

❖ Galvanic Corrosion :

Galvanic corrosion is a type of corrosion that occurs when two different metals are in electrical contact within an electrolytic environment (water, humidity, saline solutions, etc.). One of the metals (anode) corrodes faster than it would if it were alone, while the other (cathode) is protected. (It results from the contact between two metals with different electrochemical potentials).

This type of corrosion is commonly observed in systems combining metals such as steel and copper, aluminum and zinc, or other dissimilar pairs. The rate of galvanic corrosion depends on several factors, including the potential difference between the metals, the ratio of cathode to anode surface areas, and the conductivity of the electrolyte. Proper material selection and design are crucial to minimize galvanic interactions.

To prevent galvanic corrosion, engineers often use insulating materials between the metals, apply protective coatings, or employ cathodic protection techniques. Awareness of the environment, such as avoiding prolonged exposure to saline or humid conditions, also helps

reduce the risk. Understanding galvanic corrosion is essential in industries like maritime, construction, and pipelines, where different metals are frequently used together.

Figure I.6 : Electrochemical Corrosion (Galvanic Corrosion)

2. Localized Corrosion :

Localized corrosion is a type of electrochemical corrosion that affects specific areas of a metal surface, rather than spreading uniformly as in generalized corrosion. This form of corrosion is particularly dangerous because it can create deep pits, cracks, or crevices, which significantly weaken the material and may lead to sudden and catastrophic failure. The initiation of localized corrosion often occurs at points of heterogeneity on the metal surface, such as scratches, inclusions, welds, or areas with deposits and crevices where the electrolyte becomes stagnant.

❖ Stress Corrosion Cracking (SCC):

Stress corrosion cracking (SCC) is a type of localized corrosion that occurs when a material is simultaneously exposed to a corrosive environment and mechanical stress.

This combination accelerates the initiation and propagation of cracks on the metal surface, which can lead to sudden and catastrophic failure even when the applied loads are below the material's normal strength limits. SCC is particularly insidious because it often develops

without significant visible corrosion or material loss, making early detection challenging. The phenomenon is influenced by several factors, including the type of metal or alloy, the nature and concentration of corrosive agents, temperature, and the magnitude and distribution of mechanical stress.

Common metals susceptible to SCC include stainless steels, high-strength aluminum alloys, and certain nickel-based alloys, especially when exposed to chlorides, hydroxides, or other aggressive ions. Cracks typically initiate at microscopic defects, grain boundaries, or stress concentrators such as welds or notches, and can propagate rapidly under sustained stress. Preventing SCC requires a combination of strategies: reducing residual and applied stresses through proper design or heat treatment, selecting corrosion-resistant materials, controlling environmental factors (e.g., removing chloride ions), and applying protective coatings or inhibitors. Understanding SCC is critical in industries such as chemical processing, oil and gas, nuclear power, and aerospace, where undetected cracks can compromise safety and result in severe economic and operational consequences.

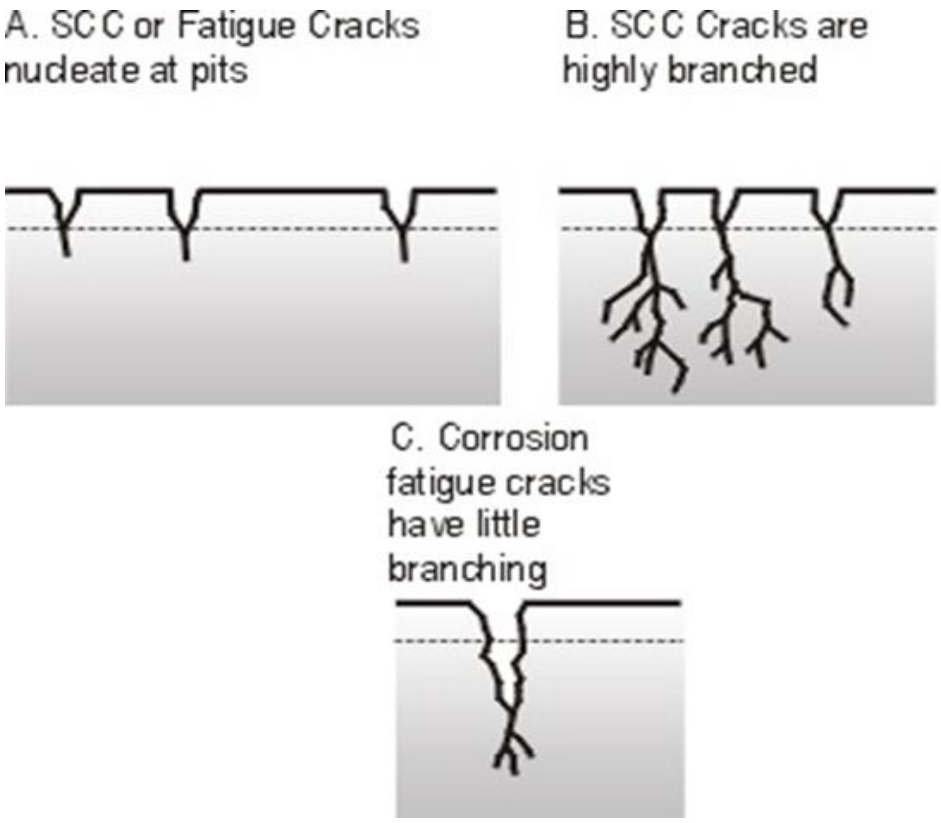


Figure I.7 : Stress Corrosion Cracking (SCC)

❖ Intergranular Corrosion :

Intergranular corrosion is a localized form of corrosion that occurs along the grain boundaries of a metal or alloy, rather than uniformly across its surface. This type of corrosion is often associated with metals that have been improperly heat-treated or welded, leading to the formation of precipitates at the grain boundaries that are more susceptible to chemical attack. As a result, the metal may appear relatively intact on the surface while the internal structure is significantly weakened, creating hidden risks of mechanical failure. Commonly affected materials include stainless steels, aluminum alloys, and nickel-based alloys, particularly when exposed to corrosive environments such as chlorides or acidic solutions. The progression of intergranular corrosion can compromise the ductility and toughness of the material, making it prone to cracking under normal loads. Detection of IGC requires careful inspection techniques, such as metallographic analysis or non-destructive testing, since visible signs may be minimal. Preventive measures include proper heat treatment to avoid sensitization, the use of stabilized or low-carbon alloys, and the application of protective coatings or inhibitors. Understanding intergranular corrosion is essential in industries such as aerospace, nuclear power, and chemical processing, where structural integrity and long-term reliability are critical.

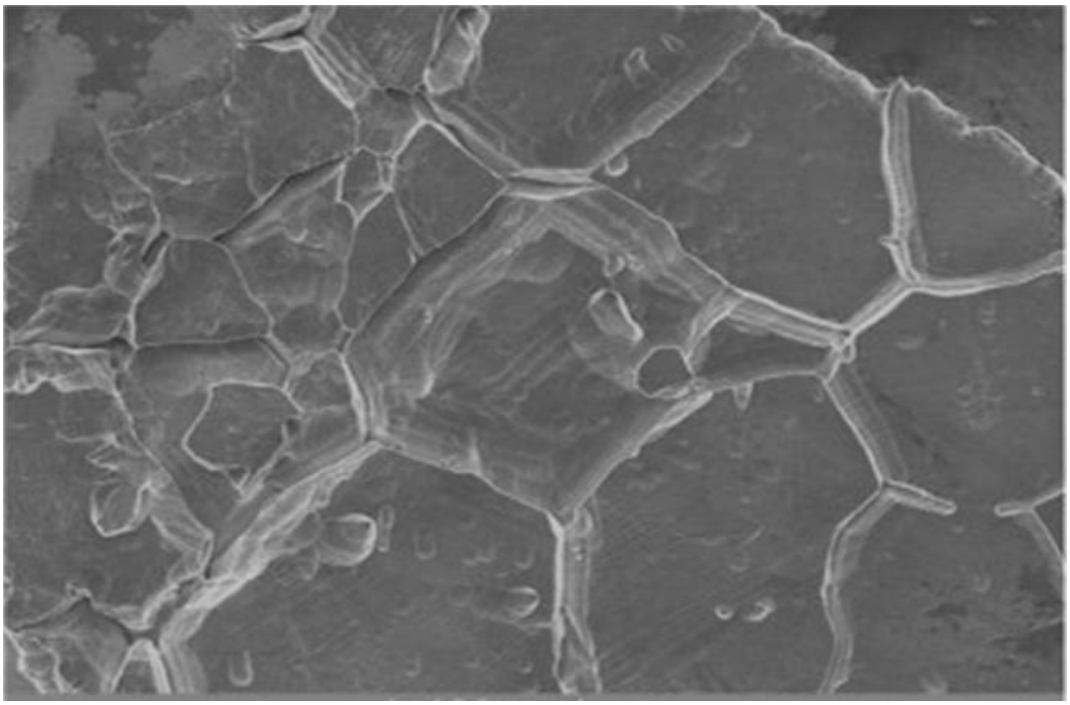


Figure I.8 : Intergranular Corrosion

❖ Pitting Corrosion:

Pitting corrosion is a form of localized corrosion that leads to the formation of small holes, known as pits, on the surface of a metal. Unlike uniform corrosion, which gradually affects the entire surface, pitting is highly localized, which makes it particularly dangerous. The pits can penetrate deeply into the material while the surrounding surface appears almost unaffected, making early detection difficult and increasing the risk of This type of corrosion often occurs in metals exposed to aggressive environments, especially in the presence of chloride ions, such as in seawater or saline industrial solutions. Pitting typically initiates at points of heterogeneity on the metal surface, including scratches, inclusions, or defects in protective coatings. Once a pit forms, it can create a microenvironment that further accelerates corrosion, leading to rapid growth and deep penetration.unexpected structural failure. Preventive measures include selecting alloys that are resistant to pitting, applying high-quality protective coatings, and controlling environmental factors such as chloride concentration. Regular inspections using non-destructive testing methods, such as ultrasonic testing or radiography, are also essential to identify pits before they compromise the structural integrity of the metal. Understanding pitting corrosion is critical in industries such as marine engineering, chemical processing, pipelines, and infrastructure, where even small, localized damage can lead to significant economic and safety consequences.

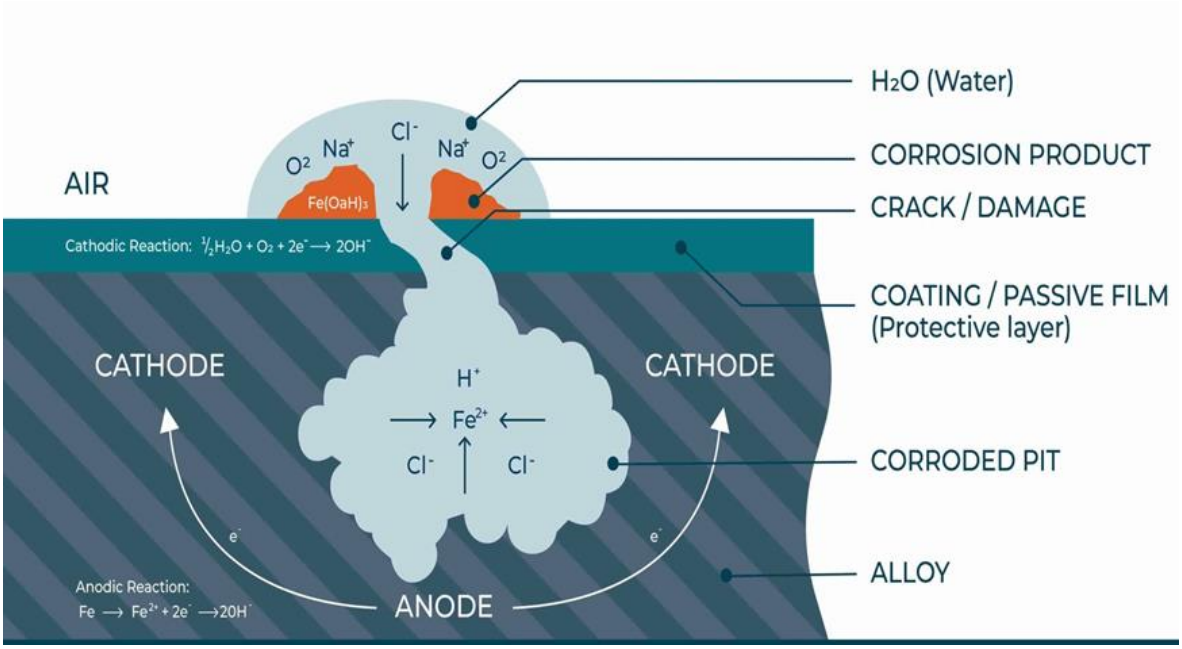


Figure I.9 : Pitting Corrosion

❖ Crevice Corrosion

Crevice corrosion is a localized electrochemical corrosion that occurs inside narrow, confined spaces where a stagnant electrolyte becomes trapped. These crevices can form under gaskets, washers, bolts, O-rings, lap joints, surface deposits, or between two contacting metal surfaces. Because the solution inside the crevice cannot freely exchange with the bulk environment, the internal chemistry changes and becomes highly aggressive.

The mechanism of crevice corrosion begins with oxygen depletion inside the crevice. As dissolved oxygen is consumed and cannot be replenished, the metal surface in the crevice loses its passive film. Metal ions then start to dissolve, and to maintain electroneutrality, chloride ions migrate into the crevice. This creates an environment that is acidic, chloride-rich, and highly corrosive. Once this stage is reached, corrosion becomes autocatalytic, meaning it accelerates rapidly and continues even if external conditions remain stable.

Crevice corrosion often affects stainless steels, aluminum alloys, titanium, and nickel-based alloys, especially in chloride-containing environments such as seawater or industrial process solutions. Materials that depend on a passive oxide film are particularly susceptible, because the crevice conditions destabilize passivity.

Several factors increase the risk of crevice corrosion: narrow crevice geometry, presence of chlorides, high temperature, low pH, and stagnant or poorly aerated conditions. Even very small crevices, sometimes only a few micrometers wide, can initiate attack.

Figure I.10: Crevice Corrosion

❖ Corrosion Fatigue

Corrosion fatigue is a combined damage mechanism that results from the interaction between cyclic mechanical loading and a corrosive environment. While metals can normally withstand repeated loading in air for a long time, their fatigue resistance decreases drastically when exposed to corrosive media such as seawater, acids, humidity, or industrial solutions. This synergy causes premature crack initiation and rapid crack propagation, leading to unexpected and often catastrophic failure.

The mechanism of corrosion fatigue involves two simultaneous processes. First, cyclic stress produces microscopic slip and deformation on the metal surface. This mechanical action weakens the protective passive film or coating, exposing fresh metal to the environment. Second, the corrosive medium attacks the newly exposed metal surfaces, forming small pits or dissolution zones. These pits act as stress concentrators that significantly accelerate crack initiation. Once cracks form, cyclic loading continues to open and close them, allowing corrosive agents to penetrate deeper, which speeds up crack growth. As a result, crack propagation in corrosion fatigue is much faster than in normal mechanical fatigue.

Corrosion fatigue affects a wide range of materials including carbon steels, stainless steels, aluminum alloys, titanium, and nickel-based alloys. It is especially critical in components subjected to fluctuating loads in harsh environments: offshore structures, pipelines, aircraft components, turbines, ships, bridges, and chemical processing equipment.

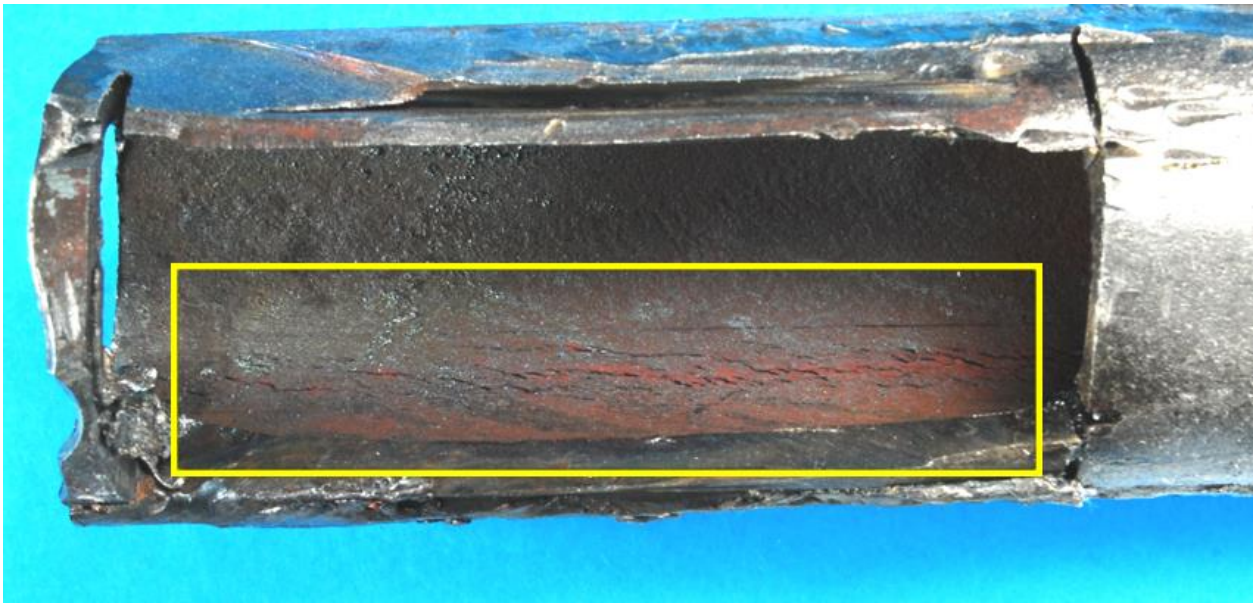


Figure I.11: Corrosion Fatigue

❖ Atmospheric Corrosion

Atmospheric corrosion is the electrochemical degradation of metals exposed to the air. It is the most common form of corrosion because almost all structures buildings, pipelines, vehicles, industrial equipment are in contact with the atmosphere. This type of corrosion occurs when a thin film of moisture, such as dew, rain, fog, or humidity condensation, forms on the metal surface, creating an electrolyte that enables electrochemical reactions.

The mechanism of atmospheric corrosion starts with the formation of an electrolyte layer containing dissolved oxygen, carbon dioxide, and airborne pollutants such as chloride ions (from marine environments) or sulfur dioxide (from industrial emissions). These species lower the pH and increase the conductivity of the moisture film. The metal surface becomes divided into anodic and cathodic areas, leading to localized oxidation of the metal at the anode and oxygen reduction at the cathode. Over time, this process produces corrosion products such as rust on steel or oxide layers on other metals.

Figure I.12: Atmospheric Corrosion

❖ Erosion Corrosion

Erosion corrosion is a synergistic damage mechanism that occurs when corrosive attack is combined with mechanical erosion caused by the relative motion of a fluid against a metal surface. Neither erosion nor corrosion alone can explain the severity of the damage: they reinforce each other, leading to rapid material loss and premature failure of components.

This phenomenon typically occurs in systems where fluids move at high velocity, including pipelines, pumps, valves, heat exchangers, turbines, and marine structures. Suspended solid particles, air bubbles, or cavitation can intensify the mechanical component of erosion, removing protective films and exposing fresh metal to aggressive environments.

The mechanism of erosion corrosion involves a continuous cycle of film breakdown and metal dissolution. Corrosion forms a thin passive or oxide layer on the metal. However, fast-flowing fluids mechanically strip this layer away, leaving the underlying metal unprotected. The fresh surface corrodes more quickly, producing new films that are again removed, accelerating the process. This repeated cycle creates severe localized attack, often appearing as grooves, directional patterns, pitting-like features, or horseshoe-shaped damage marks aligned with the flow direction.

Several factors influence erosion corrosion. On the mechanical side, fluid velocity, turbulence, impingement angle, and the presence of solid particles or bubbles strongly affect the rate of erosion. Higher velocities and sharper impact angles dramatically increase damage. On the electrochemical side, pH, temperature, chloride concentration, and oxygen content determine the corrosion contribution. High temperature and chloride-rich environments typically accelerate metal dissolution.

Figure I.13: Erosion Corrosion

❖ Cavitation Corrosion

Cavitation corrosion is a synergistic damage mechanism caused by the combined effects of cavitation the formation and collapse of vapor bubbles in a liquid and electrochemical corrosion. When a liquid flows rapidly or undergoes sudden pressure changes, vapor bubbles form and then collapse violently near a metal surface. These micro-collapses generate extremely high-pressure shock waves and micro-jets that strike the metal, damaging the surface and removing protective films. The freshly exposed metal then corrodes rapidly, leading to accelerated material loss.

The cavitation process begins when the local pressure in a flowing liquid drops below the vapor pressure, allowing bubbles to form. When the pressure rises again, these bubbles implode with great force. The repeated bubble formation and collapse creates a highly aggressive environment, causing mechanical pitting, roughening, and surface deformation. Once the protective oxide layer is removed, the underlying metal becomes anodic and undergoes electrochemical dissolution, intensifying the damage.

Cavitation corrosion is common in equipment exposed to high-velocity or fluctuating fluid flow. Typical systems include pumps, propellers, turbines, hydraulic machinery, valves, condenser tubes, and marine structures. Even small bubbles can generate pressures exceeding hundreds of megapascals when they collapse, making cavitation one of the most aggressive forms of flow-induced damage.

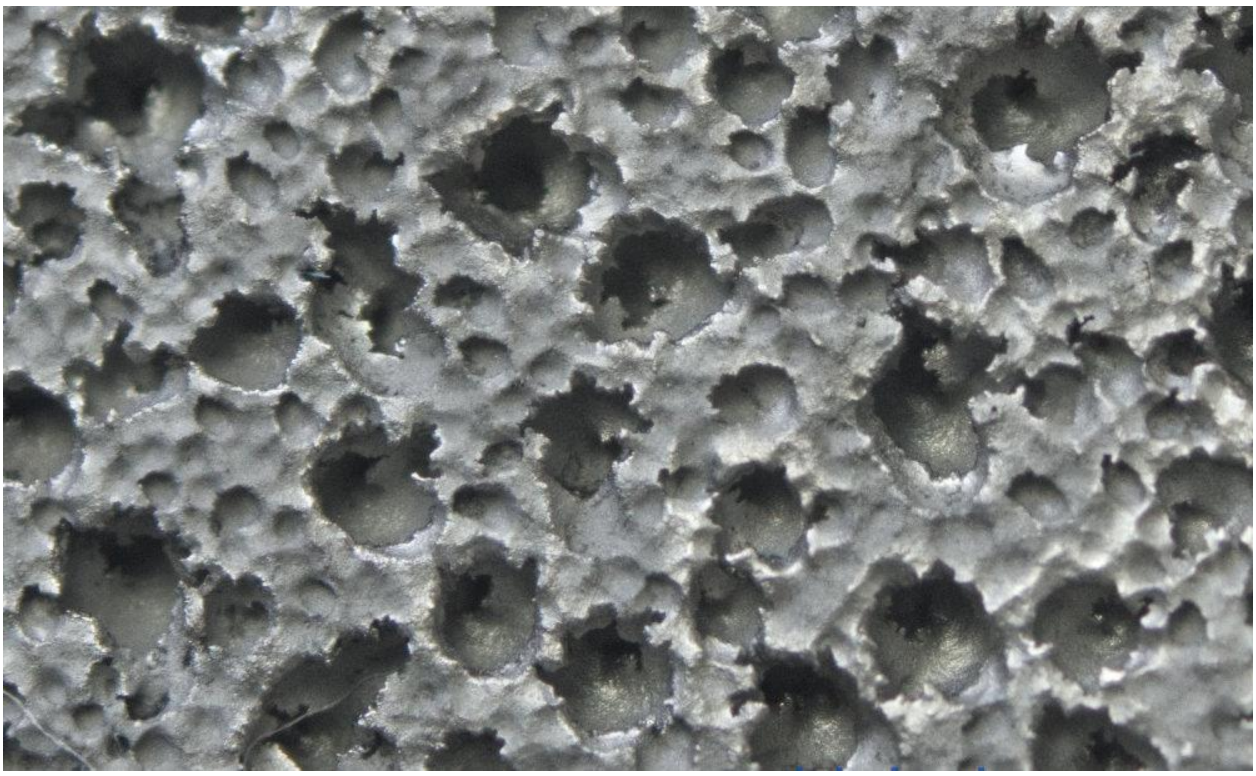


Figure I.14: Cavitation Corrosion

I.5.2 Chemical Corrosion

Chemical corrosion is a type of corrosion that occurs without the involvement of an electric current, distinguishing it from electrochemical (wet) corrosion. It results directly from chemical reactions between a metal and its surrounding environment, which may include gases, liquids, or aggressive solid substances. These reactions lead to the gradual transformation of the metal into more stable compounds such as oxides, sulfides, or other salts, depending on the nature of the environment.

Dry corrosion is commonly observed at high temperatures, where metals react with oxygen, sulfur, nitrogen, or other reactive gases. For example, the oxidation of iron to form a layer of iron oxide at elevated temperatures is a typical form of chemical corrosion. Similarly, metals like copper or aluminum can form protective oxide layers that slow further degradation, while others may continue to corrode more rapidly.

The rate and severity of chemical corrosion depend on several factors, including temperature, gas composition, pressure, and the chemical reactivity of the metal. Unlike electrochemical corrosion, which often requires moisture, chemical corrosion can occur in completely dry environments. Protective strategies include selecting corrosion-resistant alloys, applying surface coatings, and controlling environmental conditions, such as reducing exposure to oxidizing gases. Understanding chemical corrosion is essential in industries like metallurgy, high-temperature furnaces, and chemical manufacturing, where metals are exposed to reactive gases or extreme operating conditions.

Figure I.10 : Chemical Corrosion

I.5.3 Bacterial Corrosion

Bacterial corrosion, also known as microbiologically influenced corrosion (MIC) or bio-corrosion encompasses all corrosion phenomena in which microorganisms, particularly bacteria, play a direct or indirect role in metal degradation. In these processes, bacteria can accelerate existing corrosion reactions or create environmental conditions that favor the initiation of corrosion. For example, certain types of bacteria produce corrosive metabolites, such as hydrogen sulfide (H_2S) or sulfuric acid (H_2SO_4), which can attack metals like steel or iron.

This type of corrosion is particularly insidious because it often develops in hidden or confined areas, such as pipelines, storage tanks, water systems, or marine structures, where bacterial colonies can thrive in stagnant or low-oxygen conditions. The corrosion may appear localized, such as pitting or crevice corrosion, but it can progress rapidly due to the continuous metabolic activity of the microorganisms.

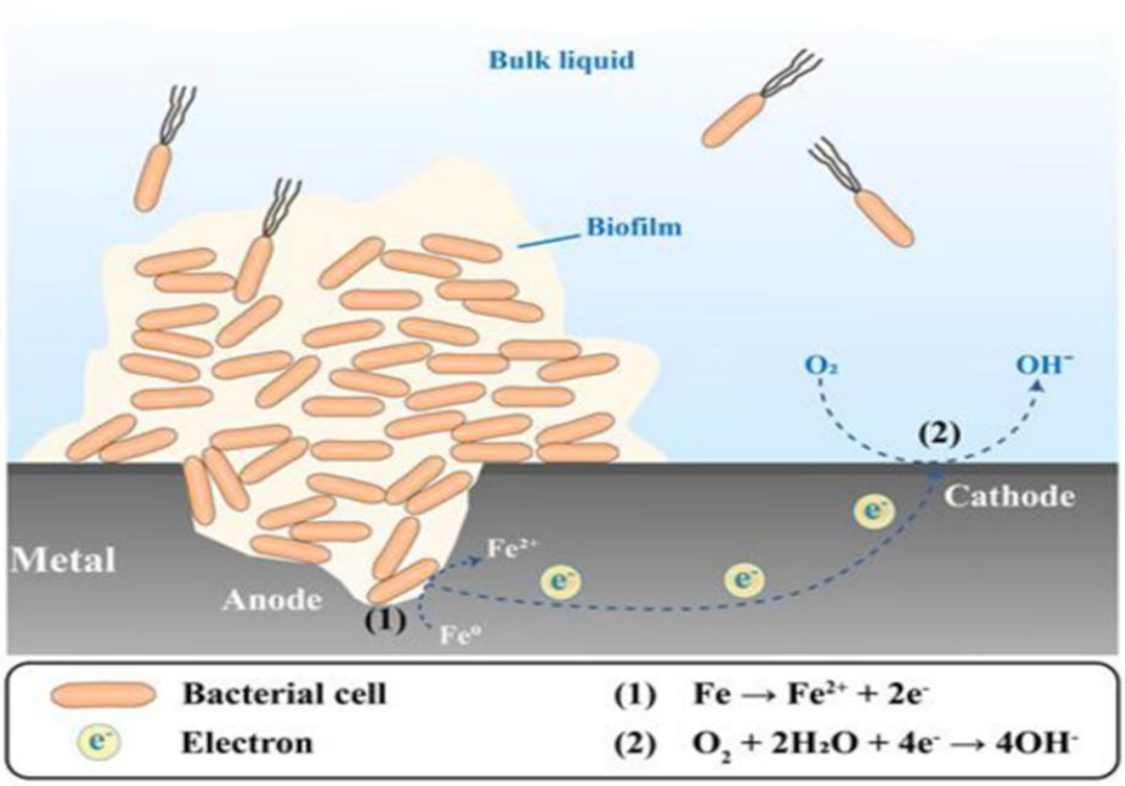


Figure I.11 : Bacterial Corrosion

I.6 Conclusion

Corrosion is an inevitable phenomenon that affects many materials, particularly metals, and it can lead to significant economic, environmental, and safety consequences. It not only reduces the structural integrity and functionality of equipment and infrastructure but also increases maintenance costs and operational downtime in industries. Understanding the mechanisms, causes, and types of corrosion is crucial for developing effective prevention and mitigation strategies, such as the application of protective coatings, the use of corrosion-resistant alloys, the control of environmental conditions, and cathodic protection techniques.

Moreover, the study of corrosion allows engineers and materials scientists to predict the lifespan of metallic structures, plan maintenance schedules, and avoid unexpected failures that could pose safety risks or environmental hazards, such as leaks in pipelines or structural collapse. Corrosion management also contributes to sustainability by reducing material waste and minimizing the need for frequent replacements of damaged components. In critical sectors such as aerospace, maritime, oil and gas, chemical processing, and infrastructure, corrosion control is essential to ensure reliability, operational efficiency, and the protection of human lives.

Overall, corrosion research and prevention are not merely technical challenges but strategic necessities, as they help preserve resources, enhance safety, and support economic efficiency across multiple industries. By combining scientific understanding with practical engineering measures, it is possible to significantly extend the service life of materials and maintain the performance and safety of essential systems.

I.7 References

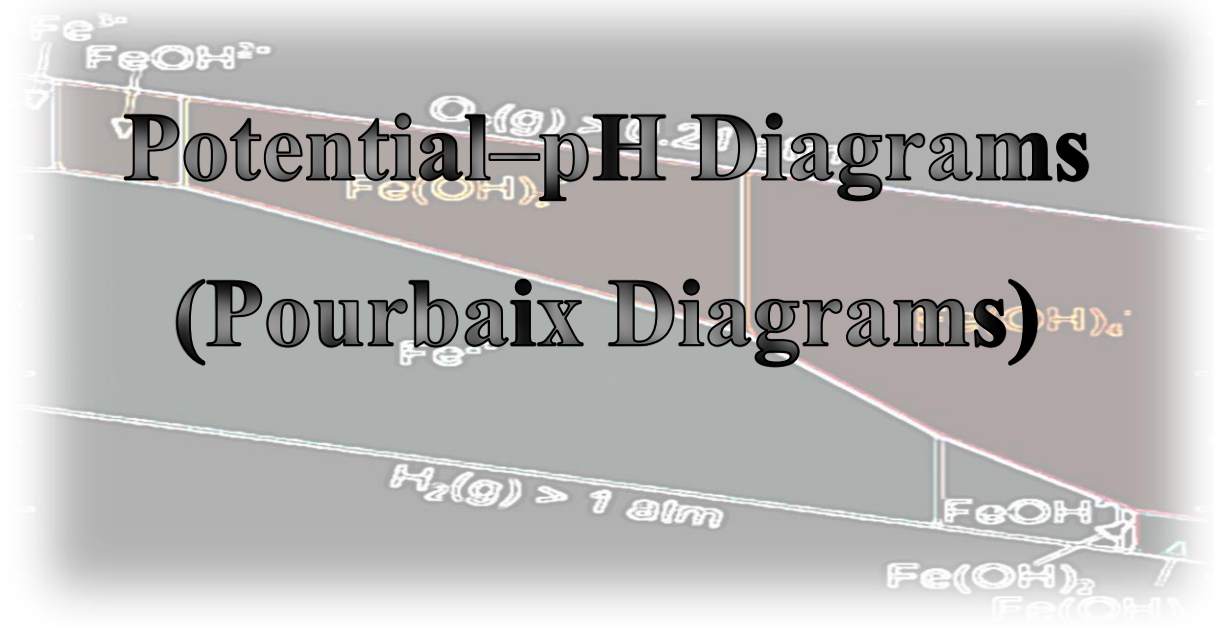
[1] *Fontana, M. G. – Corrosion Engineering (3rd Edition, McGraw-Hill, 1986).*

[2] *Uhlig, H. H. & Revie, R. W. – Corrosion and Corrosion Control: An Introduction to Corrosion Science and Engineering (4th Edition, Wiley, 2008).*

[3] *Jones, D. A. – Principles and Prevention of Corrosion (2nd Edition, Prentice Hall, 1996).*

[4] *Pierre R. Roberge – Handbook of Corrosion Engineering (McGraw-Hill, 2000)*

CHAPTER II



Potential–pH Diagrams

(Pourbaix Diagrams)

This chapter discusses the importance and application of Pourbaix diagrams in the thermodynamic analysis of corrosion reactions. It enables the student to construct and interpret this type of diagram, which is of crucial importance.

II. Chapter II: Potential–pH Diagrams (Pourbaix Diagrams)

II.1 Introduction

Phase diagrams are essential tools for understanding the stability of chemical species as a function of thermodynamic conditions. Among these diagrams, the potential–pH diagram (or Pourbaix diagram) is particularly useful for studying corrosion, the precipitation of species in aqueous solutions, and the stability of materials in different environments.

II.2 The Potential–pH Diagram

II.2.1 Definition and Principles

The reversible potential of many reactions, particularly those involving oxides, depends on the pH, as it may also depend on the occurrence of precipitation or complexation reactions.

Potential–pH diagrams, also known as Pourbaix diagrams, represent the stability domains of different chemical species as a function of the electrochemical potential (E) and pH. They are constructed from the redox and acid–base equilibria of the species considered and allow the determination of the conditions under which a species is stable in dissolved, precipitated, or gaseous form.

In a Pourbaix diagram, three types of equilibria are illustrated:

- Equilibrium between solid species: solid/solid.
- Equilibrium between two species in solution: aqueous/aqueous.
- Equilibrium between a species and another species in solution in a solid/aqueous medium.

Pourbaix diagrams consist of several regions representing these three possible states.

Corrosion domain:

In which the stable species exists in a dissolved form of the metal.

- Passivation domain: in which the stable species appears in the form of an oxide or hydroxide of the metal.

- Immunity domain: where the metal remains inactive.

Pourbaix diagrams are constructed in ideal liquid, namely chemically pure water at a temperature of 25 °C, for a metal of maximum purity, and not for an alloy. For a given metal, such a diagram is usually plotted by taking into account the various possible electrode and chemical reactions:

- Electrochemical equilibrium between a metal and its ions :

$$M^{n+} + n\acute{e} \Leftrightarrow M$$

- Electrochemical equilibrium between a metal and its oxide :

$$MO_{n/2} + nH^+ + n\acute{e} \Leftrightarrow M + \frac{n}{2}H_2O$$

- Electrochemical equation between two oxides with different oxidation states :

$$MO_{n/2} + nH^+ + n\acute{e} \Leftrightarrow MO_{(n-1)/2} + nH_2O$$

- Chemical equilibrium in an acidic medium between an oxide and dissolved ions :

$$MO_{n/2} + nH^+ \Leftrightarrow M^{n+} + \frac{n}{2}H_2O$$

- Chemical equilibrium in an alkaline medium between an oxide and dissolved ions :

$$MO_{n/2} + 2OH^- \Leftrightarrow MO^{2-}_{(n+1)/2} + H_2O$$

II.2.2 Construction of the Diagram

- Collection of thermodynamic data (standard potentials, equilibrium constants, etc.)
- Writing of redox and acid–base equilibria
- Plotting the stability boundaries of species by solving the equilibrium equations
- Identification of the predominance domains of the different forms of a chemical species (ions, complexes, precipitates, etc.).

II.2.3 Predominance (PD) or Existence (ED) Domains

Before constructing the Pourbaix diagram, it is essential to determine or define the predominance or existence domains of the species under consideration.

- A species "A" is considered predominant over a species "B" when the concentration of [A] is greater than that of [B].
- A solid species may be either present (activity equal to 1) or absent (activity equal to 0); in this case, we refer to the existence domain rather than the predominance domain.

II.2.4 Why Specify a PD or ED?

- Between two solutes (ions or complexes), OX and Red (or acid and base), there are always variable proportions depending on the equilibrium potential (E) or the pH value.
- The presence of a condensed (solid) phase in interaction with a solute is conditional: this phase may be present or absent depending on whether the solubility product is reached or not. Thus, the boundary line defines an existence domain for the condensed species.

II.2.4.1 Case of a redox equilibrium (involving electrons but not H^+ ions)

$$\alpha\ Ox + n\ e^- \rightleftharpoons \beta Red$$

For this equilibrium, the potential along the boundary line is defined as follows:

$$E_f = E^0_{Ox/Red} + \frac{RT}{nF} \lg \frac{[OX]^{\propto}}{[Red]^{B}}$$

$$E_f = E^0_{Ox/Red} + 0.059 \lg \frac{[OX]^{\propto}}{[Red]^{B}}$$

This type of equation is represented by a family of straight lines parallel to the pH axis.

Exemple : Redox couple Cu^{2+} / Cu

$$Cu^{2+} + 2e^- \Rightarrow Cu$$

$$E_f = E^0_{Cu^{2+}/Cu} + \frac{0.059}{2} \lg[Cu^{2+}]$$

$$E_f = 0{,}34 + 0{,}0295 \lg[Cu^{2+}]$$

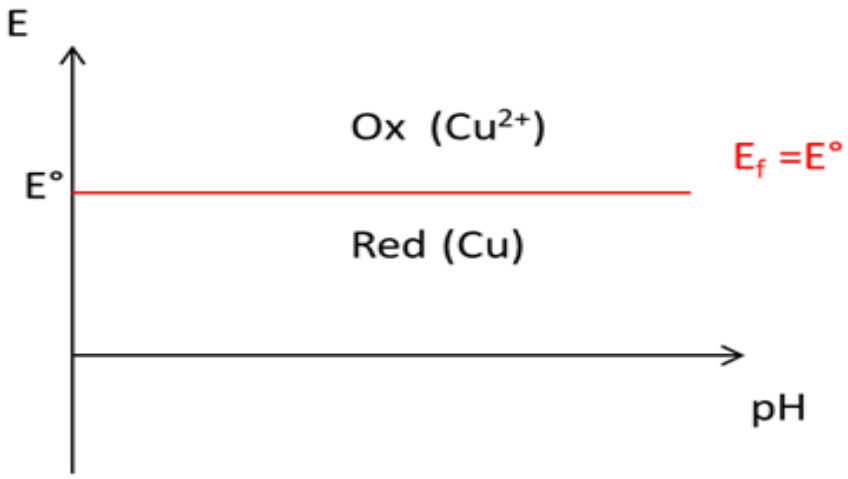


Figure II.1 : Case of redox equilibrium

- On the boundary line :[Ox] = [Red], Ef = E° → $O_x et\ R_{ed}$ en At equilibrium,
- [Ox] > [Red], Ef > E° → It is the predominance domain ofO_x.
- [Ox] < [Red], Ef < E° →It is the predominance domain ofR_{ed}.

II.2.4.2 Case of an acid–base equilibrium (involving H^+ ions but not electrons)

$$HA + H_2O \Rightarrow A^- + H_3O^+$$

$$pH = pKa + \lg\frac{[A^-]}{[HA]}$$

Exemple *: Redox couple* NH_4^+/NH_3

$$NH_4^+ + H_2O \Rightarrow NH_3 + H_2O$$

$$pH = pKa + \lg\frac{[NH_3]}{[NH_4^+]}$$

This type of equilibrium is represented by a family of straight lines parallel to the E axis.

- On the boundary line $[A^-] = [HA] \rightarrow pH = pKa$
- If $pH > pKa$, $[A^-] > [HA] \rightarrow$ it is the predominance domain of the base A^-.
- If $pH < pKa$, $[A^-] < [HA] \rightarrow$ it is the predominance domain of the acid HA.

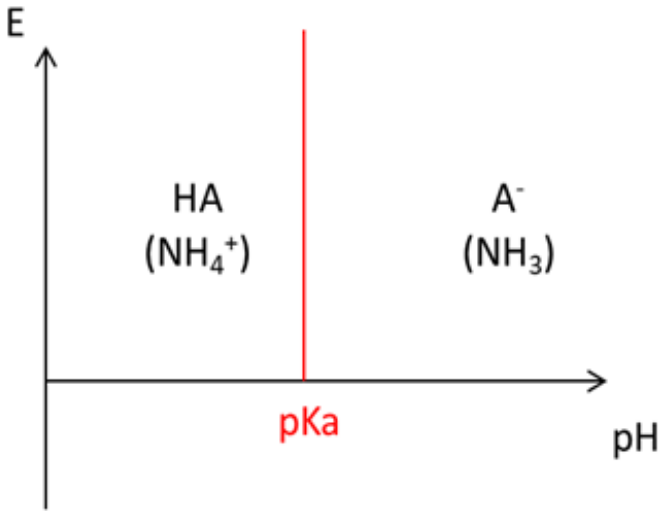


Figure II.2 : Case of acid–base equilibrium

II.2.4.3 Case of a mixed equilibrium involving both e⁻ and H⁺ ions

$$\propto \mathrm{O_x} + mH^+ + ne^- = \beta\, \mathrm{R_{ed}} + \frac{m}{2} H_2O$$

$$\mathrm{E_f} = \mathrm{E^0_{Ox/Red}} + \frac{RT}{nF} \lg \frac{[\mathrm{OX}]^{\propto}[\mathrm{H^+}]^{\mathrm{m}}}{[\mathrm{Red}]^{\mathrm{B}}}$$

$$\mathrm{E_f} = \mathrm{E^0_{Ox/Red}} - 0.059 \frac{m}{n} pH + \frac{0.059}{n} \lg \frac{[\mathrm{OX}]^{\propto}}{[\mathrm{Red}]^{\mathrm{B}}}$$

On the boundary line $[\mathrm{Ox}] = [\mathrm{Red}]$

$$\mathrm{E_f} = \mathrm{E^0_{Ox/Red}} - 0.059 \frac{m}{n} pH$$

This type of equation is represented by families of straight lines with slopes equal to: $0.059 \frac{m}{n} pH$

Exemple : *Redox couple* MnO_4^- / Mn^{2+}

We have :

$$MnO_4^- + 8H^+ + 5e^- \Rightarrow \mathrm{Mn^{2+}} + 4H_2O$$

$$\mathrm{E_f} = \mathrm{E^0_{MnO_4^-/Mn^{2+}}} - 0.059 \frac{8}{5} pH$$

- If $\mathrm{E} > Ef$: It is the predominance or existence domain of O_x,
- If $\mathrm{E} < Ef$: It is the predominance or existence domain of R_{ed}

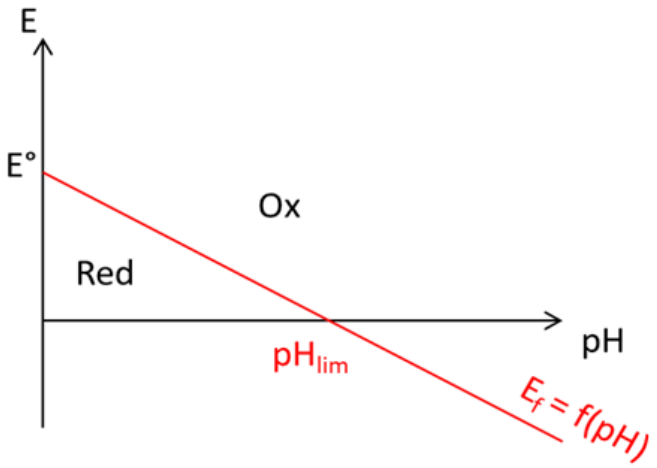


Figure II.3 : Case of a mixed equilibrium

In this way, it is possible to determine the respective stability domains of an element and its compounds, but one must first establish the arbitrary conventions for the plot and know the standard potentials of the redox couples.

II.3 Conventions for Plotting E–pH Diagrams

- **CONVENTION 1:** The total concentration of dissolved species remains constant and is denoted by C_o, also referred to as the working concentration. «C_{tr} ».
- **CONVENTION 2:** It is assumed that all gases are at a pressure of 1 bar ($P_{tr} = 1$ b).
- **CONVENTION 3:** At the boundary separating two soluble (dissolved) species, on the boundary line (BL), the concentrations of the two species are equal. In the case where the stoichiometric coefficients are identical, this is equivalent to:$\frac{C_{tr}}{2}$

  Exemple **:** *couple* Fe^{3+}/Fe^{2+}

  $$Fe^{3+}_{aq} + e^- \rightleftharpoons Fe^{2+}_{aq}$$

  In the predominance domain (PD): $[Fe^{3+}] = [Fe^{2+}] = C_{tr}$

  On the boundary line (BL): $[Fe^{3+}] = [Fe^{2+}] = \frac{C_{tr}}{2}$

- **CONVENTION 4 :** At the boundary between a soluble species and a solid, on the BL, the concentration of the soluble species$= C_t$

  Exemple **:** Redox *couple* Ag^+/Ag

  $$Ag^{+}_{aq} + e^- \rightleftharpoons Ag_s$$

  $$E_f = E^0_{Ag^+/Ag} + 0.059 \lg[Ag^+]$$

$$E_f = E^0_{Ag^+/Ag} + 0.059 \lg C_{tr}$$

❖ **CONVENTION 5 :** A At the boundary between a soluble species and a gas, on the BL, the concentration of the soluble species= C_{qr} and the pressure of the gaz $P_{gaz} = P_{tr}$

***Exemple 1* : Redox** *couple* H^+/H_2

$$2H^+_{aq} + 2e^- \rightleftharpoons H_{2g}$$

$$E_f = E^0_{H^+/H_2} + \frac{0.059}{2} \lg \frac{[H^+]^2}{P_{H_2}}$$

$$E_f = -0.059pH - \frac{0.059}{2} \lg p_{tr}$$

$$E_f = -0.059pH$$

Exemple 2* : Redox *couple Cl_2/Cl^-

$$Cl_{2g} + 2e^- \rightleftharpoons Cl^-$$

$$E_f = E^0_{Cl_2/Cl^-} + \frac{0.059}{2} \lg \frac{P_{Cl_2}}{[Cl^-]^2}$$

$$E_f = E^0_{Cl_2/Cl^-} - 0.059 \lg C_{tr}$$

II.4 Plotting the E–pH Diagram

II.4.1 Potential–pH Diagram of Water

L The stability domains of an element and its compounds are limited by the decomposition equilibria of the solvent. The most commonly used solvent is water.

Water consists of three entities in equilibrium:$H_2O, H_3O^+ et\ O$.It is a redox amphoteric species, acting as an oxidant in one couple and as a reductant in another couple.

Couple (1) : H_2O/H_2

Water is the oxidant in the H_2O/H_2 couple, i.e., H (+1)/H (0). In an acidic medium, this couple is equivalent to the H^+/H_2 couple. H_3O^+/H_2 Ou H^+/H_2

$$2H^+_{og} + 2e^- \rightleftharpoons H_{2g}$$

If we apply the plotting convention, we will have:

$$E_1 = E^0_{H^+/H_2} + \frac{0.059}{2} \lg \frac{[H^+]^2}{P_{H_2}}$$

$E_1 = -0.06pH$……..(1)

Couple (2) : $0_2/H_2O$

Water is the reductant in the O₂/H₂O couple. $0_2/H_2O$, soit $O(0)/O(-2)$

$$O_{2_g} + 4H^+_{aq} + 4e^- \rightleftharpoons 2H_2O$$

$$E_1 = E^0_{0_2/H_2O} + \frac{0.059}{2} \lg pO_2[H^+]^4$$

$$E_1 = E^0_{0_2/H_2O} + 0.059\, pH$$

$$E_2 = 1.23 - 0.06pH \ldots\ldots\ldots\ldots\ldots\ldots\ldots (2)$$

Two lines corresponding to Equation (1) and Equation (2) are plotted:

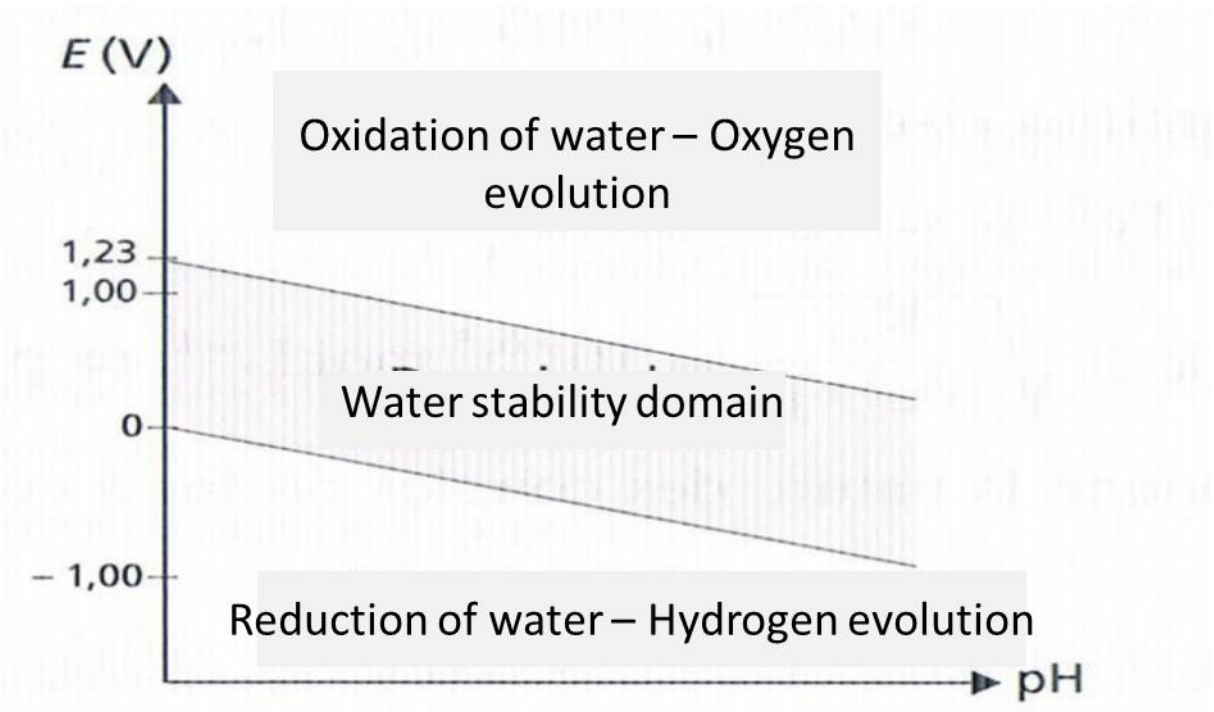


Figure II.4 : Potential–pH Diagram of Water

II.4.2 Interpretation of the Diagram

- Stability zones of soluble and solid species
- Domains of corrosion, passivation, and immunity
- Effects of pH and potential on dissolution, precipitation, and reduction of species
- Applications in environmental and industrial electrochemistry.

II.5 Applications of Potential–pH Diagrams

II.5.1 Prediction of Metal Corrosion

Predicting metal corrosion is a key aspect of materials engineering and maintenance planning. Corrosion does not occur randomly; it follows certain chemical and electrochemical mechanisms that depend on the type of metal, its environment, and the conditions it is exposed to. By understanding these factors, scientists and engineers can estimate how quickly and in what manner a metal will degrade over time. Environmental factors such as humidity, temperature, presence of salts, acids, or other chemicals, and even the flow of water or air can greatly influence corrosion rates.

Several methods are used to predict corrosion, including laboratory testing, computer simulations, and analysis of historical data from similar metals in comparable environments. These predictions help in selecting appropriate materials, designing protective measures, and planning maintenance schedules to prevent unexpected failures. Accurate prediction of corrosion is essential not only to extend the service life of metal structures but also to reduce repair costs, prevent accidents, and ensure safety in industrial, civil, and everyday applications.

II.5.2 Water Treatment and Water Quality Control

Water treatment and water quality control are essential processes for ensuring safe and clean water for drinking, industrial use, and environmental protection. Raw water from rivers, lakes, or underground sources often contains impurities such as suspended solids, microorganisms, dissolved chemicals, and other pollutants. The purpose of water treatment is to remove these contaminants and to make the water safe for its intended use.

Water treatment typically involves several steps, including coagulation and flocculation, sedimentation, filtration, and disinfection. These processes help remove particles, bacteria, and harmful substances. In addition, water quality control involves continuous monitoring and

testing of various parameters, such as pH, turbidity, microbial content, and the presence of heavy metals or chemical residues. Regular monitoring ensures that treated water meets health and safety standards and prevents waterborne diseases.

Effective water treatment and quality control are crucial not only for human health but also for industrial processes, agriculture, and the preservation of natural ecosystems. By combining advanced treatment techniques with strict quality monitoring, it is possible to provide reliable, safe, and high-quality water to meet the needs of communities and industries.

II.5.3 Metal Extraction and Refining

Metal extraction and refining are fundamental processes in metallurgy, aimed at obtaining pure metals from their ores. Raw ores contain metals combined with other elements in the form of oxides, sulfides, or other compounds. The extraction process involves separating the metal from these compounds using chemical, thermal, or electrochemical methods. Common techniques include pyrometallurgy (high-temperature smelting), hydrometallurgy (chemical leaching), and electrometallurgy (electrolytic processes).

After extraction, refining is carried out to improve the purity and quality of the metal. Refining removes remaining impurities that may affect the metal's physical and chemical properties. This can be achieved through methods such as electrorefining, chemical purification, or zone refining. The choice of extraction and refining techniques depends on the type of metal, the nature of the ore, economic considerations, and environmental impacts.

Efficient extraction and refining are essential for producing metals that meet industrial and technological requirements. High-purity metals are critical in applications ranging from construction and electronics to aerospace and medicine. Furthermore, advancements in extraction and refining processes contribute to reducing energy consumption, minimizing environmental pollution, and maximizing the recovery of valuable metals.

II.5.4 Applications in Geochemistry and Materials Science

The study of metals, their extraction, corrosion, and behavior in different environments has important applications in geochemistry and materials science. In geochemistry, understanding the chemical composition of rocks, minerals, and soils helps scientists determine the distribution and availability of metals in the Earth's crust. This knowledge is essential for

exploring mineral resources, predicting natural processes such as mineral weathering, and assessing environmental impacts of mining activities.

In materials science, knowledge of metals and their properties is used to develop new materials with specific characteristics, such as increased strength, corrosion resistance, or electrical conductivity. Metals are studied to improve their performance in construction, electronics, energy systems, and biomedical applications. Research in this field often involves designing alloys, testing their mechanical and chemical behavior, and developing surface treatments to enhance durability and functionality.

By integrating principles from geochemistry and materials science, scientists and engineers can optimize the extraction of metals, design better materials, and protect them from corrosion. This interdisciplinary approach contributes to sustainable resource management, technological innovation, and the advancement of industrial and environmental applications.

II.6 Conclusion

Potential–pH diagrams, also known as Pourbaix diagrams, are a powerful and versatile tool in the study of electrochemical phenomena. These diagrams represent the thermodynamic stability of different species of a metal as a function of the electrode potential (E) and the pH of the solution. By showing which forms of a metal are stable under specific conditions, potential-pH diagrams provide critical insights into corrosion, passivation, and redox reactions. In industrial applications, these diagrams are invaluable for optimizing processes such as water treatment, where controlling the chemical environment prevents undesirable reactions and ensures safe, high-quality water. In corrosion control, potential–pH diagrams help engineers predict the conditions under which metals will corrode, remain passive, or form protective oxide layers. This information is essential for selecting suitable materials, designing protective coatings, and implementing effective cathodic protection systems.

In metallurgy, potential-pH diagrams assist in understanding the solubility and stability of metal ions in aqueous solutions, guiding processes such as leaching, electrorefining, and selective precipitation. By predicting the formation of soluble or insoluble species, these diagrams help improve metal recovery and minimize environmental impacts associated with mining and industrial waste.

Moreover, in materials science and geochemistry, potential-pH diagrams are used to study the stability of minerals, alloys, and other solid phases in natural and engineered systems. They provide insight into the interactions between solids and aqueous environments, helping scientists develop corrosion-resistant materials and predict the behavior of metals in soils, groundwater, or seawater.

The integration of potential–pH concepts into the design of new materials and industrial processes supports technological innovation. By understanding and controlling electrochemical behavior, researchers can create materials with enhanced durability, improved energy efficiency, and reduced environmental impact. Overall, potential-pH diagrams serve as a fundamental tool in both theoretical and applied sciences, bridging chemistry, materials engineering, environmental protection, and industrial technology.

II.7 Références

[1] Pourbaix, M. (1974). Atlas of Electrochemical Equilibria in Aqueous Solutions. *NACE International.*

[2] Bard, A. J., & Faulkner, L. R. (2001). Electrochemical Methods: Fundamentals and Applications. *John Wiley & Sons.*

[3] Stumm, W., & Morgan, J. J. (1996). Aquatic Chemistry: Chemical Equilibria and Rates in Natural Waters. *Wiley-Interscience.*

[4] Bockris, J. O., & Reddy, A. K. N. (1998). Modern Electrochemistry 2A: Fundamentals of Electrodics. *Springer.*

[5] Sverjensky, D. A., & Fukushi, K. (2006). "A predictive model of solution chemistry of aqueous aluminum carbonate complexes." Geochimica et Cosmochimica Acta, *70(15), 3778-3802.*

CHAPTER III

This chapter deals with the description of various methods for preventing and protecting against different types of corrosion.

III. Chapter III: Methods of Corrosion Protection

III.1 Introduction

It is essential to take corrosion prevention into account from the very early stages of a facility's design. In fact, implementing preventive measures at the right time is crucial to avoiding many issues related to the durability of materials, particularly in sectors such as nuclear energy, the chemical industry, or aeronautics, where accidents can have extremely serious consequences for both people and the ecosystem.

Corrosion control involves various methods: prevention can be achieved through proper design of metal components, careful selection of materials, application of protective coatings, use of inhibitors, or implementation of electrochemical protection.

Before examining these various methods, we will first conduct an analysis of the main categories of alloys and their respective applications.

III.2 Protection by Coatings

Coatings are one of the most common methods used to protect metal surfaces from corrosion. They act as a physical barrier between the metal and its environment.

III.2.1 Metallic Coatings

Metallic coatings involve depositing a layer of another metal that is more resistant to corrosion. Among the techniques used are:

- **Galvanization:** the deposition of zinc on steel to protect it. .
- **Nickeling and Chroming**: improve corrosion resistance and appearance.
- **Aluminizing**: the application of an aluminum layer for high-temperature protection..

It is important to distinguish between two categories of metallic coatings:

a. Anodic Coatings :

The protective metal is less noble than the metal to be protected. The same applies to the galvanization process, that is, zinc coating, which was mentioned earlier. In the event of a coating defect, a local cell is formed, leading to the cathodic corrosion of the base metal. Thus, protection remains effective as long as an adequate amount of coating is present.

Beyond the absence of defects, thickness is a crucial parameter for this type of coating. As a general rule, it ranges between 100 and 200 μm.

b. Cathodic Coatings :

The protective metal is nobler than the metal to be protected. This can be illustrated by applying a nickel or copper coating to steel. In the event of coating failure, a corrosion cell may form, leading to rapid corrosion of the base metal a phenomenon exacerbated by the ratio between the "small anodic area" and the "large cathodic area." In this situation, maintaining the continuity of the coating is therefore the main factor to consider.

III.2.2 Inorganic Non-Metallic Coatings

These are layers formed either by a chemical change on the surface or those that are not part of the substrate. Conversion layers form when a metal reacts with a specific environment (such as phosphating, anodizing, or chromating). In contrast, layers that do not bond to the metal are created through deposition methods that do not require a reaction with the metal (such as enameling). In this case, the chemical composition of these layers does not depend on that of the metal.

III.2.3 Organic Coatings

Paints, varnishes, and polymers form an insulating layer on the metal, thereby preventing contact with corrosive agents. Organic coatings create a more or less impermeable barrier between the metal and the electrolyte environment. They are grouped into three categories: three types of coatings are commonly used for the protection of buried structures: bituminous coatings, polymeric coatings, and paints and varnishes.peintures, vernis et polymères forment une couche isolante sur le métal, empêchant ainsi le contact avec les agents corrosifs.

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Three types of coatings are commonly used for the protection of buried structures: bituminous coatings, polymeric coatings, and paints and varnishes.

Polymeric coatings are applied using various methods such as powder spraying, spray gun application, rolling, dipping, and others. Their performance depends on their intrinsic chemical resistance in the environment and the absence of defects.

Paints are presented as opaque, two-phase liquids. Some formulations contain pigments with corrosion-inhibiting properties. They protect the substrate through various mechanisms, such as the barrier effect, suppression of electrochemical cells, inhibition of electrochemical reactions, and so on.

Paints play a crucial role in corrosion protection, far surpassing other available methods. Most steel objects, as well as many items made from other materials, are coated with paint to ensure their protection.

III.2.4 Revêtements céramiques

Les céramiques et oxydes protègent contre les environnements extrêmes comme les hautes températures et les milieux acides.

III.3 Protection par inhibiteurs :

III.3.1 Definition of an Inhibitor :

An inhibitor is a chemical compound added in small quantities to an environment to reduce the corrosion rate of the metal material to be protected. Their applications include acidic environments, vapors, and cooling waters.

III.3.2 Classification of Inhibitors

Inhibitors can be categorized according to different criteria:

- Based on their field of application,
- Based on the specific reaction they target,
- Based on the reaction mechanism they involve.

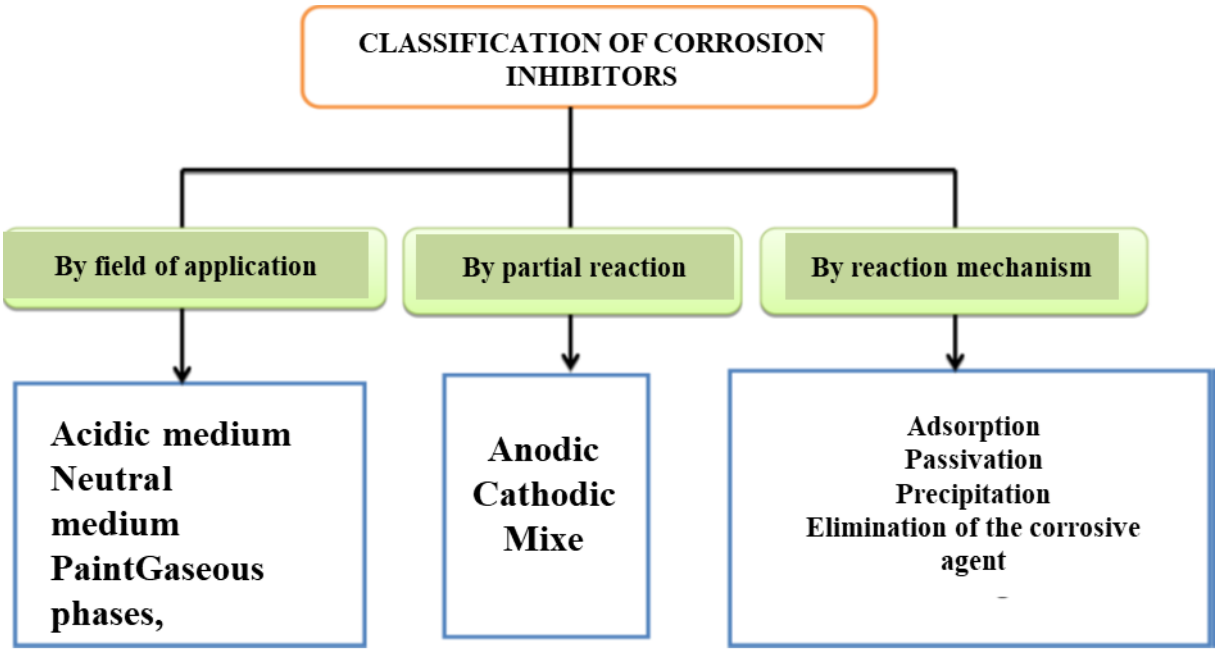

Figure III.1 : Classification of Inhibitors

III.3.2.1 By Field of Application :

Regarding classification based on the field of application, corrosion inhibitors can be categorized according to their use in aqueous, organic, or gaseous environments. Corrosion inhibitors used in aqueous environments are selected based on the pH of the medium: in an acidic environment, they aim to prevent chemical corrosion of steel during pickling or descaling operations, whereas in a neutral or alkaline environment, they are often used to protect the pipelines of cooling systems.

III.3.2.2 By Partial Electrochemical Reaction :

Three types of inhibitors can be distinguished based on their impact on the rate of partial electrochemical reactions.

a. Anodic Inhibitors: They act by reducing the current at the anodic part of the metal surface. In the case of partial blockage, a local increase in current density may occur on these surfaces. This can lead to a more intense localized corrosion process than that observed in the absence of the inhibitor, highlighting the importance of the concentration of the active element near the steel.

b. Cathodic Inhibitors: They cause an increase in cathodic overpotential, which reduces the corrosion current. Although these inhibitors never completely stop the corrosion process, they do not pose a risk of localized corrosion. They often lead to the precipitation of salts or hydroxides due to the accumulation of OH^- ions on the cathodes.

c. Mixed Inhibitors: They possess the properties of both anodic and cathodic inhibitors.

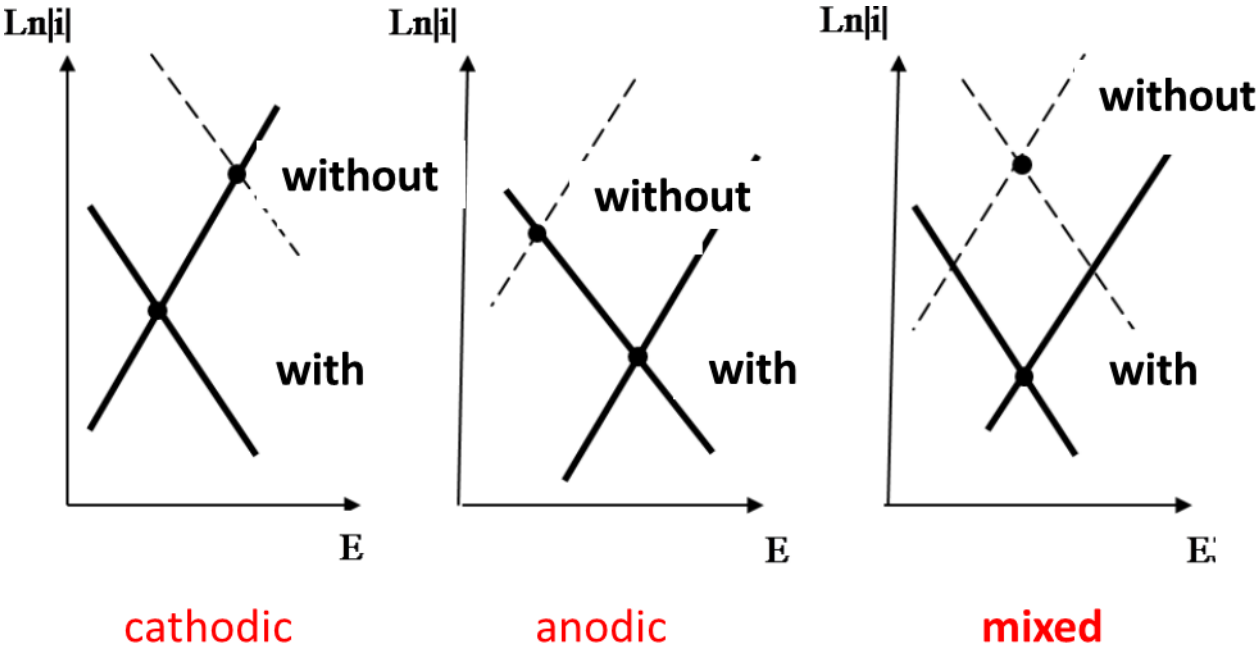

Figure III.2 : Partial Electrochemical Reaction

An anodic inhibitor reduces the anodic partial current density and shifts the corrosion potential toward more positive values. A cathodic inhibitor decreases the cathodic current intensity and shifts the corrosion potential toward more negative values. A mixed inhibitor reduces the rate of both reactions while having little effect on the corrosion potential.

III.3.3 By Reaction Mechanism

According to the reaction mechanism, inhibition can occur in different ways:

- Through adsorption or passivation,
- Through the precipitation of a protective film,
- Through the removal of the corrosive agent.

Corrosion can be slowed by the adsorption of an inhibitor on the metal surface. The level of inhibition depends on the equilibrium between the dissolved and adsorbed species, as

expressed by an adsorption isotherm. This process is particularly important in an acidic environment.

Some oxidizing inhibitor agents induce spontaneous passivation of the metal, leading to a reduction in the corrosion rate.

Other inhibitors induce the formation of surface layers through the precipitation of mineral salts or sparingly soluble complexes. These films limit the accessibility of the surface to oxygen and partially hinder anodic dissolution. Corrosion inhibition by removal of the corrosive agent is only possible in closed systems. This technique is commonly used in closed hot water loops of thermal power plants.

III.3.4 Properties

A corrosion inhibitor must reduce the corrosion rate of a metal without altering its physical and chemical properties, particularly its mechanical strength. It should remain stable with other components in the environment and should not affect the stability of species within that environment. An inhibitor is considered effective if it remains stable at the operating temperature and performs well at low concentrations. It can be used for permanent protection (requiring careful monitoring of the system) or, more commonly, for temporary protection: when the material to be protected is highly sensitive to corrosion (during storage, pickling, cleaning, etc.) or when it undergoes particularly challenging machining operations such as drilling, tapping, boring, threading, and so on..

III.3.5 Nature of Inhibitors

III.3.5.1 Organic Inhibitors

Organic inhibitors are carbon-containing molecules that interfere with a chemical or enzymatic reaction by reducing its effectiveness. These inhibitors can be of natural or synthetic origin and are widely used in biochemistry, medicine, and the chemical industry.

III.3.5.2 Inorganic Inhibitors

Inorganic inhibitors are substances of mineral origin (not containing organic carbon) that reduce or prevent a chemical or enzymatic reaction. They are widely used in chemistry, biochemistry, pharmacology, and industry.

III.3.6 Selection of an Inhibitor

The inhibitor must be selected in accordance with rules regarding toxicity and environmental impact. This calls into question the use of certain inhibitors, particularly sodium and potassium chromates, which were chosen for their high effectiveness. The same applies to the use of volatile inhibitors.

For years, research has been conducted to replace them with other mineral salts such as vanadates, molybdates, and silicates.

III.3.7 Methods for Studying Corrosion Inhibitors

The methods for studying corrosion inhibitors are the same as those used to study corrosion in general, whether electrochemical or not. Electrochemical tests provide useful information about the inhibitor's performance and, if properly interpreted, about the rate of corrosion processes at the time of measurement. This therefore requires a study over a period of time. Among these methods, one can mention corrosion risk measurement, tracing of current and potential curves, and electrochemical impedance spectroscopy (EIS).

III.4 Electrochemical Protection

III.4.1 Cathodic Protection

Cathodic protection alters the metal's potential to prevent corrosion. It involves giving the metal a low potential so that corrosion occurs very slowly. This method is mainly used to protect heavy steel structures, such as offshore drilling platforms, ships, and buried pipelines.

Cathodic protection is regulated by two main factors: the protection potential and the current density.

Protection Potential (E_{prot}) is defined by the Nernst equation.:

$$E_{prot} = E° + \left(\frac{RT}{nF}\right) Ln10^{-6}$$

T = 25°C

$$E_{prot} = E° - 0.354/n$$

When the metal potential is equal to or lower than the protection potential, the corrosion rate cannot exceed a value considered negligible. In this way, it is possible to prevent the corrosion of a metal by applying a specific potential, so that E ≤ E_{prot}

The protection current, denoted as (I_{prot}), is the cathodic current required to maintain the protection potential. Its magnitude is determined by the area to be protected, denoted, as well as by the protection current density. I_{prot} :

$$I_{prot} = \quad i_{prot} \quad \text{A}$$

The principle of cathodic protection states that the potential is shifted into the protection range (hatched area) such that E ≤E_{prot}.

The value of the partial cathodic current density at the protection potential is as follows: $i_c \quad = i_{prot}\, A$.

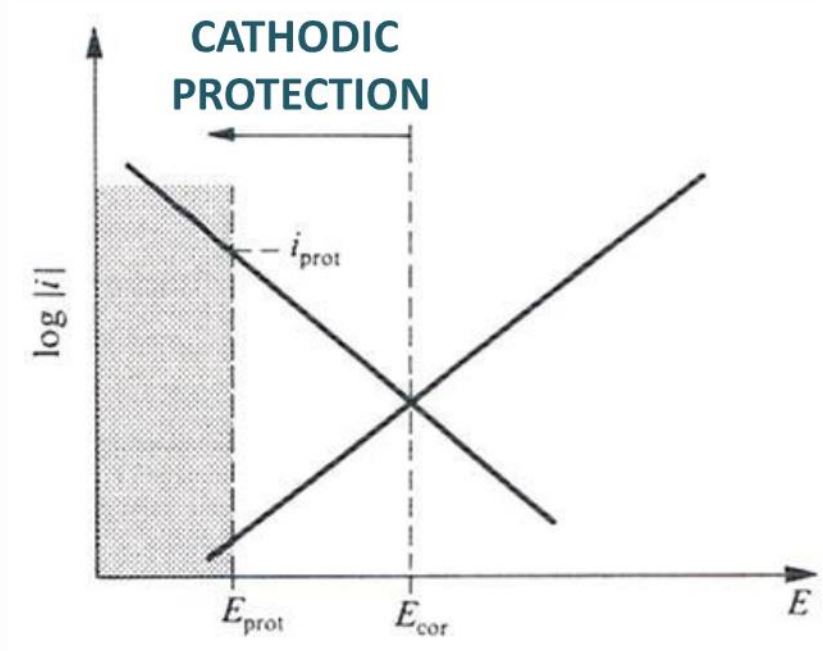

Figure III.3 : Cathodic Protection

Two methods of cathodic protection are commonly used in practice:

III.4.2 Cathodic Protection by Sacrificial Anode

The sacrificial anode and the metal to be protected from an electrochemical cell, in which the latter acts as the cathode. It is necessary for the sacrificial anode to have a lower reversible potential than that of the metal to be protected. To preserve steel, it is common to use sacrificial anodes made of zinc, magnesium, or aluminum, as well as their alloys.

❖ **Selection of Sacrificial Anodes**

Sacrificial anodes must meet the following criteria:

- They must have a sufficiently negative electrode potential to allow rapid polarization of the material to an adequate level.
- They must not undergo polarization during current flow. More specifically, it is essential that corrosion products do not form an adherent coating that could alter the electrochemical potential. Additionally, they should corrode uniformly in the specific environment, without being severely attacked in the absence of current.
- They must also exhibit good conductivity, adequate mechanical strength, and be easily manufactured in various shapes and sizes.
- Finally, their cost must be economically viable.
- In practice, only three materials meet these criteria: zinc, aluminum, and magnesium.

III.4.3 Impressed Current Protection

It requires the use of a rectifier. This method has the advantage of allowing the voltage or current to be adjusted according to the requirements.

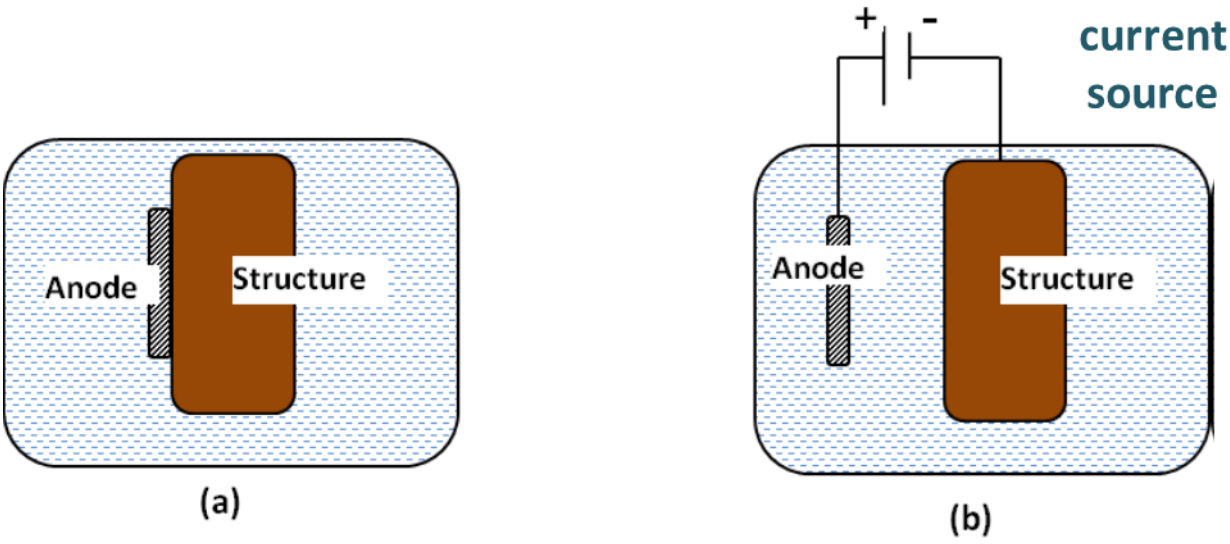

Figure III.4 : La protection par courant imposer

III.4.4 Impressed Current Protection

The anodic protection method is used for passivable metals whose corrosion potential lies within the active range, where $E_{corr.} \leq E_{pass}$. In this situation, anodic polarization is used to shift the potential into the passive range. Maintaining cathodic protection requires only a low current intensity.

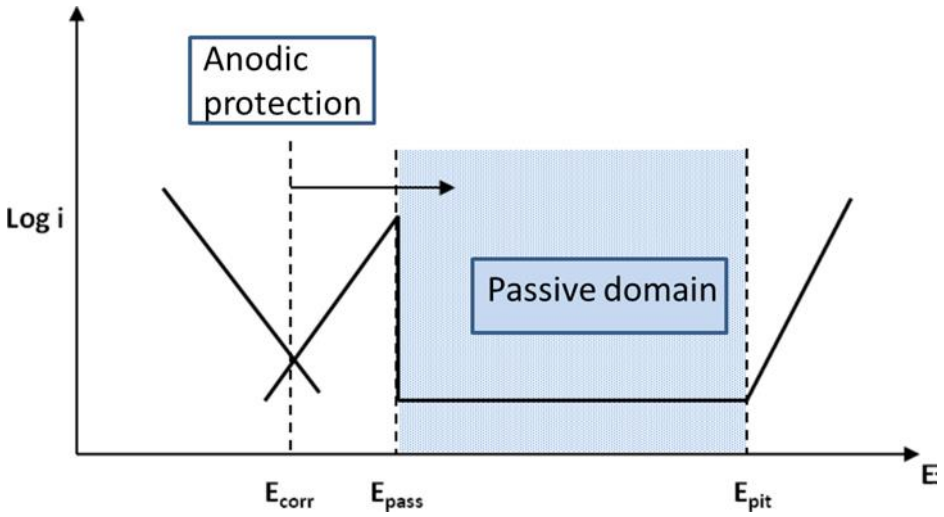

Figure III.5 : Anodic Protection

III.5 Conclusion

Corrosion protection relies on strategies specifically designed to suit the operating conditions and environmental exposure of materials. Employing coatings, chemical inhibitors, and cathodic protection systems offers effective solutions to mitigate corrosion processes. These approaches not only extend the service life of infrastructures and industrial equipment but also enhance their operational reliability and reduce long-term maintenance costs. By carefully selecting the appropriate protection method according to material type, usage conditions, and environmental aggressiveness, industries can ensure the safety, efficiency, and durability of their installations.

III.6 Références

[6] Pierre R. Roberge, "Handbook of Corrosion Engineering", McGraw-Hill, 2000.

[7] Denny A. Jones, "Principles and Prevention of Corrosion", Pearson, 1996.

[8] Mars G. Fontana, "Corrosion Engineering", McGraw-Hill, 1986.

[9] Uhlig H. H., "Corrosion and Corrosion Control", Wiley, 1985.

[10] Revues scientifiques et articles récents sur la protection contre la corrosion

III.7 Exercices and Their Solutions

➢ Exercice 01

Find the oxidation reactions and the reduction reactions:

a) $2I^- \longrightarrow I_2 + 2e^-$

b) $Al \longrightarrow Al^{3+} + 3e^-$

c) $Na^+ + e^- \longrightarrow Na$

d) $Br^{2+} + 2e^- \longrightarrow Br$

For each reaction, indicate which species is the oxidizing agent and which is the reducing agent.

➢ Solution 01

a and b: Oxidation occurs because electrons are released.

I^- and Al are reducing agents.

c and d: Reduction occurs because electrons are gained.

Na^+ and Br are oxidizing agents.

➢ Exercice 02

Write the oxidizing/reducing couples and the corresponding half-reactions:

Ag^+, H_2, Sn^{2+} , Fe, Ag, NO, Al, Cl_2, H^+, Zn, Fe^{2+} , NO^{3-} , Cl^-, Sn, Zn^{2+} , Al^{3+} .

➢ Solution 02

Ag^+/Ag; H^+/H_2; $Sn^{2+/}Sn$; $Fe^{2+/}Fe$; $NO_{3-/}NO$; $Al^{3+/}Al$; Cl_2/Cl^- ; $Zn^{2+/}Zn$.

$Ag^+ + e^- = Ag$

$2H^+ + 2e^- = H_2$

$Sn^{2+} + 2e^- = Sn$

$Fe^{2+} + 2e^- = Fe$

$NO_{3-} + 4H^+ + 3e^- = NO + 2H_2O$

$Al^{3+} + 3e^- = Al$

$Cl_2 + 2e^- = 2Cl^-$

$Zn^{2+} + 2e^- = Zn$

➢ Exercice 03

A 500 mg nail is immersed in 50 mL of hydrochloric acid at 1.0 $mol \cdot L^{-1}$.

a) Write the overall reaction equation.

b) Calculate the volume of hydrogen gas released when the entire nail has been oxidized.

c) Calculate the concentration of all ionic species present in the solution at the end of the reaction.

➢ Solution 03

a)

$$Fe = Fe^{2+} + 2e^-$$

$$2H^+ + 2e^- = H_2$$

$$2H^+ + Fe = H_2 + Fe^{2+}$$

b) The stoichiometric coefficients show that one mole of Fe corresponds to the release of one mole of H_2, therefore:

n(Fe) = n(H2)

n(Fe) = m(Fe)/M(Fe) = 0,5/55,8 = 8,96.10-3 mol.

If we take the standard molar volume as 22,4 l :

$V(H_2)$ = 8,96.10-3.22,4 $V(H_2) = 200\ cm^3$

d) The solution contains Fe^{2+}, $H_3O^+(H^+)$, Cl^-,OH^-.

n(Fe) = n(Fe2+)

$[Fe^{2+}]$= 8,96.10-3/50.10-3 $[Fe^{2+}] = 0,179\ mol.l^{-1}$

At the beginning [HCl] = $[H^+]$ = $[Cl^-]$ = 1 $mol.l^{-1}$

Since Cl^- does not react, at the end we still have $[Cl^-]$ = 1 $mol.l^{-1}$

On the other hand

$[H^+]$ remaining = $[H^+]$ initial – $[H^+]$ disappeared

$[H^+]$ initial = 1 mol.l-1

$[H^+]$ disappeared = $2[Fe^{2+}]$ = 0,359 mol.l-1 $[H^+]$ = 0,64 mol.l-1

➢ Exercice 04

To protect a cast-iron pipeline, it is connected by a conducting wire to a zinc block. In the absence of the zinc block, the annual iron loss would be 0.274 $kg \cdot m^{-2}$. The pipeline has an external diameter of 0.80 m. What is the mass of zinc consumed per year per meter of the pipeline?

➢ Solution 04

Surface length of one meter of pipeline:

S = pd.l

l = S/pd = 0,398 m.

For 1 meter of length, the mass of iron lost will be:

m (Fe) = 0,274/0,398

m (Fe) = 0,689 kg.m-1

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

$Zn = Zn^{2+} + 2\ e^-$

Thus, 1 mole of iron corresponds to 1 mole of zinc.

m (Zn) = 0,689.65,4/55,8 m (Zn) = 0,807 kg.m-1

➢ Exercice 05

A 1 kg zinc anode is placed on the hull of a ship. The corrosion current has an average intensity of 500 mA.

Calculate the maximum lifetime of the anode.

Zn = 65,4 g.mol-1 ; 1 faraday = 96500 C

➢ Solution 05

$Zn = Zn^{2+} + 2\ e^-$

We thus have Q = 2.96500.103/65,4 = 2,951.106 C

t = Q/I = 5,902.106 s t = 68 jours 8 h