

1. Definition

Corrosion, derived from the Latin term "corrodere", 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. Galvanic Corrosion : Galvanic corrosion is the result of an electrical contact between two dissimilar metals in the presence of an electrolyte. The cathode, which is the more

noble metal with lower susceptibility to corrosion, and the anode, which is the less noble metal, leading to accelerated corrosion of the anode.

2.3.2. Electrolyte Conductivity : Electrolyte, such as water or moisture, is essential for the electrochemical reactions that cause corrosion. Electrolytes facilitate the flow of ions from the anode to the cathode, so establishing an electrical circuit. High electrolyte conductivity accelerates corrosion by facilitating the mobility of ions and electrons. The presence of salts, acids, and other dissolved ions in water can have a considerable impact on the conductivity of electrolytes and, as a result, the rate of corrosion.

2.3.3. Polarization : Polarization affects the rate of electrochemical reactions occurring at the surface of the metal. The corrosion rate of an electrode can either grow or decrease, depending on the direction of polarization. Anodic polarization enhances the rate of corrosion at the anode, whereas cathodic polarization inhibits it.

2.3. Mechanical Factors

Mechanical factors, such as the simultaneous presence of mechanical stress and a corrosive environment, can result in stress corrosion cracking. In addition, mechanical wear has the potential to eliminate protective coatings, so exposing the underlying metal to the process of corrosion.

2.4. Microbial Activity

Microbial activity can accelerate corrosion by the generation of corrosive byproducts or modification of the surrounding environment.

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, it is a natural phenomenon that primarily affects metals, where the materials degrade as a result of chemical reactions with their surroundings.

The most often attack of a metal (M) is by a gas (G), according to a reaction of the type :



Where **X** is a corrosion product that is most often solid.

The gas considered is often oxygen, although other gases such as SO₂, Br₂, Cl₂ and H₂S must be taken into account. This form of corrosion primarily happens in furnaces, boilers, 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%.

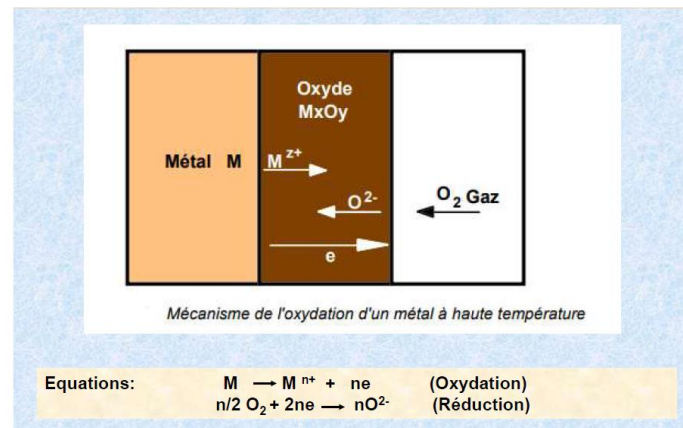


Fig.1. Chemical corrosion

3.2. Biological Corrosion

Biological corrosion, or microbiologically influenced corrosion, also known as biocorrosion. 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 as a 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.

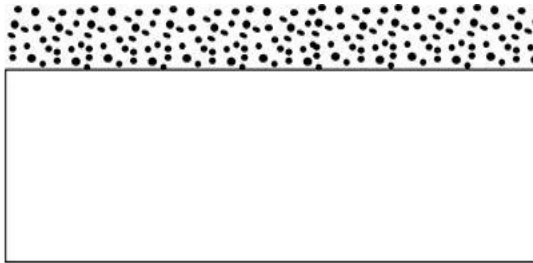


Fig. 4. General corrosion affecting the surface of a metal

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.

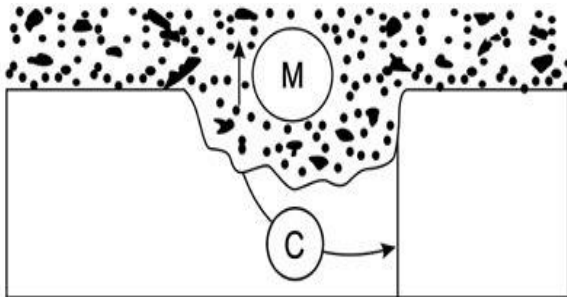


Fig 5. The puck is the element that exhibits the lowest resistance to corrosion.

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 example, stainless steel, nickel, titanium, aluminum, and certain alloys are susceptible to pitting corrosion.

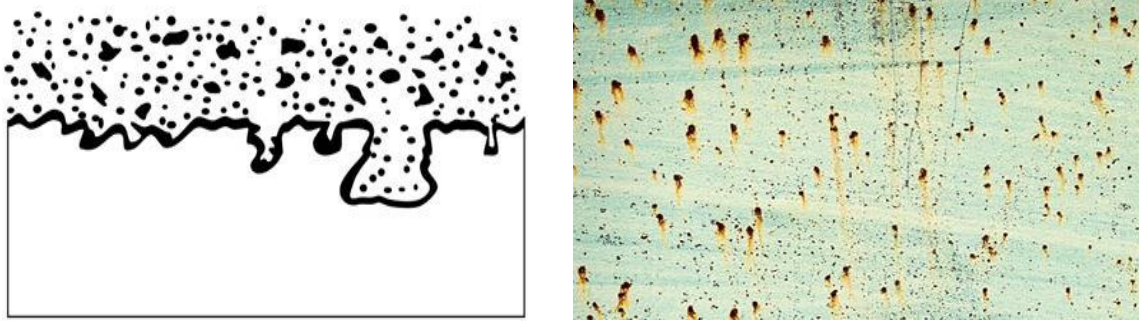


Fig 6. Pitting corrosion of metallic piece

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.

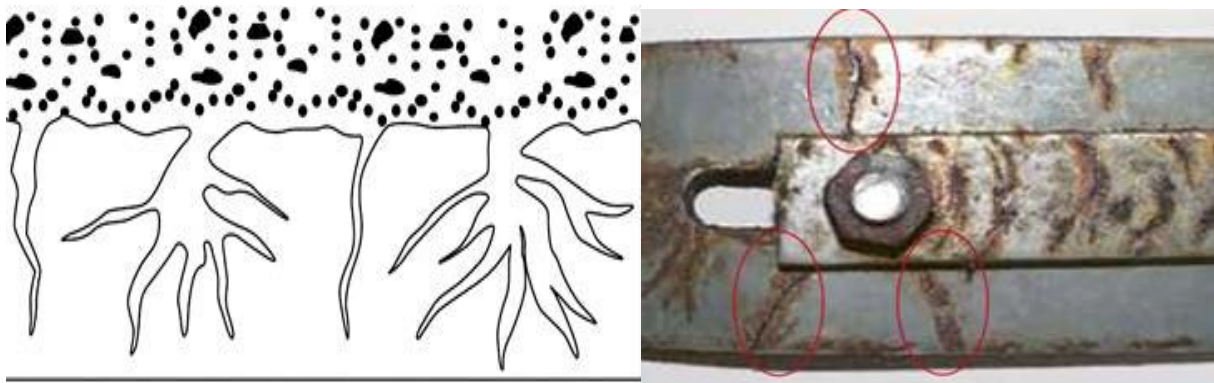


Fig.7. Stress corrosion cracking of an assembly after 4 years

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 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.

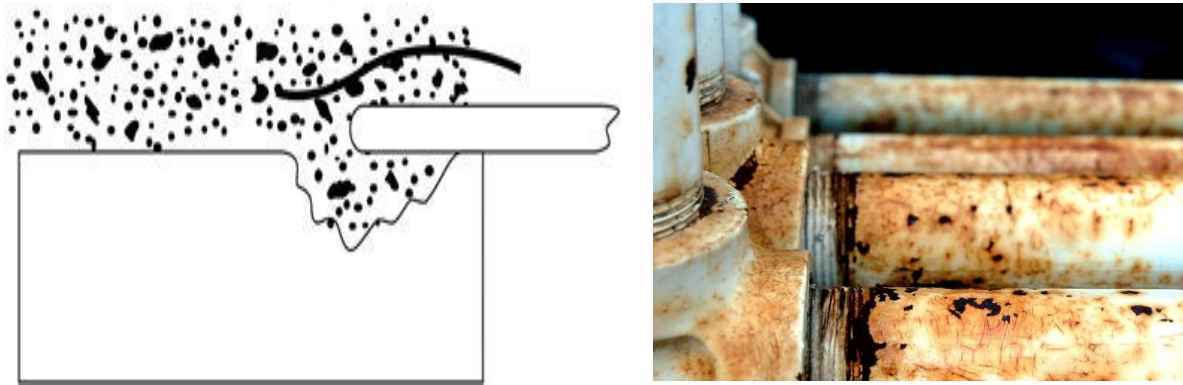


Fig.8. Crevice corrosion

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.

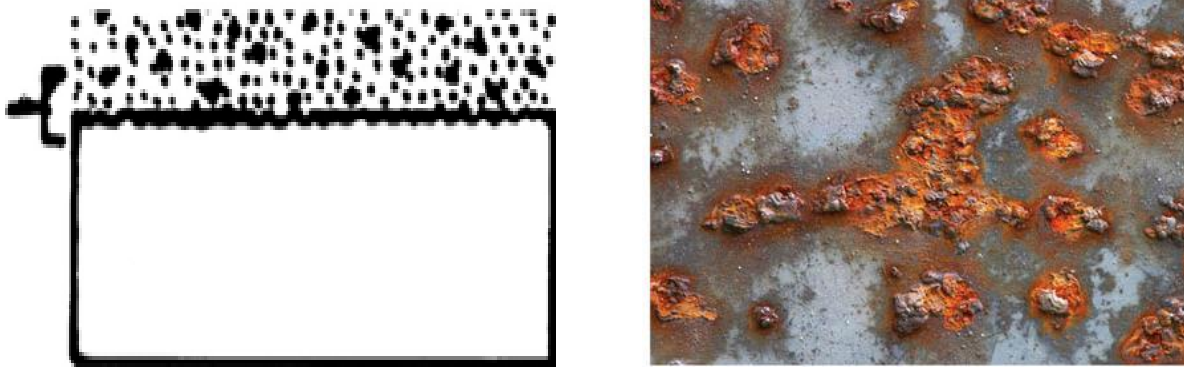


Fig.10. Intergranular corrosion

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.

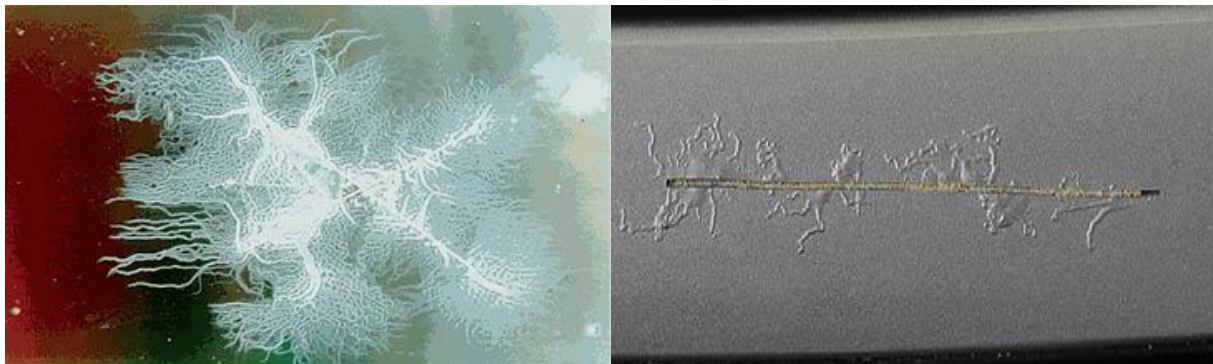


Fig.11. Filiform corrosion

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.

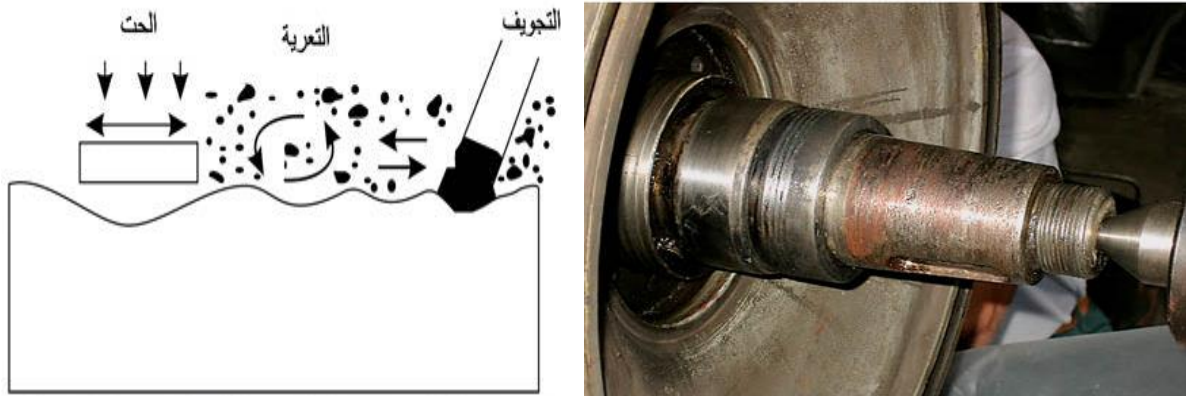


Fig.12. Fretting corrosion

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 as 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.

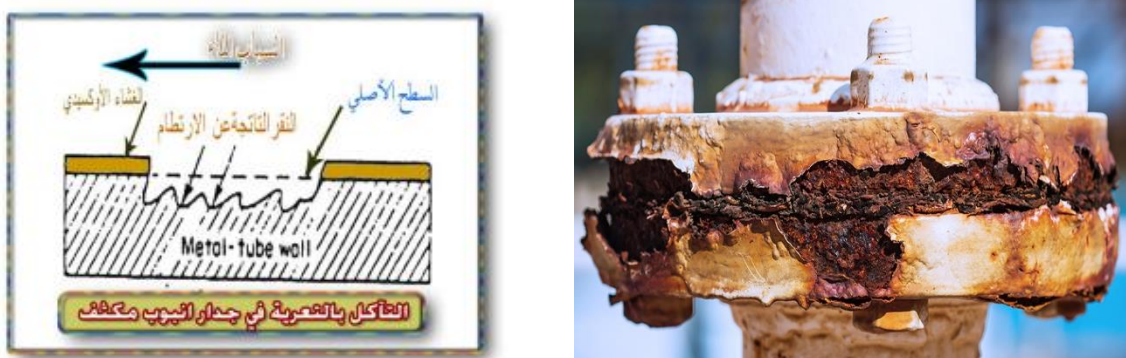


Fig.13. Erosion Corrosion

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 cm² (μA/cm²), 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 :

$$W = \frac{\Delta m}{S \times t} \quad (I.1)$$

Where

The symbol Δm denotes the difference between the initial mass m_1 and the final mass m_2 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 1

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

Calculation

$$\Delta m = M_1 - m_2 = 2.47987 - 1.99870 = 0.48117 \text{ mg}$$

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

$$W = \frac{\Delta m}{S \times t} = 7.6011 \cdot 10^{-4} \frac{\text{mg}}{\text{cm}^2 \cdot \text{h}}$$

5.2. Electrochemical Methods

This method is regarded as a more advanced and contemporary approach compared to the previous method. It is considered somewhat cost-effective in terms of both the time required for the experiment and the amount of metal sample utilized. To execute this method, we employ one of two approaches :

5.2.1. Potentiodynamic Polarization

5.2.2. Electrochemical Impedance Spectroscopy

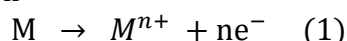
6. Theoretical foundations of corrosion

Corrosion is a chemical process that may be analyzed from both thermodynamic and kinetic perspectives. By studying corrosion, we can discover several features, including the rate and frequency at which it occurs.

6. 1. Corrosion's thermodynamic aspect

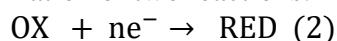
6. 1. 1. Corrosion reactions

Corrosion of metal is its oxidation



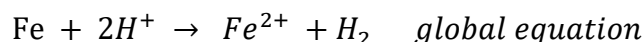
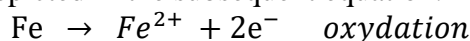
The M metal reaction is only possible when the electrons are grabbed by another pair known as the corrosion motor.

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

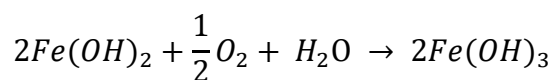
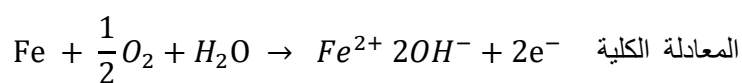
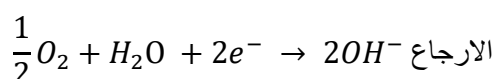
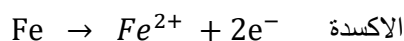


Example 2

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

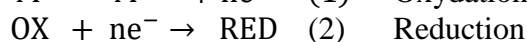
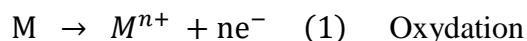


- Under conditions that are neutral or basic, iron undergoes corrosion, resulting in the creation of iron hydroxide Fe(OH)₃.



6.1.2. Thermodynamic equilibrium potential

When a metal M is exposed to a solution containing Mⁿ⁺ 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.



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 : The thermodynamic equilibrium potential (volts).

E° : The standard potential (volts).

n : The number of electrons exchanged in the reaction.

R : The ideal gas constant (J.mol⁻¹.K-18.314).

F : The Faraday's constant (96500 C/mol).

T : The absolute temperature (degrees Kelvin).

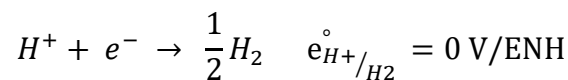
Corrosion occurs only when its potential value is: $E_2 > E_1$ in general $E^\circ_2 > E^\circ_1$

6.1.3. Engine of corrosion

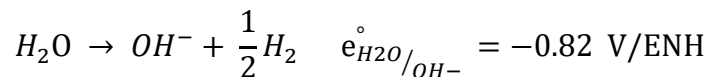
Hydrogen ions (H^+) oxygen (O_2), together with water (H_2O) are the primary causes of corrosion, and there are two distinct forms of corrosion.

❖ **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**

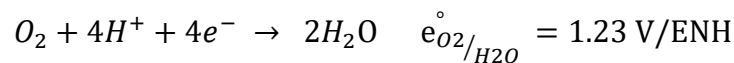


- **Basic solution**

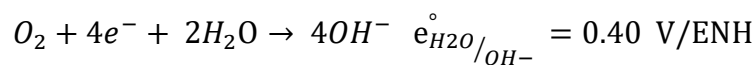


❖ **Aerobic Solutions** : Aerobic solutions are liquid solutions that have a high concentration of dissolved oxygen.

- **Acidic solution**

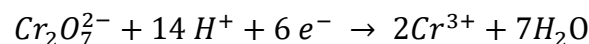


- **Basic or neutral solution**



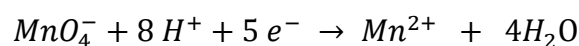
In addition, we can cite other examples of oxidizing agents (engines), such as :

- **Dichromate ions**



$$e^\circ_{Cr_2O_7^{2-}/2Cr^{3+}} = 1.33 \text{ V/ENH}$$

- **Permanganate**



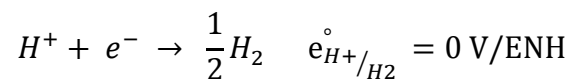
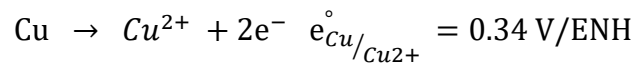
$$e^\circ_{MnO_4^-/Mn^{2+}} = 1.51 \text{ V/ENH}$$

Example 3: 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 $e_{Cu/Cu^{2+}}^{\circ} = 0.34 \frac{V}{ENH}$

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 is : $Cu / Cu^{2+} ; H^+ / H_2$
2. The equations that depict the oxidation and reduction processes are :



3. Corrosion cannot occur because $E_2^{\circ} < E_1^{\circ}$
4. Indeed, corrosion can take place when the copper plate is exposed to air solutions due to the fact that $E_2^{\circ} > E_1^{\circ}$

