1. Definition

Corrosion, derived from the Latin term "corrodère", means to corrode, to attack, it refers to the process of gradually deteriorating a material or a metallic alloy and its environment ; it is a natural phenomenon that affects most metallic materials, resulting in deterioration of their properties. Given the growing utilization of metals and alloys in modern life, this phenomena has acquired significant importance today. Corrosion is not limited to steel, but corrosion may occur to non-metallic materials such as concrete and plastic [1].

Corrosion is not limited to steel, but impacts various metals, plastics, and ceramics. It has affects throughout all sectors of the economy, ranging from integrated circuits to reinforced concrete bridges.

Why the study of corrosion ?

The study of corrosion is crucial and it has broad implications for diverse industries and fields, encompassing economic, safety, and environmental considerations. Here are some key reasons why the study of corrosion is crucial :

1. Economic Impact

Corrosion results in material degradation, necessitating regular maintenance, repairs, and replacements, where, understanding and mitigating corrosion can greatly decrease these costs significantly. Also, corrosion-related problems can cause downtime and decreased production in various sectors.

2. Safety Considerations

Corrosion can compromise the structural integrity of buildings, bridges, pipelines, and other critical infrastructure. Furthermore, in sectors such as aerospace and automotive, the presence of corrosion in vital components can present significant hazards to safety.

3. Environmental Impact

Failures caused by corrosion frequently lead to the depletion of important resources and materials, where, reducing corrosion helps in this resources conservation. Furthermore, corrosion can result in the discharge of dangerous substances into the environment.

4. Infrastructure Sustainability

Understanding corrosion mechanisms allows for the development of materials and coatings that resist degradation, leading to longer lifespans for infrastructure and minimizing the necessity for frequent replacements. Also, materials can be used more efficiently, hence contributing to sustainable resource management.

5. Innovation and Advancements

Technology development and progress of innovative technologies and methodologies, leading to the development of new alloys, coatings, and materials that are more resistant to corrosion.

6. Public Health

Corrosion research plays a crucial role in preserving the reliability of essential public health infrastructure, such as water distribution networks and storage tanks.

2. Corrosion Influencing Factors

Corrosion is impacted by a variety of factors, and comprehending these factors is essential for managing the deterioration of materials. These are the primary elements that influence corrosion :

2.1. Environmental Conditions

2.1.1. Humidity : Corrosion often requires the existence of moisture. Elevated levels of humidity can accelerate the progression of corrosion mechanisms. Corrosion is more likely to occur in humid conditions, such as coastal locations or regions that get frequent rainfall.

2.1.2. Oxygen Concentration : Oxygen plays a vital role in numerous corrosion processes. Oxygen is capable of promoting cathodic reactions, which are crucial elements of the entire corrosion process. Oxygen reacts with metal to form metal oxides, these oxides can weaken the structural integrity of the material.

2.1.3. Temperature : Higher temperatures can expedite corrosion reactions, this is because higher temperatures decrease the areas where metals remain stable and increase the speed at which reactions and charge transport occur.

2.1.4. pH Levels : Corrosion can be affected by the acidity or alkalinity of the environment (pH), acidic conditions can cause acid corrosion, while alkaline conditions can trigger alkali corrosion.

2.1.5. Pollutants and Contaminants : The existence of pollutants, salts, and other contaminants can accelerate the occurrence of corrosion processes. For example, the presence of salts, particularly chloride ions, can increase the corrosivity.

2.1.6. Atmospheric Conditions : The corrosion rates can be influenced by the composition of the atmosphere, including pollutants, gases, and airborne particles (gases such as CO2, SO2, SO3 etc).

2.2. Material Factors

2.2.1. Metal Type : Different metals exhibit varying degrees of susceptibility to corrosion. Some metals, like stainless steel and aluminum, form protective oxide layers that slow down corrosion, while others, like iron, can corrode more rapidly.

2.2.2. Alloy Composition : The corrosion resistance of alloys can be influenced by their composition. Gold and platinum, being noble metals, exhibit greater resistance to corrosion due to their stability. Alloying elements are often added to improve corrosion resistance. Adding chromium to iron produces stainless steel, a material more resistant to corrosion.

2.2.3. Metal surface : The roughness of the material surface can impact the rate of corrosion. Irregular and rough surface offers a greater number of sites for corrosion attack. Conversely, a sleek and unblemished surface can exhibit greater resistance to corrosion. Additionally, many metals and alloys can develop protective films, such as oxide layers, on their surfaces, which act as a barrier against corrosion.

2.2.4. Microstructure : The internal structure of the metal, including grain size and orientation, can influence its vulnerability to corrosion.

2.3. Electrochemical factors

2.3.1. Electric Current : Corrosion often occurs due to electric currents, which may arise from electrochemical cells or from potential differences across different areas of a metallic surface. This leads to oxidation and reduction reactions at various parts of the metal surface.

2.3.2. Electric Potential : The electric potential between a metal and its surrounding environment can contribute to corrosion. Changes in electric potential (for example, due to varying environmental conditions) can promote oxidation-reduction reactions, leading to corrosion of the material.

2.3.3. Ion Concentration in Solution : The ion concentration in the surrounding medium significantly affects electrochemical reactions. Salt solutions, like seawater, are favorable for corrosion due to the high concentration of chloride ions. These ions increase the rate of reaction between the metal and the solution.

2.3.4. Acidic or Alkaline Environment : Acidic solutions increase the rate of corrosion because of their ability to transfer positive ions such as hydrogen, which enhances oxidation reactions on the metal. In contrast, alkaline environments might be less corrosive but can contribute to the formation of non-protective oxide layers.

2.3.5. Composition Differences in Metal : When the metal surface contains areas with different chemical compositions, potential differences may arise between these regions, leading to the formation of electrochemical corrosion cells within the metal. These cells are responsible for the electrochemical processes that cause corrosion.

2.3.6. Interaction with Oxygen : Oxygen plays a crucial role in many electrochemical corrosion reactions. In aqueous environments, oxygen interacts with the metal to form oxides or hydroxides, which leads to corrosion of the metal.

2.3. Mechanical Factors

Mechanical factors are those related to the forces and mechanical stresses that affect materials, especially metals, in their various environments.

2.3.1. Mechanical Stresses : Internal and **external stresses** are two types of stresses that affect metals. Internal stresses arise from manufacturing processes or thermal expansion and cooling, while external stresses are forces applied to the metal, such as tension, compression, or bending. These external forces change the surface of the metal and help in the formation of cracks, which may lead to localized corrosion such as stress corrosion cracking.

2.3.2. Friction : This type of corrosion occurs when friction between moving parts removes protective layers or coatings on the metal surface. This exposes the metal to corrosive environments and increases the rate of corrosion. In environments containing moisture or aggressive chemicals, this process is accelerated.

2.3.3. Erosion Corrosion : Erosion corrosion happens when the metal surface is exposed to a continuous flow of liquids or gases. This leads to the removal of the protective layer and increases the exposure of the metal to corrosive agents. It is commonly seen in piping **systems**, marine environments, and industrial equipment exposed to flowing fluids.

2.3.4. Mechanical Pressure : Mechanical pressure or load can increase the likelihood of corrosion in metals, especially when the pressure is high or varies periodically. For example, in pipeline systems, pressure changes can cause the metal to expand or contract, leading to crack formation and corrosion. Under continuous pressure, corrosion can occur in cracks or crevices, especially in tight or stagnant spaces where exposure to oxygen is limited.

2.4. Microbial Activity

It is a phenomenon known as microbiologically influenced corrosion (MIC). This type of corrosion occurs due to the activity of microorganisms such as bacteria, fungi, and algae, which interact with materials, particularly metals, in various environments.

3. Different types of corrosion

The causes of corrosion are multiple and complex and result from chemical and/or physical interactions between the material and its environment. There are several different corrosion processes, each with its own mechanisms and contributing factors. Corrosion can be classified into three categories : chemical corrosion, bacterial corrosion, and electrochemical corrosion.

3.1. Chemical Corrosion

Chemical corrosion refers to the deterioration or breakdown of materials, especially metals, due to their direct chemical interaction with surrounding substances such as gases or liquids. Chemical corrosion primarily occurs in environments containing reactive materials like acids, alkalis, salts, or oxidizing gases.

Example

$\mathrm{M} + \mathrm{HCl} \rightarrow \mathrm{MCl}_n + \mathrm{H}_2$

$\mathrm{M} + OH^- \rightarrow \mathrm{M(OH)}_n$

$4\mathrm{Fe} + 3\mathrm{O}_2 + + 6\mathrm{H}_2\mathrm{O} \rightarrow 4\mathrm{Fe(OH)}_3$

The gas typically considered in these reactions is oxygen, although other gases such as SO_2, Cl_2, and H_2S must also be considered at elevated temperatures.

This form of corrosion primarily happens in furnaces, and gas turbines. It is a phenomenon that primarily affects metals, although polymers and ceramics can also corrode under specific conditions. It is important to know that chemical corrosion accounts for just 3% of occurrences of industrial corrosion, whereas electrochemical corrosion accounts for the remaining 97%.

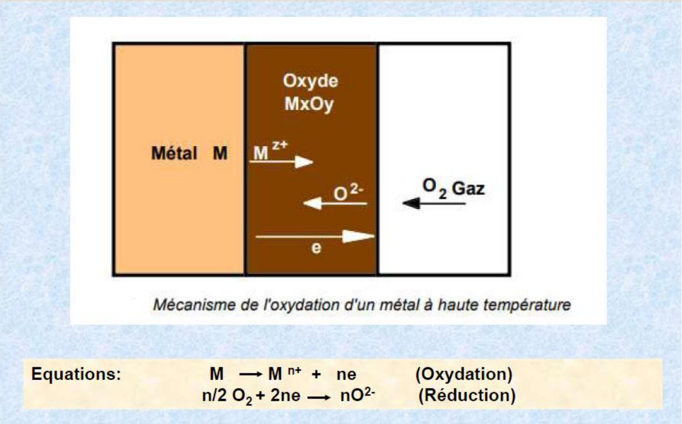

Fig.1. Chemical corrosion

3.2. Biological Corrosion

Biological corrosion, or microbiologically influenced corrosion, also known as bio-corrosion. It is a form of corrosion that is induced or influenced by the actions of microorganisms that can contribute to the corrosion of materials, especially in situations with dampness. The most common cases are described below.

3.2.1. Sulfate-reducing bacteria

One notable example is the corrosion caused by sulfate-reducing bacteria, which is a wellencountered kind of microbiological corrosion commonly found in industrial cooling circuits and waste water transportation networks. The class of bacterial associated with this phenomenon are Desulfovibrio, Desulfomonas, and Desulfomaculum. These anaerobic bacteria possess the unique ability to metabolize sulfates and sulfites, resulting in the formation of sulfides.

3.2.2. Acidogenic bacteria

Furthermore, acidogenic bacteria refer to a group of bacteria that generate mineral or organic acids asa part of their metabolic processes. The resultant decrease in pH leads to expedited corrosion via chemical reactions. The genera Thiobacillus, Thiooxidans, and Clostridium are frequently associated with microbiological corrosion of steel.

3.2.3. Iron and manganese bacteria

The bacteria belonging to this category encompass species such as Gallionella, Sphaerotilus, Crenothrix, and Leptothrix. Their function is to convert naturally occurring dissolved ferrous ions (Fe^{2+}) into the ferric state (Fe^{3+}) through oxidation. These bacteria aid in the process of corrosion by facilitating corrosion under deposits.

3.2.4. Bacteria that generate biofilms

Biofilms are formed by numerous bacterial species. The latter consist primarily of water bound to extracellular polymers. Biofilms have the ability to rapidly proliferate by trapping other materials, such as colloids and detritus.

3.2.5. Algae

Algae only grows in sufficient light conditions. Under favorable conditions, they have the ability to produce dense fibrous layers that block the channels and create ideal conditions for the growth of anaerobic bacteria at the bottom of the layer. Dead algae undergo decomposition, resulting in the production of corrosive organic acids.

3.2.6. Nitrifying bacteria

Nitrifying bacteria are a category of microorganisms that may convert ammonia (NH_3) or nitrites (NO_2^-) into nitrates (NO_3^-) through their metabolic processes. The most widely recognized genera are Nitrosomonas and Nitrobacter. These organisms facilitate corrosion by lowering the pH through the conversion of ammonia into nitric acid.

Fig.2. Biological corrosion

3.3.Electrochemical Corrosion

Electrochemical corrosion refers to the phenomenon where metals corrode as a result of electrochemical processes taking place at the boundary between the metal and its surrounding environment. This type of corrosion occurs when electric current flows between anodic and cathodic sites on a metal surface, resulting in material degradation. Electrochemical corrosion is the most common form of corrosion and occurs in various environments, such as aqueous solutions, air conditions, and soil.

Fig.3. Electrochemical corrosion

4. Different forms of corrosion

Causes of corrosion are multiple and complex and result from chemical and/or physical interactions between the material and its environment. There are several different processes of corrosion, each with its own mechanisms and contributing factors. Generally, the various corrosion processes can be summarized as follows :

4.1. Uniform corrosion

Uniform corrosion is the most common type of corrosion, and general attack corrosion are other names for general corrosion. This kind of corrosion occurs on the surface of the whole metal. It is often caused by the metal's exposure to the corrosion-causing conditions, such as moisture, oxygen, and pollutants, it does so almost at the same rate. Because of this, the corroded surfaces seem mottled. Examples include the corrosion of iron and the oxidation of silver.

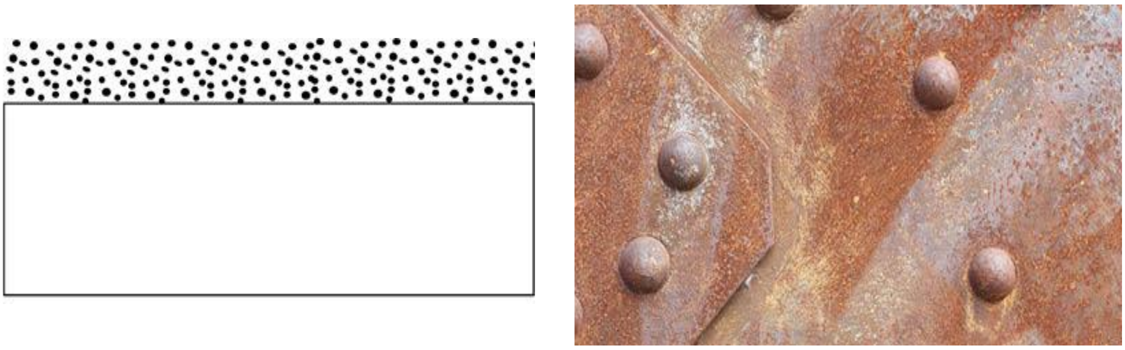

Fig.4. General corrosion affecting the surface of a metal

4.2. Galvanic Corrosion

Galvanic Corrosion is form manifests itself particularly in aqueous environments, it arises when two dissimilar metals are in electrical contact while exposed to an electrolyte (such as water or a conductive solution). Corrosion occurs in the more reactive of the two metals while the less reactive metal is essentially unaffected. An instance of this type of corrosion is frequently observed in water pipes, particularly in cases when steel and copper tubes or copper-based alloys are joined.

Fig.5. The puck is the element that exhibits the lowest resistance to corrosion.

4.3. Pitting Corrosion (localized)

Pitting corrosion, also known as localized corrosion, refers to the corrosion that occurs in specific areas of a metal. It is typically triggered by the presence of small defects in the protective oxide layer, which allow corrosive substances to penetrate the metal and cause damage. For exemple, stainless steel, nickel, titanium, aluminum, and certain alloys are susceptible to pitting corrosion.

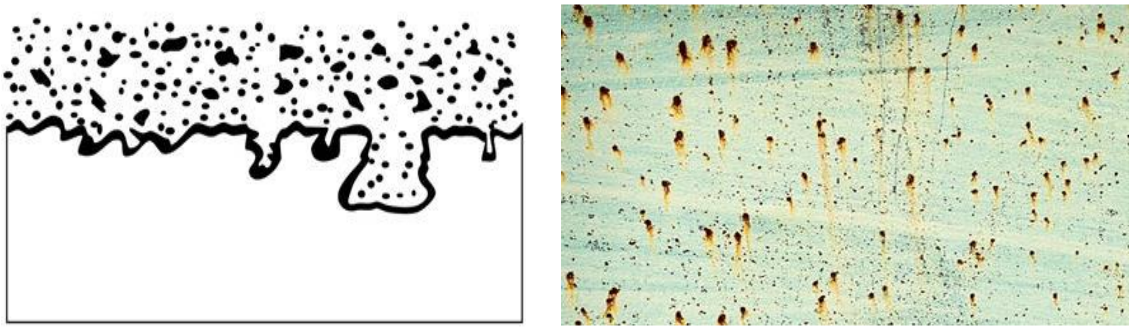

Fig.6. Pitting corrosion of metallic piece

4.4. Stress corrosion

Also, known under the term CSC, it refers to the phenomenon where a metal undergoes cracking due to the combined effects of mechanical stress and the aggressive environment. This form of corrosion is very harmful, it leads to the breakdown of installations by the propagation of the crack which can be inter- or trans-granular. For example, stress corrosion cracking can occur in some metals, such as alloys made of aluminum and certain kinds of stainless steel.

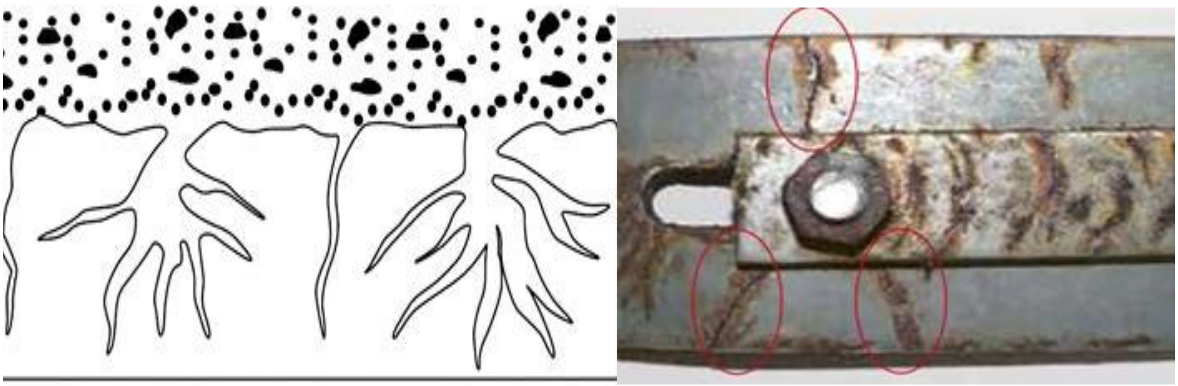

Fig.7. Stress corrosion cracking of an assembly after 4 years

4.5. Crevice Corrosion

Crevice corrosion, often referred to as two-metal corrosion, it is an electrochemical oxidation-reduction (redox) process, it occurs when a metal or alloy is exposed to a corrosive environment, such as the presence of humid air, salt water and acidic solutions. It can happen at any location where there is a gap or crevice in the metal or alloy surface, where corrosive agents are trapped, leading for localized attack on the surface material. This phenomenon, occurs in restricted spaces, gaps, and regions with limited fluid movement, such as joints, gaskets, and and under deposits and it is difficult to detect because it often occurs in tight, visually inaccessible spaces. Crevice corrosion is highly accelerated if chloride, sulphate or bromide ions are present in the electrolyte solution. In order to mitigate crevice corrosion, it is necessary to periodically clean surfaces and ensure that all gaps are effectively sealed with protective coatings such as paint or sealants.

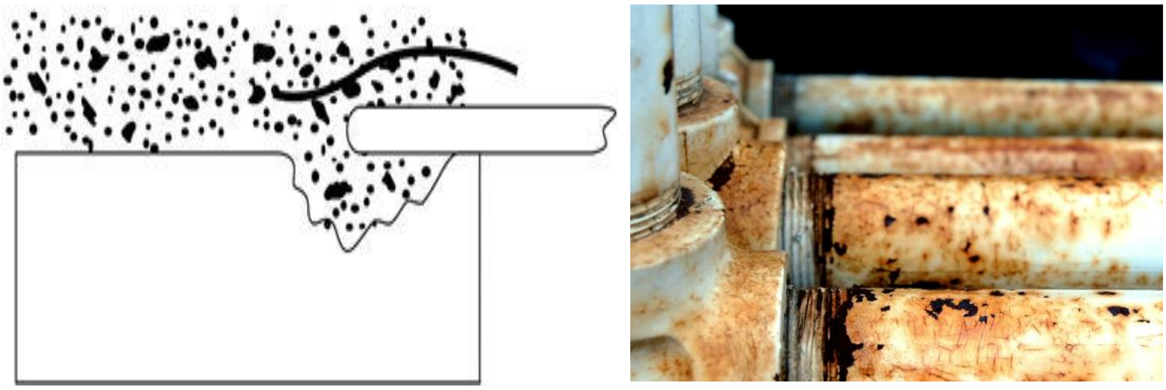

Fig.8. Crevice corrosion

4.6. Hydrogen Embrittlement

Hydrogen embrittlement is the deterioration of structural properties of solid metals due to the presence of hydrogen, where the hydrogen atoms infiltrate the metal structure, resulting in brittleness. It can be induced by variables like electroplating or exposure to hydrogen-rich environments, it is commonly associated with high-strength steels. Hydrogen embrittlement occurs most notably in steels, as well as in iron, nickel, titanium, cobalt, and their alloys. Copper, aluminium, and stainless steels are less susceptible to hydrogen embrittlement.[1][2][3][4],

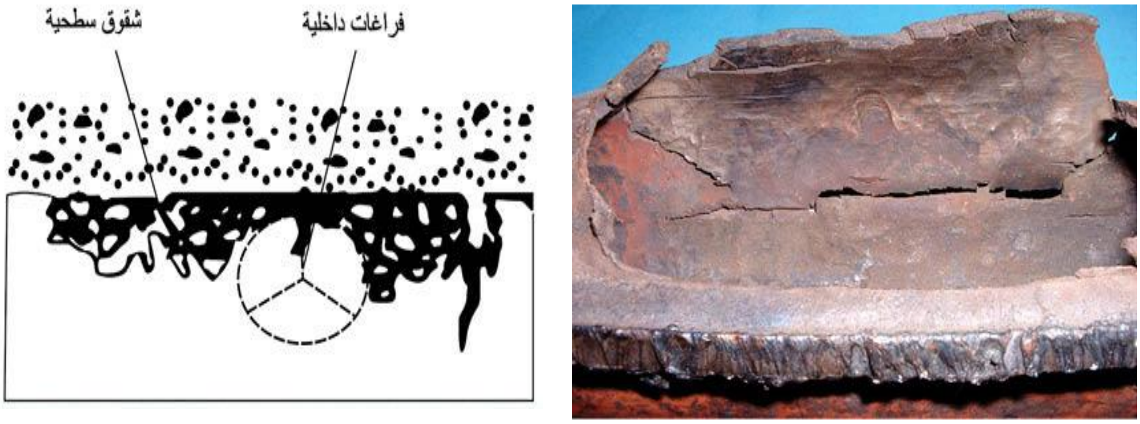

Fig.9. Hydrogen embrittlement

4.7. Intergranular Corrosion

Intergranular corrosion : Is a form of corrosion that occurs specifically at the boundaries between grains in a metal. Grain boundaries are the interfaces that exist between individual crystals or grains inside a polycrystalline material. The attack typically arises from impurities present at the interfaces between grains, as well as the concentration of one alloying element or the depletion of another in these interfacial regions. Stainless steels, namely those with low carbon content (such as AISI 304 and AISI 316), and aluminium alloys with high levels of certain impurities, might be susceptible to intergranular corrosion under specific conditions.

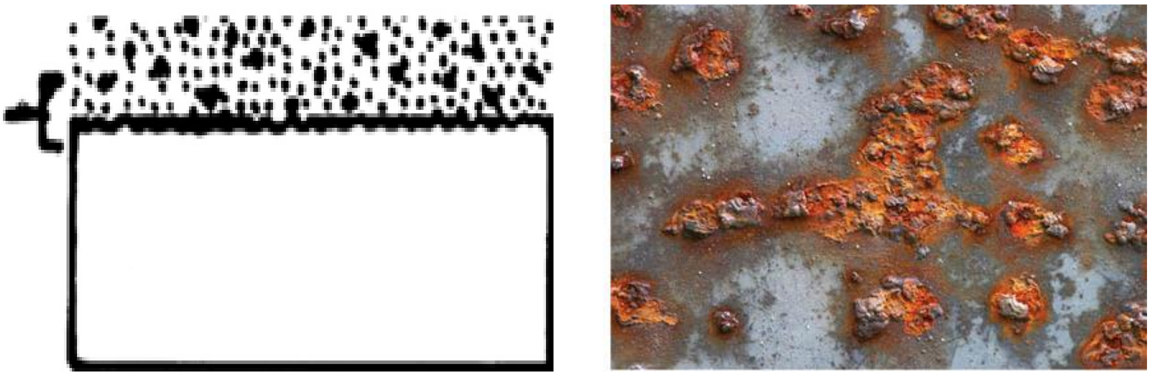

Fig.10. Intergranular corrosion

4.8. Filiform corrosion

The filamentous corrosion appears as a capillary network that is filamentous both on the painted metal's surface and beneath the paint layer, where the hairs spread out in certain directions and in straight lines.This kind of corrosion is most commonly caused by humid atmospheres with humidity levels between 65 and 90% and if the humidity level rises above 90%, this corrosion appears in the form of ulcerated swellings. This rusting can be observed on the surfaces of food containers exposed to a humid environment.

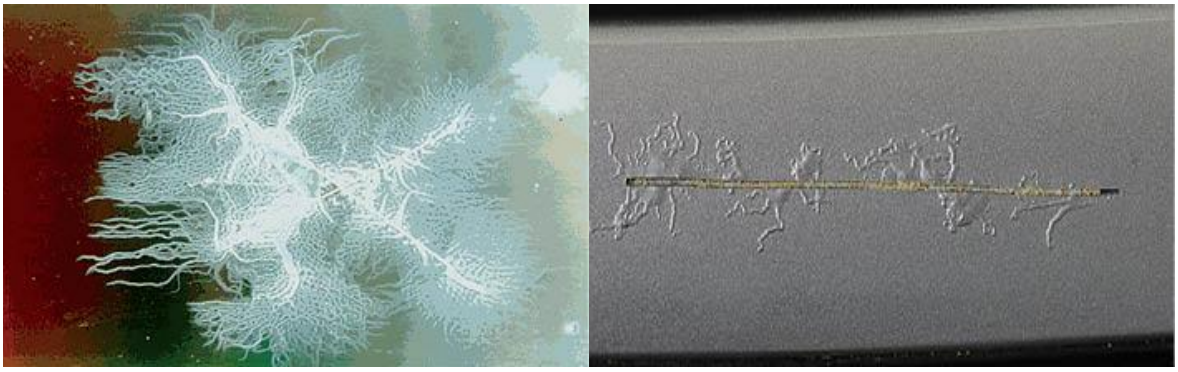

Fig.11. Filiform corrosion

4.9. Fretting Corrosion

Fretting corrosion is a specific form of wear-related corrosion that occurs at the interface of two contacting surfaces that experience small, repetitive relative motions or vibrations. This type of corrosion is often characterized by fine particles or wear debris generated at the contact points between the surfaces. Fretting corrosion typically occurs in environments where the surfaces are subject to cyclic loading, such as in mechanical components like bearings, joints, or electrical connectors. in this case not only is mechanical damage of the surface possible, but the protective surface film of the metal is also removed and this in turn hastens electrochemical corrosion processes.

Fretting corrosion happens at the two exposure zone of metals which will connect jointly, and this usually looks when the exposure space will pacify to fall and difference. This corrosion can be straightforward in fastening and engaging, secure floor, etc.

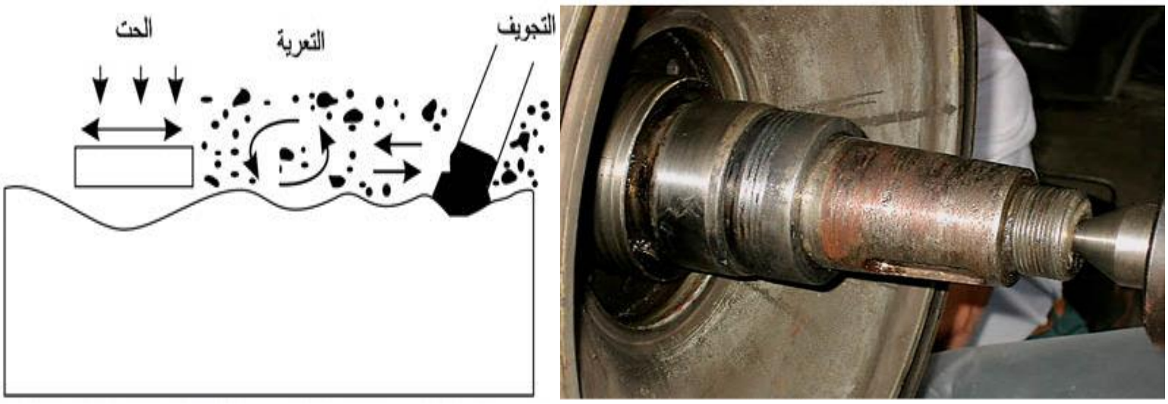

Fig.12. Fretting corrosion

4.10. Erosion Corrosion

This type of corrosion occurs as a result of relative movement between the metal surface and the corrosive medium due to two factors, one chemical and the other mechanical. The defining feature of this corrosion is the formation of grooves, ripples, or rises and falls on the metal surface, and their direction is in the same direction as the medium's movement, and its severity increases when there are air bubbles or suspended solid particles such the sand. The process of erosion by stripping relies on the formation of an oxide layer on the metal's surface, which is then damaged and destroyed by mechanical activity and as a result, the medium starts attacking the metal.

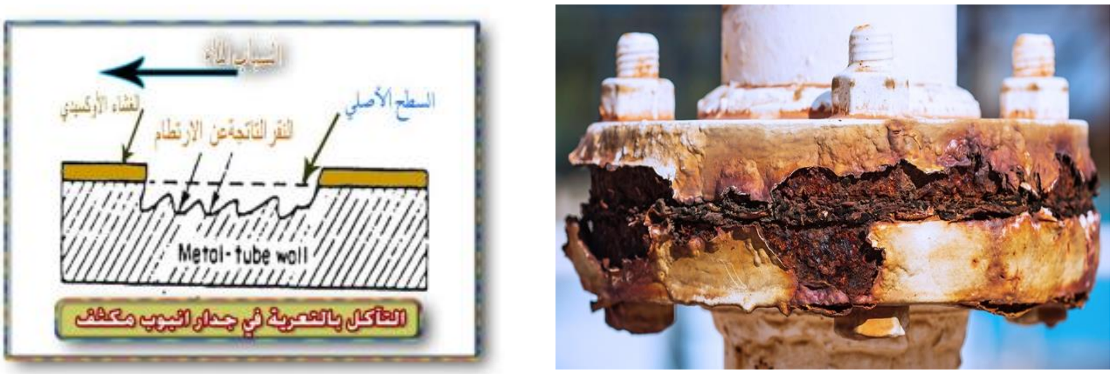

Fig.13. Erosion Corrosion

4.11. Selective corrosion

Selective corrosion is a preferential attack of a particular component of an alloy in presence of electrolyte as a result of an electrochemical oxidation-reduction process. Alloys prone to selective corrosion are composed of components with a great difference between their Electrode potentials (eg.Cu-Zn). The component having lower value of electrode potential (higher position in the table of Electrochemical series) will oxidize (anodic reaction) and dissolve in the electrolyte when the component having higher value of electrode potential will provide cathodic reaction (reduction).

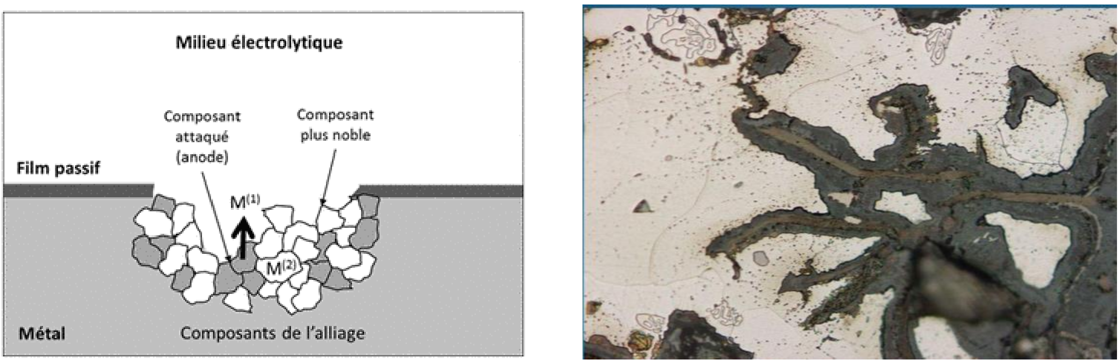

Fig.13. Selective Corrosion on cast iron

5. Calculation of corrosion rate

The corrosion rate of a certain metal in a specific medium refers to the quantity of weight that the metal loses per unit area and per unit time in that particular medium. It is a quantitative indicator, determining the degradation of a metal in certain conditions, such as in acidic or salty solutions. This numerical value is very useful for understanding how each metal reacts, which helps engineers and scientists in their selection of materials, and in making decisions regarding the necessity of protective coatings. The basic units used to express corrosion rate are usually millimeters per year (mm/y), inches per year (inch/y), microamperes per cm^2 ($\mu A/cm^2$), micrometers per year (µm/y) and millimeters per year (mm/y). Different techniques are used to evaluate the corrosion rate, depending on the specific conditions and type of material being studied, and the commonly used methods are weight loss and electrochemical methods.

5.1. Weight Loss Method

This approach is straightforward and precise, relying on the measurement of the initial and final weights of a metal sample before and after it is exposed to the corrosive medium. Using the recorded data, we can compute the rate of weight loss or decrease in mass. This allows us to determine the quantity of corrosion that took place over a specific time period.

While this method is regarded as precise and the most efficient means of corrosion testing, it is time-consuming due to the slow nature of the corrosion process. Conducting weight-based measurements can be a lengthy process, lasting from weeks to months or even years, until experiments are fully completed.

The wear rate is determined using the following formula :

$$W = \frac{\Delta m}{S \times t}$$

Where

The symbol **Δm** denotes the difference between the initial mass m1 and the final mass m2 of the metal. The symbol **S** represents the surface area of the metal that is in contact with the corroded solution and **t** the time.

Example

Calculate the corrosion rate of a metal sample with a diameter of 3 cm and a height of 1.3 cm, immersed in hydrochloric acid solution for 24 hours. The initial mass of the sample was 2.47987 mg, and its final mass after immersion was 1.99870 mg.

Calculation

$\Delta m = M1 – M2 = 2.47987 – 1.99870 = 0.48117$ mg

$S = 2.\ S_{cercle} + S_{latéral} = 2.\pi.r^2 + 2.\ .\pi.r.h = 2.\pi.r\ (r + h) = 26.376\ cm^2$

$$W = \frac{\Delta m}{S \times t} = 7.6011.10^{-4}\ \frac{mg}{cm^2.h}$$

5.2. Electrochemical Methods

Electrochemical methods are among the advanced and modern techniques used for corrosion analysis. They are characterized by their high efficiency and speed compared to traditional methods. Additionally, these techniques require only small sample sizes for experimentation, making them economical and effective.

These methods are used to analyze the properties of metals and their interaction with corrosive environments, providing a precise understanding of corrosion mechanisms and evaluating the performance of materials in various environments. Two primary techniques used in this method are :

5.2.1. Potentiodynamic Polarization Curves

This technique involves recording the changes in voltage and current on the metal surface exposed to corrosion. A polarization curve is plotted by applying current intensity between the working electrode (metal) and the reference electrode (platinum or graphite), measuring the current density at each instance. The curve is represented as $i = f(E)$. The scientist **Tafel** was able to plot the relationship between the voltage difference and the logarithm of the current density using the Butler-Volmer equation, resulting in the following graph :

Polarization curves are used to determine key corrosion parameters such as:

- **Corrosion Potential (Ecorr) :** The potential at which corrosion starts to occur on the metal.
- **Corrosion Current Density (Icorr) :** The rate of corrosion, which is related to Faraday's law.

5.2.2. Electrochemical Impedance Spectroscopy (EIS)

Electrochemical impedance spectroscopy is an advanced, non-destructive technique used to analyze corrosion mechanisms and the surface properties of metallic materials. The method is based on studying the system's response to the application of an alternating voltage over a wide frequency range, which allows for measuring resistance, capacitance, and the dynamic properties of surface interactions. Key parameters measured include :

- **Polarization Resistance (Rp) :** Represents the metal's resistance to corrosion. The higher the value, the lower the corrosion rate.
- **Double Layer Capacitance (Cdl) :** Represents the surface properties of the metal, such as the presence of an oxide layer or inhibitors.
- **Electrolyte Resistance (Rs) :** Represents the resistance of the solution surrounding the sample.
- **Diffusion Resistance (W) :** Relates to the movement of ions or reacting materials to and from the metal surface.

From electrochemical impedance spectroscopy, we can obtain two types of plots :

- **Nyquist Plot :** Represents the electrochemical impedance by plotting the real part (Zreal) against the imaginary part (Zimag).
- **Bode Plot :** Represents the total impedance |Z| and phase angle versus frequency.

6. Fundamental Theoretical Principles of Corrosion

Corrosion is a chemical reaction that can be studied from both thermodynamic and kinetic perspectives, allowing for the determination of various characteristics such as corrosion current and the corrosion rate. The speed of this reaction can be measured through several methods, which we will discuss below.

6.1. Corrosion's Kinetic Aspect

The kinetic aspect of corrosion focuses on studying the rate and interactions of corrosion in different materials under the influence of various environmental factors. This aspect is essential for understanding the corrosion mechanism, as it helps assess the impact of external factors such as humidity, temperature, acidity, the presence of oxygen, and the presence of salts on the rate of corrosion.

6. 2. Corrosion's Thermodynamic Aspect

6. 2. 1. Corrosion reactions

Corrosion of metal is its oxidation

$$\mathrm{M} \rightarrow M^{n+} + \mathrm{ne}^{-} \quad (1)$$

The M metal reaction is only possible when the electrons are grabbed by another pair known as the corrosion motor.

Corrosion is the result of the combination of two reactions : metal oxidation and corrosion drive.

$$\mathrm{OX} + \mathrm{ne}^{-} \rightarrow \mathrm{RED} \qquad (2)$$

Example

- Iron undergoes corrosion in an acidic environment, leading to the liberation of dihydrogen gas, as depicted in the subsequent equation :

$$\mathrm{Fe} \rightarrow Fe^{2+} + 2\mathrm{e}^{-} \quad oxydation$$

$$2H^{+} + 2e^{-} \rightarrow H_2 \quad reduction$$

$$\mathrm{Fe} + 2H^{+} \rightarrow Fe^{2+} + H_2 \quad global\ equation$$

- Under conditions that are neutral or basic, iron undergoes corrosion, resulting in the creation of iron hydroxide Fe(OH)3.

$$\mathrm{Fe} \rightarrow Fe^{2+} + 2\mathrm{e}^{-} \quad oxydation$$

$$\frac{1}{2}O_2 + H_2\mathrm{O} + 2e^{-} \rightarrow 2OH^{-} \quad reduction$$

$$\mathrm{Fe} + \frac{1}{2}O_2 + H_2\mathrm{O} \rightarrow Fe^{2+}\, 2OH^{-} + 2\mathrm{e}^{-} \quad global$$

$$2Fe(OH)_2 + \frac{1}{2}O_2 + H_2\mathrm{O} \rightarrow 2Fe(OH)_3$$

6.2.2. Thermodynamic equilibrium potential

When a metal M is exposed to a solution containing M^{+n} metal ions, a difference in electrical potential arises between the two phases. This potential is known as the thermodynamic potential or thermodynamic equilibrium potential, and it is expressed by Nernst's law.

$$\mathrm{M} \rightarrow M^{n+} + \mathrm{ne}^- \quad (1) \quad \text{Oxydation}$$
$$\mathrm{OX} + \mathrm{ne}^- \rightarrow \mathrm{RED} \quad (2) \quad \text{Reduction}$$

According to Nernst's law

$$E_1 = E_1^\circ + \frac{RT}{nF}\ln[M^{n+}]$$

$$E_2 = E_2^\circ + \frac{RT}{nF} ln \frac{[OX]}{[RED]}$$

Where

E_1: Thermodynamic Equilibrium Potential (volts).
E°: Standard Potential (volts).
n: Number of Electrons exchanged in the reaction.
R: Ideal gas Constant (8.314 $J.mol^{-1}.K^{-1}$).
F: Faraday's Constant (96500 C/mol).
T: Absolute Temperature (Degrees Kelvin).

Corrosion occurs only when its potential value is : $E_2 > E_1$ in general $E°_2 > E°_1$

6.2.3. Engine of corrosion

Hydrogen ions (H^+) oxygen (O_2), together with water (H_2O) are the primary causes of corrosion, and there are two distinct forms of corrosion.

- **Deaerated Solutions :** Also known as oxygen-free or oxygen-depleted solutions, these solutions, play a vital role in managing corrosion and there are two distinct states that we can differentiate between :

- **Acidic solution**

$$H^+ + e^- \rightarrow \frac{1}{2}H_2 \quad \mathrm{e}^\circ_{H+/H2} = 0 \text{ V/ENH}$$

- **Basic solution**

$$H_2O \rightarrow OH^- + \frac{1}{2}H_2 \quad \mathrm{e}^\circ_{H2O/OH-} = -0.82 \text{ V/ENH}$$

- **Aerated Solutions :** Aerated solutions are liquid solutions that contain a significant concentration of dissolved oxygen.

- **Acidic solution**

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \quad \mathrm{e}^\circ_{O2/H2O} = 1.23 \text{ V/ENH}$$

- **Basic or neutral solution**

$$O_2 + 4e^- + 2H_2O \rightarrow 4OH^- \quad \mathrm{e}^\circ_{H2O/OH-} = 0.40 \text{ V/ENH}$$

In addition, we can cite other examples of oxidizing agents (engines), such as :

- **Dichromate ions**

$$Cr_2O_7^{2-} + 14\,H^+ + 6\,e^- \rightarrow 2Cr^{3+} + 7H_2O$$

$$\overset{\circ}{e}_{Cr_2O_7^{2-}/2Cr^{3+}} = 1.33\ \mathrm{V/ENH}$$

- **Permanganate**

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

$$\overset{\circ}{e}_{MnO_4^-/Mn^{2+}} = 1.51\ \mathrm{V/ENH}$$

Example

A copper plate is submerged in a beaker filled with a hydrochloric acid (HCl) solution. Throughout the experiment, we observed the release of hydrogen gas (H^2) and the existence of copper ions (Cu^{2+}) in the solution. The standard voltage for copper is $\overset{\circ}{e}_{Cu/Cu2+} = 0.34\,\frac{\mathrm{V}}{\mathrm{ENH}}$

1. Which redox pairs are involved ?

2. Provide the equation that symbolizes the process of oxidation and reduction.

3. Can corrosion occur ?

4. Is corrosion possible in the presence of a copper plate in air solutions ?

Calculation

1. The redox couple involved are : Cu / Cu^{2+} ; H^+/ H_2

2. The equations that depict the oxidation and reduction processes are :

$$\mathrm{Cu} \rightarrow Cu^{2+} + 2\mathrm{e}^- \quad \overset{\circ}{e}_{Cu/Cu2+} = 0.34\ \mathrm{V/ENH}$$

$$H^+ + e^- \rightarrow \frac{1}{2}H_2 \quad \overset{\circ}{e}_{H+/H2} = 0\ \mathrm{V/ENH}$$

3. Corrosion cannot occur because $\overset{\circ}{E}_2 < \overset{\circ}{E}_1$

4. Indeed, corrosion can take place when the copper plate is exposed to air solutions due to the fact that $\overset{\circ}{E}_2 > \overset{\circ}{E}_1$

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \quad \overset{\circ}{e}_{O2/H2O} = 1.23\ \mathrm{V/ENH}$$