

PEOPLE'S DEMOCRATIC REPUBLIC OF ALGERIA  
MINISTRY OF HIGHER EDUCATION AND SCIENTIFIC RESEARCH  
M'HAMED BOUGARA UNIVERSITY BOUMERDES



**Faculty of Sciences-Department of Chemistry**

**End of study thesis**

**In order to obtain the Master's Degree in:**

**Field: Sciences of Matter**

**Secter: chemistry**

**Option: Analytical Chemistry**

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**Theme**

**Effect of chromium and molybdenum content on the  
corrosion resistance of stainless steels in Ablien  
water used in the petroleum industry**

Defense date:05/11/2020 Before the Jury composed of:

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**University Year: 2019/2020**

## Acknowledgements

Sincerely, I would like to thank my supervisor Dr. FAHIM HAMIDOUCHE, for his time, patience, constructive criticism, and supervision. I am indebted beyond measure to him for his unceasing guidance and critical insight without which this work could have never been achieved.

I am grateful to the members of the board of examiners for their kind acceptance of reading and evaluating my thesis despite their tight schedules during such unprecedented circumstances.

My further thanks to all my teachers at the **M'HAMED BOUGARA** university for their kindness, commitment, valuable support and devotion which will continue to inspire me to be the best version of myself; both academically and professionally.

I would also like to extend my warm thanks to my graduate and postgraduate colleagues with whom I was fortunate to share the spirit of hard work in the quest for knowledge.

Last but not least, I would like to express my deepest gratitude to my family and friends for their unfaltering support and trust. Special thanks to my parents for believing in me and did everything to pave an unforgettable and delightful intellectual journey.

## **Dedication:**

**This work is dedicated to:**

**To my parents**

**To my family**

**To my friends.**

## Abbreviations list

PVC = Poly (vinyl chloride)

SCC = stress corrosion cracking

F = Faraday

E = potential

n = number of electrons

ICCP = impressed current cathodic protection

MPI = Magnetic Particle Inspection

FSM = Field Signature Method

HIC = hydrogen induced cracking

Wt = the mass fraction of the species times 100

°C = Degree Celsius

°F = Fahrenheit

NG = Natural gas

PWHT = post-weld heat treatment

DSS = Duplex stainless steels

SDSS = super duplex stainless steels

LDSSs = lean duplex stainless steels

FSS = Ferritic stainless steel

HAZ = heat affected zone

LPR = linear polarization resistance

EIS = electrochemical impedance spectroscopy

EN = electrochemical noise

R<sub>p</sub> = Polarization resistance

i<sub>corr</sub> = Electric power of corrosion

E<sub>corr</sub> = potential of corrosion

V<sub>corr</sub> = speed of corrosion

C = capacitance of a planar electrode

R<sub>TC</sub> = Load transfer resistance

R<sub>e</sub> = Electrolyte resistance

E<sub>mf</sub> = electromotive force

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# General introduction

## General Introduction

We Live in a Metals-Based Society, Residents of industrialized nations live in metal-based societies. Various types of steel are used in residential and commercial structures, in bridges and trusses, in automobiles, passenger trains, railroad cars, ships, piers, docks, bulkheads, in pipelines and storage tanks, and in the construction of motors [1].

In some cases, during the production of energy, the environments are very harsh; for example, in the nuclear sector, the materials are in contact with high-temperature coolants under irradiation. In the fossil sector, some hydrocarbons, such as natural gas, have to be obtained from deep wells that are sour and hot. In other sectors, such as in the case of the renewable energy sector, corrosion issues seem to be less pervasive or central to the issue of power generation [2].

The oil and gas industry uses various materials, including metals and non-metals. Over 90% of the materials used are metals, but non-metals serve critical functions in the industry and they are increasingly replacing metals in some key areas. The materials properties required to construct components for the oil and gas industry are relatively well established, and various standards are available to ensure that the materials possess the properties required for the application [3].

Corrosion is the chemical or electrochemical reaction between a material, usually a metal, and its environment that produces a deterioration of the material or its properties. Attack, decay, or becoming unserviceable by physical, mechanical, or biological causes are therefore excluded. Examples of such phenomena are superheating, wear, erosion, cavitation, swelling of plastics, decay of wood, and so on. On the other hand, corrosion is considered as including combined forms of attack in which the simultaneous occurrence of corrosion by chemical or electrochemical attack and the effect of the other previously mentioned causes leads to an item becoming unserviceable at an above-normal rate [4]. Pipelines play an extremely important role through the world as a means of transporting gases and liquids over long distances from their sources to ultimate consumers. So that corrosion problems exist in the oil industry at every stage of production from initial extraction to refining and storage prior to use requiring the application of corrosion inhibitors [5].

## References

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# **Chapter I: Bibliographic Research**

## Chapter I: Bibliographic Research

### I.1. General information about corrosion

#### I.1.1. Introduction:

The history of mankind is distinguished by the pronounced effort to understand the processes of nature and to manipulate these processes for the improvement of the human condition and survivability [1]. There for, Corrosion, from the Latin *corrodere*, means “to chew away”, “to attack”. It is estimated that corrosion destroys one quarter of the world’s annual steel production, which corresponds to about 150 million tons per year, or 5 tons per second. Of course, corrosion is not limited to steel but affects all materials: metals, polymers and ceramics. It is the result of chemical and/or physical interactions between the material and its environment [2]. Examples of the corrosion phenomena include:

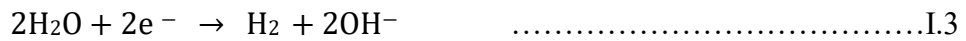
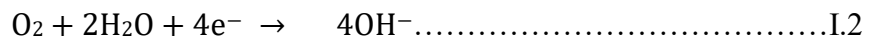
- transformation of steel into rust;
- cracking of brass in the presence of ammonia;
- oxidation of an electrical contact made of copper;
- weakening of high-resistance steel by hydrogen;
- hot corrosion of a super-alloy in a gas turbine;
- swelling of PVC in contact with a solvent;
- chemical attack of a nylon tube by an oxidizing acid;
- alkaline attack on refractory bricks;
- chemical attack of mineral glass by an alkaline solution.

Most people are familiar with corrosion in some form or another, particularly the rusting of an iron fence and the degradation of steel pilings or boats and boat fixtures. Piping is another major type of equipment subject to corrosion. This includes water pipes in the home, where corrosion attacks mostly from the inside, as well as the underground water, gas, and oil pipelines that crisscross our land. Thus, it would appear safe to say that almost everyone is at least somewhat familiar with corrosion [3].

#### I.1.2. Definition:

The term “corrosion” has its origin in Latin. The Latin word *rodere* means “gnawing,” and *corrodere* means “gnawing to pieces.” In daily life, corrosion manifests

itself in many forms, such as corroded automobiles, nails, pipes, pots, pans, and shovels [4]. One general definition of corrosion is the degradation of a material through environmental interaction. This definition encompasses all materials, both naturally occurring and man-made and includes plastics, ceramics, and metals. Corrosion of most common engineering materials at near ambient temperatures occurs in aqueous (water-containing) environments and is electrochemical in nature. The aqueous environment is also referred to as the electrolyte and, in the case of underground corrosion, is moist soil. The corrosion process involves the removal of electrons (oxidation) of the metal [Equation (1)] and the consumption of those electrons by some other reduction reaction, such as oxygen or water reduction [Equations (2) and (3), respectively]:



There are four necessary components of a differential corrosion cell:

- a. There must be an anode
- b. There must be a cathode
- c. There must be a metallic path electrically connecting the anode and cathode. (Normally, this will be the pipeline itself.)
- d. There must be a metallic path electrically connecting the anode and cathode. (Normally, this will be the pipeline itself.) [5].

Corrosion is a global problem for any metallic structure or material, which has become one of the most prevailing issues that need to be addressed in the present times. During the course of corrosion, there is considerable deterioration of materials used in equipment, and the costs incurred thereof in replacing the corroded parts have escalated over the years [6].

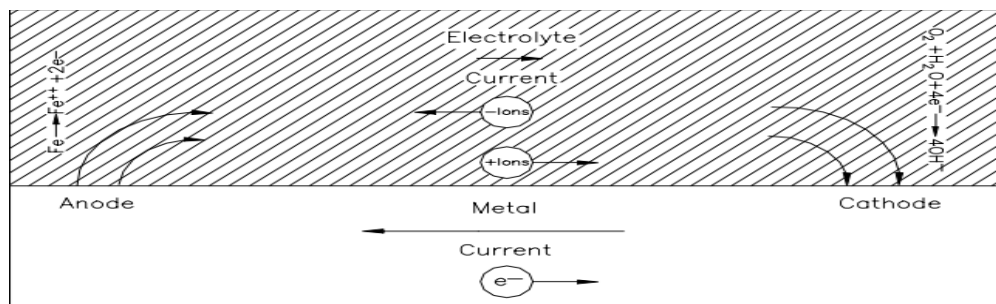


Figure 1: Schematic showing a differential corrosion cell

### **I.1.3. Corrosion Classifications:**

First consider whether the metal is generally corroded over all its exposed surface or whether the attack is localized, with some surface undamaged. Corrosion products may have to be removed before it is evident that the metal underneath is damaged. Particularly in flowing systems, rust or other solid corrosion products may deposit on areas that are unattacked, while corroded areas may be out of sight. Most corrosion, however, is general in nature, with all exposed metal surface corroding [7].

### **I.1.4. Types of Corrosion:**

Corrosion occurs in several forms, depending upon the metal involved, its size and shape, specific function, atmospheric conditions, and the corrosion producing agents present. The corrosion types described in this section are the most common forms found in pipeline weldments which have caused numerous failures in the oil and gas industries.

#### **I.1.4.1. Localized Corrosion:**

Localized corrosion is defined as the selective removal of metal by corrosion at small areas or zones on a metal surface in contact with a corrosive environment, usually a liquid. It usually takes place when small local sites are attacked at a much higher rate than the rest of the original surface. In order to operate the oil and gas pipelines under safe and reliable conditions, it is important to predict the internal corrosion that occurs in an environment containing CO<sub>2</sub>. In oil and gas industry, localized corrosion is the most serious and frequent cause of pipeline failure. Therefore, it is necessary to predict the occurrence of localized CO<sub>2</sub> corrosion of carbon and low alloy steel materials [8].

Forms of localized corrosion:

- ✓ Intergranular Corrosion: It is a preferential attack on the grain boundary phases or the zones immediately adjacent to them. Little or no attack is observed on the main body of the grain. This results in the loss of strength and ductility. The attack is often rapid, penetrating deeply into the metal and causing failure.
- ✓ Crevice Corrosion: Crevice corrosion is a localized type of corrosion occurring within or adjacent to narrow gaps or openings formed by metal-to-metal-to-nonmetal contact. It results from local differences in oxygen concentrations, associated deposits on the metal surface, gaskets, lap joints, or crevices under a bolt or around rivet heads where small amounts of liquid can collect and become stagnant [9].



Figure 2: **Localized corrosion**

#### **I.1.4.2. Uniform Corrosion:**

Uniform corrosion processes include many corrosion phenomena that are encountered in the practice of corrosion engineering and corrosion science. The majority of those phenomena deal with either aqueous or gaseous corrosion, although there are concerns about materials for use in molten salt and liquid metal environments. Gaseous corrosion is usually associated with high-temperature environments. Atmospheric corrosion is not considered a part of gaseous corrosion because the corrosion reaction occurs in a thin aqueous layer on the surface of the metal. Galvanic and stray current corrosion are not environment specific but rather can occur in any of the environments mentioned earlier [10].

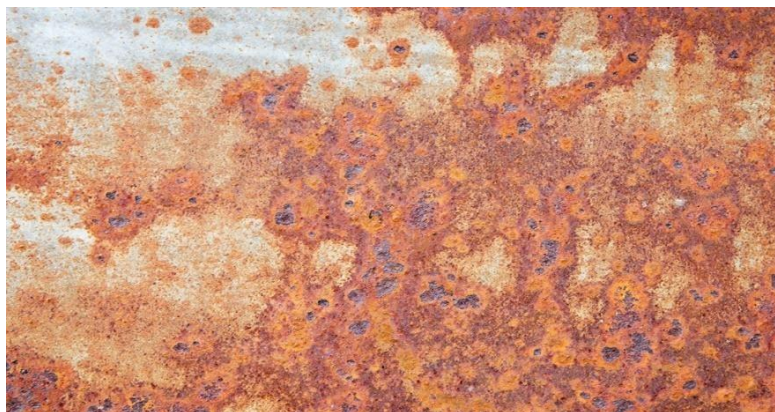


Figure 3: **Uniform corrosion**

#### **I.1.4.3. Galvanic Corrosion:**

This form of corrosion is sometimes referred to as dissimilar metal corrosion, and is found in unusual places, often causing professionals the most headaches.

Galvanic corrosion is often experienced in older homes where modern copper piping is connected to the older existing carbon steel lines. The coupling of the carbon steel to the copper causes the carbon steel to corrode. The galvanic series of metals provides details of how galvanic current will flow between two metals and which metal will corrode when they are in contact or near each other and an electrolyte is present (e.g., water). When two different metallic materials are electrically connected and placed in a conductive solution (electrolyte), an electric potential exists. This potential difference will provide a stronger driving force for the dissolution of the less noble (more electrically negative) material. It will also reduce the tendency for the more noble metal to dissolve [9].

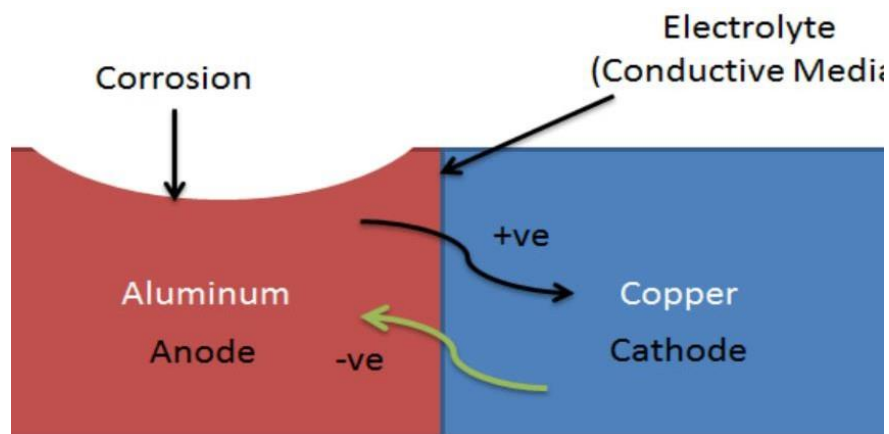


Figure 4: Galvanic Corrosion

#### I.1.4.4. Pitting Corrosion:

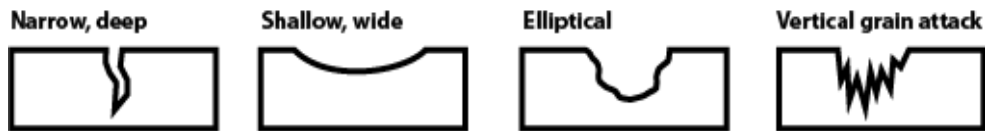
Pitting corrosion is in itself a corrosion mechanism, but it is also a form of corrosion often associated with other types of corrosion mechanisms. It is characterized by a highly localized loss of metal. In the extreme case, it appears as a deep, tiny hole in another wise unaffected surface. The initiation of a pit is associated with the breakdown of the protective film on the metal surface.

The depth of the pit eventually leads to a thorough perforation or a massive undercut in the thickness of the metal part. The width of the pit may increase with time, but not to the extent to which the depth increases. Most often, the pit opening remains covered with the corrosion product, making it difficult to detect during inspection. This, along with a negligible loss in weight or absence of apparent reduction in the overall wall thickness, gives little evidence as to the extent of the damage. Pitting may result

in the perforation of a water pipe, making it unusable even though a relatively small percentage of the total metal has been lost due to rusting.

Pitting can also cause structural failure from localized weakening effects even though there is considerable sound material remaining. Pits may also assist in brittle failure, fatigue failure, environment-assisted cracking like stress corrosion cracking (SCC), and corrosion fatigue, by providing sites of stress concentration [9]. The causes of pitting corrosion can be divided into four categories: physical factors, chemical factors, biological factors, and metallurgical factors [11].

**TROUGH PITS**



**SIDEWAY PITS**



Figure 5: Types of pitting corrosion

**I.1.4.5. Erosion corrosion:**

Is the result of an electrochemical reaction combined with a material loss by mechanical wear due to impingement of solids or a fluid [2]. The term “erosion” applies to deterioration due to mechanical force. When the factors contributing to erosion accelerate the rate of corrosion of a metal, the attack is called “erosion corrosion.” Erosion corrosion is usually caused by an aqueous or gaseous corrodent flowing over the metal surface or impinging on it. The mechanical deterioration may be aggravated by the presence of a corrodent, as in the case of fretting or corrosive wear.

The attack takes the form of grooves, i.e., scooped-out rounded areas, horseshoe-shaped depressions, gullies, or waves, all of which often show directionality. At times, attack may be an assembly of pits. Ultimate perforation due to thinning or progression of pits, and rupture due to failure of the thinned wall to resist the internal fluid pressure

are common. All equipment exposed to flowing fluid is subject to erosion corrosion, but piping systems and heat exchangers are the most commonly affected.

Erosion corrosion is affected by velocity, turbulence, and impingement, presence of suspended solids, temperature, and prevailing cavitation conditions. The acceleration of attack is due to the distribution or removal of the protective surface film by mechanical forces exposing fresh metal surfaces that are anodic to the uneroded neighboring film. A hard, dense adherent and continuous film, such as on stainless steel, is more resistant than as oft brittle film, as that on lead. The nature of the protective film depends largely on the corrosive itself [9].

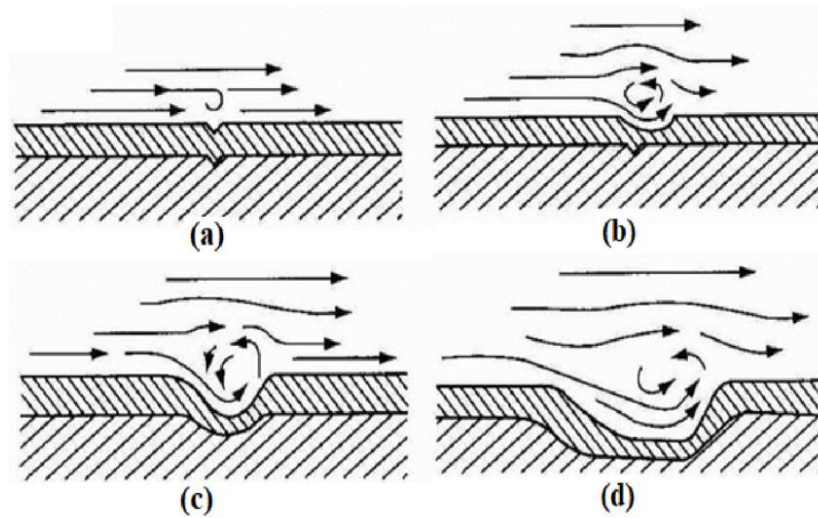


Figure 6: Erosion corrosion stages

#### I.1.4.6. Stress Corrosion Cracking (SCC):

Stress-corrosion cracking is defined as the growth of cracks under the combined influence of a non-cyclic tensile stress and a reactive environment. Usually the environment is an aqueous solution, and for the purposes of this review we shall restrict ourselves to metals. All SCC failures have in common a macroscopic appearance of brittleness, in the engineering sense that the ductility of the material is impaired, but the degree to which they involve microscopic cleavage or brittleness remains unclear. The rate of SCC can vary from  $10^{-11}$  to  $10^{-1}$  m/s, but normally lies within the range of  $10^{-10}$ - $10^{-7}$  m/s. SCC is a formidable engineering problem, especially in the nuclear power and chemical industries.

There are several processes that can contribute to the growth of stress-corrosion cracks, including anodic dissolution, film growth and hydrogen effects. These have

often been expressed as a “spectrum” of behavior ranging from obvious anodic dissolution control to obvious hydrogen embrittlement [12].

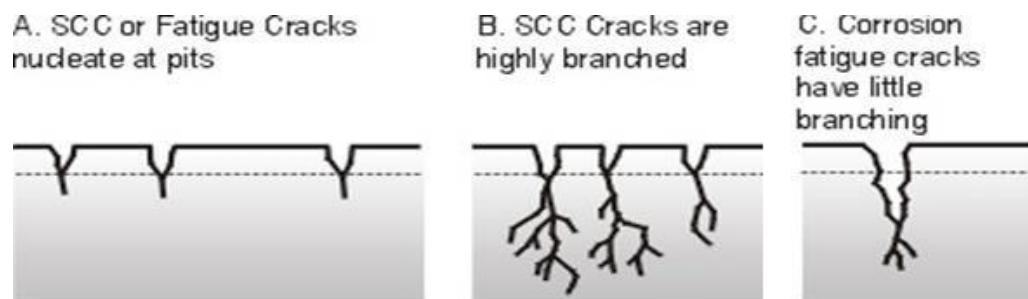


Figure 7 : **Schematic view of Stress Corrosion Cracking (SCC) and corrosion fatigue cracking**

#### 1.1.4.7. **Biological Corrosion:**

Corrosive conditions can be developed by living microorganisms as a result of their influence on anodic and cathodic reactions. This metabolic activity can directly or indirectly cause deterioration of a metal by the corrosion process. This activity can:

- ❖ Produce a corrosive environment
  - ❖ Create electrolytic cells on the metal surface
  - ❖ Alter the resistance of surface films
  - ❖ Have an influence on the rate of anodic or cathodic reaction
- Alter the environmental composition

Because this form of corrosion gives the appearance of pitting, it is first necessary to diagnose the presence of bacteria. This is also referred to as microbial corrosion [9].

#### 1.1.5. **Corrosion Inhibitors:**

By definition, a corrosion inhibitor is a chemical substance that, when added in small concentration to an environment, effectively decreases the corrosion rate [3]. Corrosion inhibitors are compounds containing heteroatoms like nitrogen, oxygen, sulfur, and phosphorus as well as aromatic rings. The inhibitory activity of these molecules is due to the formation of a monolayer on the metal surface or even to the formation of a mixed compound, as for example, Cu-benzotriazole on the Cu surface, *vide infra*. Free electron pairs on heteroatoms or p electrons are readily available for sharing to form a bond and act as nucleophile centers of inhibitor molecules and greatly facilitate the adsorption process over the metal surface, whose atoms act as electrophiles[1].

A different approach to corrosion control is chemical treatment to modify the environment, making it less corrosive by removing much of the cathode reactant. If the dissolved oxygen or hydrogen ions are tied up, they will be unavailable to receive electrons from the metal cathodes, and corrosion practically ceases [7].

### I.1.6. Corrosion Mechanisms:

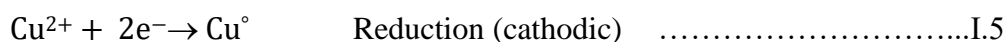
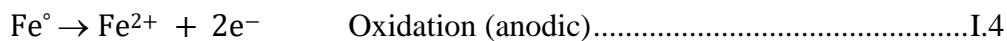
Most of the commonly used metals are unstable in the atmosphere. These unstable metals are produced by reducing ores artificially; therefore, they tend to return to their original state or to similar metallic compounds when exposed to the atmosphere. Exceptions to this are gold and platinum that are already in their metallic state. Corrosion, by its simplest definition, is the process of a metal returning to the material's thermodynamic state. For most materials, this means the formation of the oxides or sulfides from which they originally started when they were taken from the earth, before being refined into useful engineering materials. Most corrosion processes are electrochemical in nature, consisting of two or more electrode reactions: the oxidation of a metal (anodic partial reaction) and the reduction of an oxidizing agent (cathodic partial reaction). The study of electrochemical thermodynamics and electrochemical kinetics is necessary to understand corrosion reactions [9].

#### I.1.6.1. Nature of Corrosion Reactions:

Consider the system in which metallic iron is immersed in a solution of copper sulfate. In course of time metallic copper begins to appear. This process is known as a cementation reaction. The species present initially and after a lapse of time are as follows:

Initial	$\text{Fe}^\circ$	$\text{Cu}^{2+}$
Final	$\text{Fe}^{2+}$	$\text{Cu}^\circ$

Then, we may write the reactions occurring as:



The equilibrium constant K and the free energy change in the overall cementation reaction may be written as:

$$\Delta G = \Delta G^\circ + RT \ln \frac{[\text{Fe}^{2+}][\text{Cu}^\circ]}{[\text{Fe}^\circ][\text{Cu}^{2+}]} \dots\dots\dots \text{I.7}$$

Since the corrosion of iron in copper sulfate solution involves an oxidation and reduction reactions with exchange of electrons, the reaction must involve an electro-

chemical potential difference, related to the equilibrium constant. This relationship may be written as:

$$\Delta G = -nFE \dots\dots\dots I.8$$

In addition, is known as the Faraday's law. Here F (the Faraday) = 96 494 coulombs, E is the potential difference, n, the number of electrons transferred. Under standard state conditions:

$$\Delta G^\circ = -nFE^\circ \dots\dots\dots I.9$$

Neglecting solids, we may write, for the reaction of iron in copper sulfate solution:

$$-nFE = -nFE^\circ + RT \ln \frac{[Fe^{2+}]}{[Cu^{2+}]} \dots\dots\dots I.10$$

Division by nF leads to:

$$E = E^\circ - \frac{RT}{nF} \ln \frac{[Fe^{2+}]}{[Cu^{2+}]} \dots\dots\dots I.11$$

In general terms

$$E = E^\circ - \frac{RT}{nF} \ln \frac{[Products]}{[Reactants]} \dots\dots\dots I.12$$

Converting to log and T = 298K, and inserting numerical F; R values

$$E = E^\circ - \frac{0.059}{n} \ln \frac{[Products]}{[Reactants]} \dots\dots\dots I.13$$

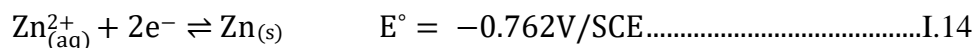
This equation is known as the Nernst equation, and is extensively used in electrochemical measurements. Under equilibrium conditions  $E = E^\circ$  and the experimentally obtained values of  $E^\circ$  are tabulated in the literature.  $E^\circ$  values can be used to determine whether a reaction will occur or not [13].

### I.1.6.2. Electrochemical Cells

Consider the two half-cells shown in Figure 8. (a). In the compartment on the left, zinc ions are in equilibrium with the solid zinc electrode. This means that the rate at which

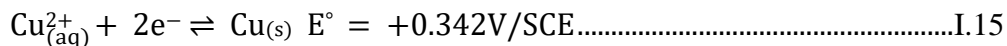
$Zn^{2+}$  ions pass into solution is equal to the rate at which they are reduced to solid zinc.

The standard reduction potential is



In the compartment on the right, copper ions are in equilibrium with the solid copper electrode. Thus, the rate at which  $Cu^{2+}$  ions pass into solution is equal to the

rate at which they are reduced to solid copper. The standard reduction potential is:



When the two unconnected half-cells are coupled by closing the switch in the external circuit, as in Figure 8. (b), an electrochemical cell is formed. One of the metals will be the anode and the other will be the cathode, although we cannot yet tell which is which. First suppose that the zinc electrode is the anode. Then

At the cathode



At the anode

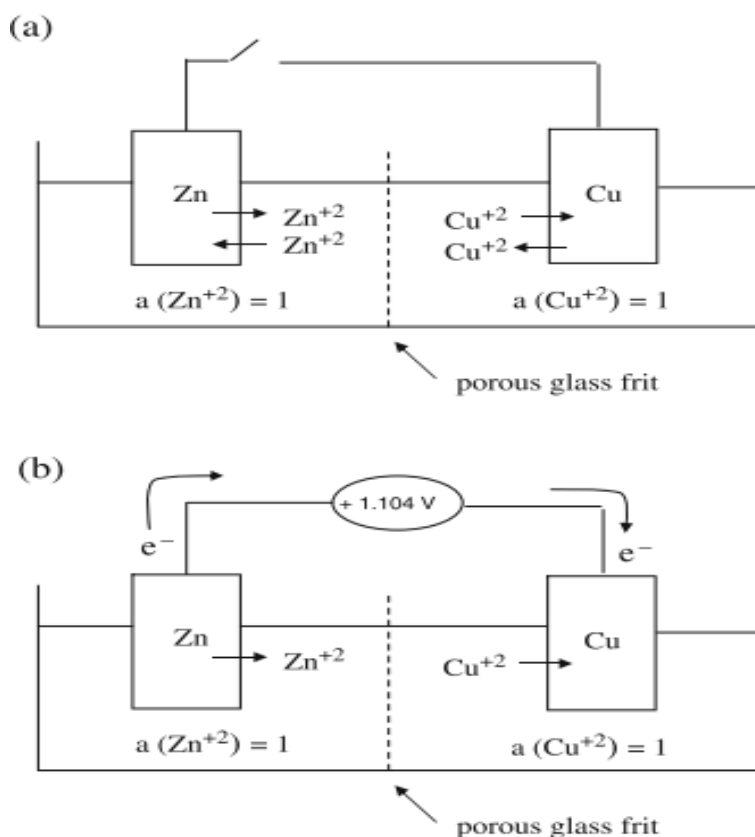
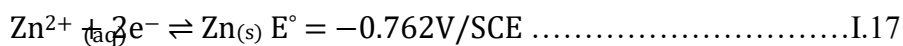


Figure 8 : An electrochemical galvanic cell

Adding the two half-cell reactions gives the overall chemical reaction:



And adding the half-cell potentials gives

$$E_{cell}^{\circ} = E_{cathode}^{\circ} - E_{anode}^{\circ} \dots\dots\dots I.19$$

Or  $E_{cell}^{\circ} = +0.342V/SCE - (-0.762 V/SCE) = +1.104 V/SCE \dots\dots I.20$

From:

$$\Delta G_{cell} = nFE_{cell} \dots\dots\dots I.21$$

The free energy change is negative because the cell potential is positive. Thus, the reaction proceeds spontaneously as written above in I.18, and we have correctly identified the anode and the cathode in the coupled cell.

If we had assumed initially that the copper electrode was the anode and the zinc electrode the cathode, then the calculated cell potential would be  $E^{\circ} = -1.104 V/SCE$ . But then the calculated change in free energy would have been positive so that the assumed reaction would not be spontaneous.

Thus, we would have reached the same conclusion as above.

The following general conclusions can be drawn:

- A. In an electrochemical cell, the metal with the lower electrode potential (more negative reduction potential) in the emf series is the anode; the metal with the higher electrode potential (more positive reduction potential) is the cathode.
- B. The cell potential (also called the cell voltage or cell emf) is given by

$$E_{cell} = E_{cathode} - E_{anode} \dots\dots\dots I.22$$

Where both  $E_{cathode}$  and  $E_{anode}$  are reduction potentials.

If the concentration of dissolved ions is not unit activity, the half-cell potentials can be calculated using the Nernst equation, and the procedure is then continued as described above [14].

## **I.1.7. Cathodic and anodic Protection:**

### **I.1.7.1. Cathodic Protection:**

Cathodic protection is widely used on small to extremely large structures to protect metals and particularly steel against corrosion. This can often be accomplished by using a protective current that is either generated by a power supply in what is called impressed current cathodic protection (ICCP) or by using another metal that corrodes more readily than the metal being protected and therefore is sacrificed in the process.

### **I.1.7.2. Anodic Protection:**

In contrast to cathodic protection, anodic protection is relatively new. The feasibility of anodic protection was first demonstrated in 1954 and tested on a small-scale stainless steel boiler designed to handle sulfuric acid [3].

## **I.1.8. Corrosion detection:**

Corrosion can cause serious failures, which lead to large economic loss, sometimes combined with environmental pollution, or risk of personnel injuries. The most important steps in order to hinder or reduce the extent of such failures are sufficiently early detection, proper diagnosis and effective prevention measures [15].

the most known methods are:

- ✓ Visual Inspection
- ✓ Radiography
- ✓ Ultrasonic Testing
- ✓ Eddy currents
- ✓ Magnetic Particle Inspection (MPI)
- ✓ Liquid Penetrant
- ✓ The Electric Field Signature Method (FSM)
- ✓ Acoustic Emission
- ✓ Leak Detection

## **I.2. Types of steel and their uses in the piping industry:**

The demand for energy has increased in recent decades which forced the industry to develop high resistance pipeline steels. Such steels show better mechanical properties and a higher corrosion resistance compared with normal carbon steels. However, these steels still suffer from two important failure modes including hydrogen induced cracking (HIC) and stress corrosion cracking (SCC) [16]. Steels are mainly composed of iron and carbon and special properties are reached by introducing additional alloying elements [17]. Iron and the most common iron alloy, steel, are from a corrosion viewpoint relatively poor materials since they rust in air, corrode in acids and scale in high temperature furnace atmospheres [18]. There are several grades of steel available [19].

### **I.2.1. Carbon steel:**

Carbon steel is one of the most widely used materials in the industry. This material is used not only in many of the water- and steam-pressure- containing systems in power plants but also in the supports for these systems [20]. Carbon steel is extensively used in oil and gas pipelines due to the merit of low cost. These pipelines are frequently exposed to the aqueous environments containing aggressive species, such as CO<sub>2</sub>, H<sub>2</sub>S and organic acids which pose significant threat to the normal operation of pipelines [21]. Carbon steel pipelines are considered the most cost-efficient solution. The mechanical properties and low cost are important considerations when long distances are planned. However, carbon steels are susceptible to corrosion in flue gas environments due to carbon dioxide (CO<sub>2</sub>), water (H<sub>2</sub>O), oxygen (O<sub>2</sub>), sulfur dioxide (SO<sub>2</sub>) and other constituents that can cause the formation of corrosive products [22].

### **I.2.2. Alloy steel:**

Since their invention in 1865, alloy steels have found broad application in multiple industries; the automotive, aerospace, heavy equipment, and pipeline industries to name a few. Alloy steels include a tremendous variation in alloying content. They range from the 1–2 wt. % Cr or Ni in some low alloy steels to the 15–18 wt. % Cr content of many stainless steels. The topic of alloy steels contains both the common 4140 and 316 alloys to more exotic alloys such as the Hadfield steels. These steels can form a wide variety of microstructures such as pearlite, bainite, or martensite, which result in an equally broad range of properties.

It is this range that has made them useful to so many industries. In some cases, these are the only steel alloys that can provide the required combination of properties [23]. Corrosion cracking is one of the most dangerous types of corrosive damage, which significantly impairs the physicommechanical properties of alloy steel. Despite many years' research, no progress has been made in preventing the corrosion cracking of equipment and pipelines, which has serious economic and environmental consequences [24].

### **I.2.3. Tool steel:**

Tool steels are iron-based alloys with properties, which are different from those of carbon steels due to the presence of alloying elements. They belong to a large group of steels which, upon heat treatment exhibit high strength, high hardness and high wear resistance relative to other steel types. Moreover, many tool steel types have good microstructural stability at elevated temperature (red hardness), and they retain their properties to an appreciable depth in the material [25]. Despite of a fast development of material engineering and searching for new metallic materials for various tools, such as: moulding tools, dies, punches, shear knives, etc., the hot work tool steels are still widely used [1÷6]. A properly designed chemical composition and heat treatment conditions ensure that these steels attain the required combination of properties, such as: high hardness and fracture toughness, high strength at elevated temperatures, structural stability, and resistance to formation of heat cracks [26].

### **I.2.4. Stainless steel:**

Stainless steel is an alloy of iron that has superior resistance to corrosion and this is what it is normally identified by. In fact, it is known that the resistance to oxidation as well as resistance to creep at high temperatures by stainless steel are normally excellent as compared to other alloys [27]. Since the microstructure has a decisive effect on properties, stainless steels have traditionally been divided into categories depending on their microstructure at room temperature. This gives a rough division in terms of both composition and properties. The Outokumpu stainless steels can be divided into four main groups: ferritic, martensitic and precipitation hardening, duplex (ferritic- austenitic) and austenitic stainless steels [18].

Stainless steel, termed as ‘miracle metal’ is all around us in numerous applications ranging from everyday household items to sophisticated biomedical applications. In earlier days, stainless steel was used to produce the finest, the most durable products that money can buy at that time and was only accessible by the upper class of the society. With time, both the production and the application of stainless-steel increase as well as its availability to wider people. The unique combination of corrosion resistance and retention of strength in a range of temperatures, from cryogenic to high temperature, expand the dramatic increase in the use of stainless steel [27].

### I.3. Corrosion in the Petroleum Production:

#### I.3.1. Introduction:

The business of the producing and transporting crude oil requires the use of thousands of tons of steel most of it in the form of tubular goods. Corrosion losses are an appreciable of the oil industry and it is difficult to determine which suffers the greatest economic loss [28]. Corrosion in the hydrocarbon processing industries may be conveniently divided in to two parts: “wet” and “dry.” Wet corrosion is that which occurs in the presence of liquid water. Corrosion in the absence of water is considered dry.

Wet corrosion normally implies low temperatures, i.e. below the boiling point or dew point of water. This temperature will, of course, be a function of the system pressure, as well as its composition. In practice, wet corrosion is limited to about 232 °C (450°F) as an upper temperature [29]. Underground corrosion of pipelines and other structures is often the result of differential corrosion cells of which a variety of different types exist. These include differential aeration cells, where different parts of a pipe are exposed to different oxygen concentrations in the soil, and cells created by differences in the nature of the pipe surface or the soil chemistry [5].

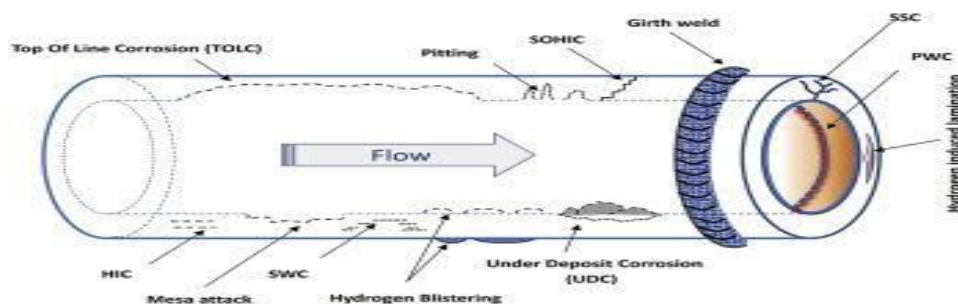


Figure 9: pipelines corrosions

Corrosion is a worldwide, crucial problem that strongly affects natural and industrial environments, in particular the oil and gas industry. Natural gas (NG) is a source of energy in industrial, residential, commercial and electric applications. The abundance of NG in many countries augurs a profitable situation for the vast energy industry. NG is considered friendlier to the environment and with lesser greenhouse gas emissions as compared with other fossil fuels [30]. Transporting products comprised of multiple constituents can lead to significant problems.

In the natural gas industry, additional engineering is needed for natural gas pipelines when even small amount of heavier hydrocarbons are present. The composition of the product to be transported has a great impact on pipeline design, compressor power, recompression distance, pipeline capacity, and could also have implications on decompression behavior at potential points of pipeline failure [22]. Natural gas is not corrosive, provided it remains in the vapor state, but most gas fields are considered corrosive from the beginning of production. Wells may not be corrosive if the production streams reach the surface under appropriate temperature and pressure conditions once lowered temperature and pressure conditions allow condensation of higher-end organic molecules and water, gas condensates usually become very corrosive. Corrosion often appears at intermediate levels in production tubing (Figures 10 and 11) as localized corrosion at imperfections in iron carbonate or other protective films [31]

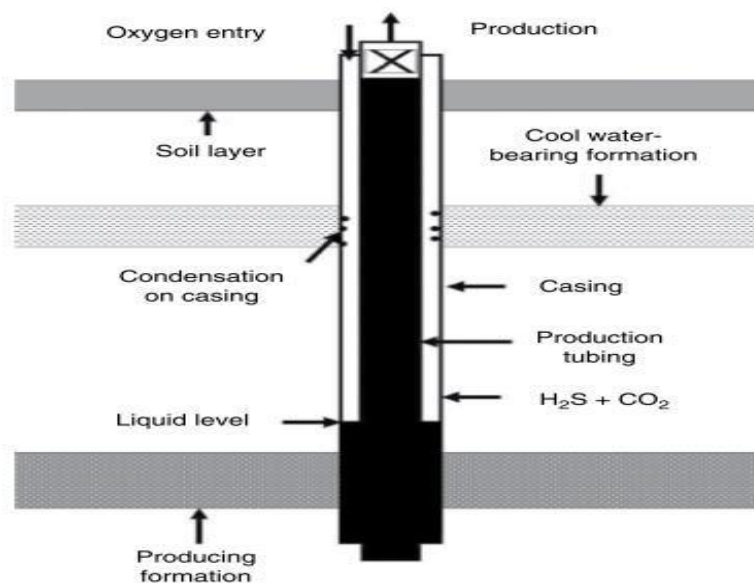


Figure 10: Locations where down hole components of an oil well are likely to corrode

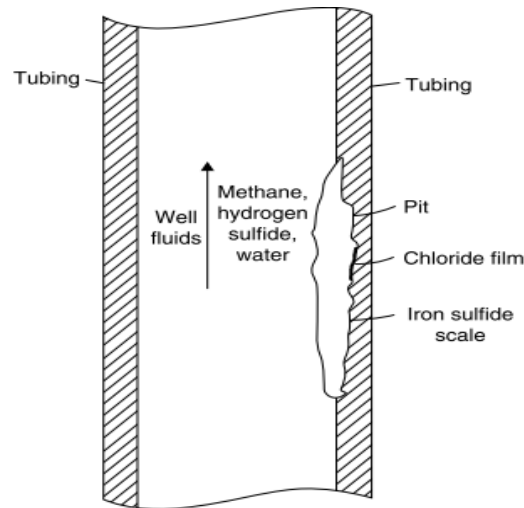


Figure 11: **Barnacle corrosion in production tubing**

### **I.3.2. Corrosion of stainless steel in the petroleum industry:**

In the petroleum industry, metallic materials are exposed to highly aggressive environments. In the absence of water at relatively low temperatures, the petroleum and its derivatives are not aggressive to most metals. However, if water is present, some chemicals present in these environments can be dissolved in the aqueous phase, making this water very aggressive to the metals [32]. Natural gases always have water associated with them, as they are saturated with water in the reservoir. When the hydrocarbons are extracted from underground water is also produced straight from the reservoir.

Generally, the water contents of sour gases are defined as a molar average of the solubility of water in the hydrocarbons, hydrogen sulfide, and carbon dioxide (Robinson et al.,1977). The accurate prediction of equilibrium water contents of natural gases is extremely important, especially for sour gases [33]. Stainless steels have a great variety of potential applications in the petroleum industry, mainly as an alternative to carbon steel in corrosive environments. Within a number of media that can cause corrosion problems with these materials, only chloride solutions and hydrogen sulfide are of importance in oilfield service [34]. Stainless steels are corrosion-resistant iron- base alloys containing a maximum of 1.2% carbon and a minimum of 10.5% chromium by weight. This is the minimum amount of chromium that prevents the formation of rust in humid unpolluted atmospheres, hence the designation “stainless.” The corrosion resistance of stainless steels is provided by a very thin and protective surface film, known as the passive film, which is self-healing when

damaged in a wide variety of environments [35].

### **I.3.2.1 Few Alloying Elements used in stainless steel:**

Stainless steels contain a number of different alloying elements, each of which has a specific effect on the properties of the steel. The properties of a specific steel grade will thus be determined by the combined effect of the alloying and trace elements in that specific grade. A brief overview of the alloying elements and their effects on the structure and properties of the steel are given in the following sections together with an explanation of why various elements are added to certain grades. It should also be noted that the effect of the alloying elements differs in some aspects between the hardenable and the nonhardenable stainless steels.

#### **I.3.2.1. a. Chromium (Cr):**

This is the most important alloying element as it provides stainless steels with their basic corrosion resistance. Generally speaking, the higher the chromium content, the better the corrosion resistance. Chromium also enhances the steel's resistance to oxidation at high temperatures and promotes a ferritic structure.

#### **I.3.2.1. a. Molybdenum (Mo):**

Molybdenum substantially enhances the resistance to both general and localized corrosion and increases the mechanical strength of steels. In addition to promoting a ferritic structure, molybdenum promotes the formation of secondary phases in ferritic, duplex, and austenitic steels. In martensitic steels, it will increase the hardness at higher tempering temperatures because of its effect on carbide precipitation.

#### **I.3.2.1. b. Carbon (C):**

Carbon is a strong austenite former and strongly promotes an austenitic structure. It also substantially increases the mechanical strength. Increasing carbon content reduces the resistance to intergranular corrosion. In ferritic stainless steels carbon will strongly reduce both toughness and corrosion resistance. In the martensitic and martensitic–austenitic steels, carbon increases hardness and strength. In the martensitic steels, an increase in hardness and strength is generally accompanied by a decrease in toughness and in this way carbon reduces the toughness of these steels [36].

### **I.3.3. Types of steels used in gas pipelines:**

The importance of stainless steels in industrial applications drives the interest in this present work. Stainless steel belongs to a family of corrosion and heat resistant steels containing a minimum of 10.5 % chromium. There is a wide range of stainless steels with progressively higher levels of corrosion resistance and strength that also meets with other mechanical characteristics [37]. Welded super martensitic stainless steels with low carbon content and varying Mo content are now being used increasingly for oil and gas transmission pipelines. The weld metal is usually super duplex stainless steel, but matching weld metal (13%Cr material) is also used, in both cases with or without post-weld heat treatment (PWHT) [38]. Duplex stainless steels, DSS, are a group of stainless steels with a microstructure of almost equal amount of austenite and ferrite. These materials show an attractive combination of excellent corrosion resistance and high mechanical properties comparing with either austenitic stainless steels or ferritic stainless steels, especially super duplex stainless steels. They have been widely used oil-gas industry. Due to its high ratio of property to cost, super duplex stainless steels have become an alternative to other higher performance materials such as super austenitic stainless steels and Ni-based alloys, and have had an about 20 years' very successful applications or experiences in the oil-gas industry [39].

#### **I.3.3.a. Duplex stainless steels (DSS):**

DSS is a popular constitutional material in the oil, gas, and manufacturing sectors. In particular, DSS is employed in chemical, wastewater, and marine engineering fields, as well as in desalination industries and marine constructions. Given the high corrosion resistance of DSS, this material is favorable for shipbuilding, petrochemical, paper, and nuclear industries and can gradually substitute the expensive 300 ASS. DSS is also the preferred material for petroleum and refining industries. The important mechanical properties of DSS help reduce thickness and are especially required in transportation to address the demand of the industry sector [40].

Duplex stainless steels (DSS) are steels that present biphasic microstructure containing ferrite and austenite in volumetric fractions approximately equal to 50%. Due to their biphasic microstructure, these steels present a favorable combination of the properties of ferritic and austenitic stainless steels. They present high mechanical strength, good toughness and ductility and good corrosion resistance in various media.

This favorable combination of properties makes this class of stainless steels widely used in the petrochemical, pulp and paper and, more recently, hydro generation industries [41].

Duplex steels are a form of weldable stainless steel that combine good corrosion resistance, typical of the austenitic stainless steels, with improved resistance to chloride stress corrosion cracking, crevice attack, and pitting. The mixed structure arises because the nickel content is insufficient to fully austenitize the steel, and as a result, the steel is an intimate mixture of the ferrite and austenite phases. This structure results from careful selection of alloy composition and very controlled heat treatments. The optimum corrosion and mechanical properties arise when the phase balance is 50:50 [42]. Fusion welding of duplex (DSS) and super duplex (SDSS) stainless steels can lead to disruption of the equilibrium of the ferrite and austenite phases, with precipitation of intermetallic phases reducing the corrosion resistance and fracture toughness of the welded joint [43].

### **I.3.3.a. austenitic stainless steels:**

Austenitic stainless steels are an extraordinary family of alloys that have exceptional corrosion resistance and equally impressive mechanical properties. They have unsurpassed strength, toughness, and formability among the commercially viable alloys from cryogenic to elevated temperatures. They are also valued aesthetically and are environmentally benign [44]. The most familiar example of intergranular corrosion is connected with certain austenitic stainless steels, particularly 18–8 CrNi steels with 0.06–0.08% C. After cooling the steel from high temperature, Cr and C are in solid solution in the austenite.

At room temperature the austenitic phase is supersaturated with these elements, and when the material is heated again to 500–800 °C, a chromium carbide,  $\text{Cr}_{23}\text{C}_6$  is precipitated at the grain boundaries [45]. Austenitic stainless steels are, usually, indicated for high temperature applications. However, it is important to emphasize that duplex stainless steels are not recommended for high temperature applications, due to the fact that these stainless steels are prone to the precipitation of deleterious phases [46]. The continuing development of austenitic stainless steels has resulted in complex compositions with substantial amounts of alloying elements, which are introduced for diverse specific reasons in order to obtain better mechanical properties and/or corrosion resistance. However, these additions invariably induce pitfalls resulting from microstructural instability [27].

**I.3.3.b. ferritic stainless steels:**

Owing to their lower cost with respect to austenitic stainless steels, ferritic stainless steels are more and more requested. They are nowadays used in many applications facings with strength/ductility requirements coupled with high targets of corrosion resistance. In particular, they are employed in automotive, construction and building, energy, aeronautical, food, and 3D printing applications [47]. The ferritic steels are characterized by good corrosion properties, very good resistance to chloride-induced stress corrosion cracking (SCC), and moderate toughness. The toughness of ferritic stainless steels is generally not particularly high. Lower carbon and nitrogen levels give a considerable improvement in both toughness and weld ability, although toughness is limited for thicker dimensions. Consequently, ferritic steels are usually only produced and used in thinner dimensions [36]. These steels can also be liable to intergranular corrosion. In addition to Cr carbides, Cr nitrides may be precipitated and thus contribute to the depletion of Cr at the grain boundaries [35].

**I.3.4. comparison between the 3 types of stainless steels:**

Duplex stainless steels (DSSs) have a dual phase structure composed of approximately equal amounts of ferrite ( $\alpha$ ) phase and austenite ( $\gamma$ ). The DSSs possess good combination of mechanical and corrosion properties, and they are well known for excellent resistance to stress corrosion cracking in comparison with single-phase stainless steels (SSs). In addition, DSSs are economically attractive because commercial DSSs commonly contain only 1–7 wt% Ni, which is less than the Ni content of FeCrNi-based  $\gamma$ -SS (8–24 wt%). These advantages of DSSs make them promising alternatives to  $\gamma$ -SSs, and thus, demands for DSSs show a continuous increase in various industrial fields such as the on/off-shore oil and gas industry and chemical process industry. Economic feasibility of DSSs can be further achieved by reducing the amount of expensive alloying elements, particularly Ni. Thus, various lean-DSSs (LDSSs), in which Ni is replaced with other  $\gamma$  stabilizers, such as Mn and N, have been developed and investigated [48]. Ferritic stainless steel (FSS) contains chromium between 11% and 30% (weight percentage) in solid solution without or with a small amount of nickel. FSS is widely used in elevators, automobiles, water tanks, pressure vessels, etc [1]. However, there are some problems in joining of FSS, especially, coarse grains will form in the weld zone and in the heat affected zone (HAZ).

Studies have shown that coarse grain HAZ of AISI 430 stainless steel was still observed at a low heat input level [49]. Improved mechanical and corrosion properties of ferritic stainless steels, such as toughness, high temperature or creep resistance and intergranular corrosion, have been attained through the reduction of solid solution carbon and nitrogen. Therefore, ultra-purified FSS stabilized with micro-alloy elements such as Nb and/or Ti are believed to be the suitable replacement for conventional Cr-Ni austenitic stainless steels in specific applications. However, FSS possess lower formability as compared to austenitic stainless steels [50].

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## Chapter II: **Materials and Methods**

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### **II. 1. Introduction:**

In this chapter, we will be talking about the materials and experimental methods that helped us to do this work. We will see corrosion effects on the stainless steels in its 3 different types of steel (13% Cr, 18%Cr and 21% Cr). We will use electrode contains the stainless steels. We will expose them to corrosion and we will see their resistance during all our experiments.

### **II. 2. Electrochemical chain (Materials):**

Electrochemistry deals with the conversion between chemical and electrical energy. This is achieved by two electrodes, an anode and a cathode, and an interconnecting electrolyte. At the electrode/electrolyte interfaces, chemical reactions take place, either driven by electrical energy or, on the contrary, yielding electrical energy. For such a process to function, the electrodes are to have high electronic conductivity while the electrolyte should have as low electronic conductivity as possible but instead high ionic conductivity [1]. By means of electrochemical reactions the chemical energy stored in chemical bonds is converted to electrical energy. The electrochemical reactions occur in two different places that are known as electrodes. At one electrode, the active material is oxidized, and a specific amount of electrons is produced. At the other electrode, the produced electrons are consumed, and the active material is reduced [2].

In electrochemical dissolution, depending on the electrochemical potential, the metal can undergo either trans passive or active dissolution. All forms of electrochemical corrosion, require the presence of aggressive ionic species (as reactants, products, or both), which in turn requires the existence of an aqueous environment capable of stabilizing them [3]. The concept of an electrochemical cell comes from the fact that different materials have different potentials to release or accept electrons. When two different materials are placed in a container, filled with electrolyte, because of their different potential in electron releasing, a potential difference takes place between them. This phenomenon makes the concept of batteries [4].

#### **II.2. 1. Electrolyte Conductivity:**

The electrical conductivity of an environment is determined by the concentration of ions in the environment, and the resulting changes in corrosivity can be understood by considering Ohm's law:

$$E = IR \dots \dots \dots I.1$$

Where:

E = the potential difference between anode and cathode, measured in volts.

I = the electrical current, measured in amperes.

R = the resistance of the electrical circuit, determined by the distances between anode and cathode and by  $\rho$ , the resistivity of the electrolyte, which is usually expressed in ohm-centimeters ( $\Omega$ -cm). In most cases the distance between anode and cathode is not known, but the changes in the corrosion rate can be monitored and correlated in changes in resistivity e.g. the changes in resistivity of soils caused by changes in moisture content, which alter the ionic content of the soil electrolyte.

The resistivity (inverse of conductivity) of liquids and solids is determined by the ions dissolved in the bulk solution. Hydrocarbons such as crude oil, natural gas, and natural gas condensates are covalent in nature and very poor electrolytes, because they have very high resistivities. Oilfield corrosion is usually caused by chemicals in the water phase that, among other things, lower the natural resistivity of water, which is also mostly covalent [5].

❖ **Albian water:**

Albian water is water with a special formula of minerals (table 1) that exist here in the south of Algeria.

Table 1: Albian Drilling Water Analysis

Cation	Mg/l	Anion	Mg/l
$Na^+$	17500	$HCO_3^-$	195.2
$k^+$	420	$Cl^-$	34991.8
$Ca^{++}$	2144	Total	35187
$Mg^{++}$	1337.6		
$Ba^{++}$	73		
$Sr^{++}$	90		
Total	21564.6	pH	8.13

### II.2. 2. Electrodes:

In real electrochemical reactions, the concentration of the species at the electrode continues to change as the reaction proceeds. This change in concentration is a result of the slow transport of species from the bulk solution to the surface of the electrode. Because the electrode potential is governed by the solution composition near the electrode surface, a change in the activity of species at the interface alters the equilibrium potential [6].

#### II.2. 2. a. Anode:

One of the two dissimilar metal electrodes in an electrolytic cell, represented as the negative terminal of the cell. Electrons are released at the anode, which is the more reactive metal. Electrons are insoluble in aqueous solutions and they only move, through the wire connection into the cathode

#### II.2. 2. b. Cathode:

One of the two electrodes in an electrolytic cell represented as a positive terminal of a cell. Reduction takes place at the cathode and electrons are consumed [7].

#### II.2. 2. c. Reference Electrodes:

Reference electrodes are commonly used with a saturated solution and an excess of salt crystals. The extra salt dissolves into the half-cell solution as some of the ions diffuse out of the reference cell body through the liquid junction during normal use. This extra buffer of salt extends the time before the reference cell starts to drift due to the depletion of ions as predicted by Nernst equation [8]. When a metal is immersed in an electrically conducting liquid, it takes up an electrochemical potential (also known

as the corrosion potential). This is determined by the equilibrium between the anodic and cathodic reactions occurring on the surface and it is usually measured with reference to a standard electrode, such as the saturated calomel electrode (SCE) or silver/silver chloride ( $Ag/AgCl_2$ ) [9].

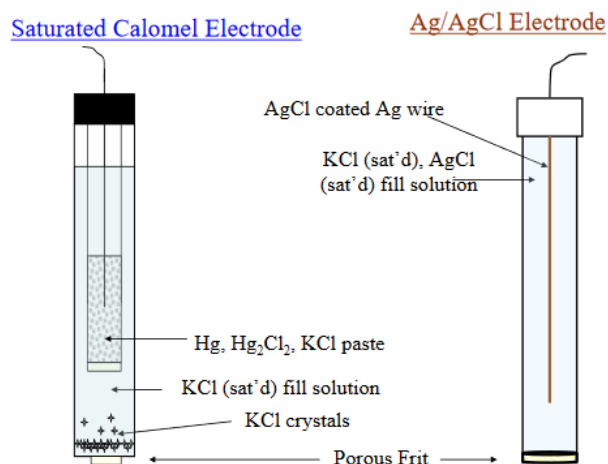


Figure 12 : Saturated calomel electrode and Ag/AgCl electrode

#### II.2.2.d. Counter electrode (Auxiliary electrode):

For research into electrochemical reactions, three electrode systems are employed. A reference electrode is used to control the potential applied to the working electrode (the electrode under study) and the current flow occurs between working and auxiliary electrodes. It is only possible for the auxiliary electrode to simultaneously act as a reference electrode in special situations, when the current flow is very small (pA or less) in order that the concentrations of soluble species hardly vary and the potential of the auxiliary/reference electrode is essentially constant [10].

#### II.2.2.e. work electrode:

In this case, it will be the electrodes of stainless steels that we want to expose to corrosion.

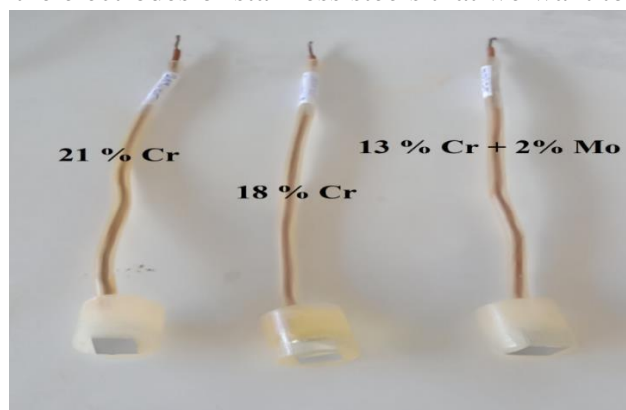


Figure 13: Electrodes made with different types of stainless steels (13%Cr, 18%Cr and 21%Cr).

### **II. 3. Tafel extrapolation procedure:**

The Tafel extrapolation method provides a direct measurement of the corrosion rate and of the corrosion potential, and it is very useful in predicting the corrosion properties of various corrosion systems. This technique monitors the corrosion rates with an accuracy that is equal to or greater than conventional weight loss methods. Using the Tafel extrapolation method, it is possible to measure extremely low corrosion rates. The rapid determination of corrosion rates with Tafel plots can be advantageous for the evaluation of inhibitors and the comparison of alloys. The cathodic and anodic polarization data are obtained by using a three-electrode electrochemical cell containing working, counter, and reference electrodes. The corrosion measurements are performed by using a potentiostat that is connected to the electrochemical cell [11].

### **II. 4. Few techniques for monitoring corrosion processes:**

Corrosion is an inevitable issue in the petroleum industry due to the complex service environments and operating conditions that include the simultaneous actions of high pressures and temperatures, water with dissolved salts and gases (particularly CO<sub>2</sub> and H<sub>2</sub>S), entrained sands, corrosion-influencing microbes, and complex multiphase flow regimes [12]. The corrosion of metallic materials is a major issue due to the huge economic losses it causes. Continuous monitoring of corrosion is particularly important for water treatment and oil and gas transportation because it provides early warnings for treatment to prevent losses. Electrochemical techniques such as linear polarization resistance (LPR), electrochemical impedance spectroscopy (EIS) and electrochemical noise (EN) have been widely used to for corrosion monitoring in the field [13]. Subsequently, microstructural characteristics and composition information are used to determine the corrosion mechanism. These asynchronous techniques for corrosion analysis are feasible but tedious and time consuming because of the pre- processing required and the repeated sampling steps [14].

On this basis, electrochemical techniques have found great importance for the characterization of the corrosion phenomena of metallic materials in the different media to which they are exposed. Such characterization involves analyzing the behavior of the metallic material in the active, passive and trans-passive states (which includes locali-

-zed phenomena like pitting, cracking corrosions) by applying a potential or frequency perturbation and measuring the value of resultant exchange current density (which is a measure of electron transfer between the cathode and anode).

The value of current density at the active, passive and trans-passive regions, as well as the values of the potential at which these phenomena occur, are important tools for the corrosion analyst in understanding the corrosion rate and susceptibility in the given corrosion environment. Such information is pertinent, especially, for metallic materials which are to be subjected to industrial application [15]. Practical examples are described of how a number of electrochemical techniques could be used to forecast corrosion or tribocorrosion behavior in practical case studies. The focus is on laboratory tests for rapid corrosion or tribocorrosion tests. The examples do not provide bit-by-bit procedures for screening most or all potentialities. Also, the discussion is not about how to set up and conduct electrochemical corrosion or tribocorrosion experiments. Such information can be readily found in instruction guidelines manual or standard references [16].

## Materials and Methods References

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## Chapter III: Results and discussion

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### III. 1. Comparison between steels:

#### III.1.1. Open-circuit potential

Figure 14 shows the change of potential during period of time. For different type of stainless steels (13% Cr + 2% Mo, 18% Cr and 21% Cr).

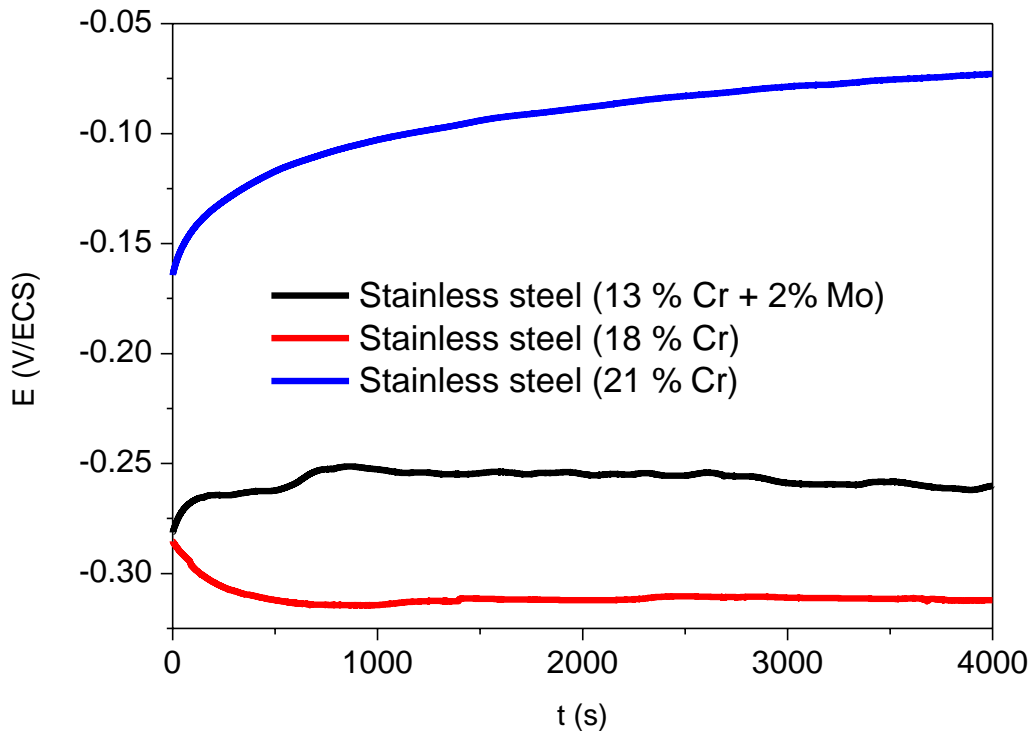


Figure 14: **Monitoring of the open-circuit potential of stainless steels immersed in a 3.5% mass solution of NaCl**

Potential of stainless steel (13%Cr + 2%Mo) rises starting from (-0.17(V/ECS)) and it keeps on rising with the change of time. For the potential of stainless steel (18%Cr) start rising for a bit to stop after 1000s and it stays stable with the change of time. While the potential of the stainless steel (21% Cr) drops below (-0.30 (V/ECS)) to stop after 1000s and it gets stabilized with the change of time.

### III.1.2. Impedance spectroscopy:

Figure 15 shows Nyquist diagram of stainless steels where we see the radius of the capacitive loop growth is different for each one of the stainless steels. Experiment was performed in a solution of NaCl with a 3.5% mass.

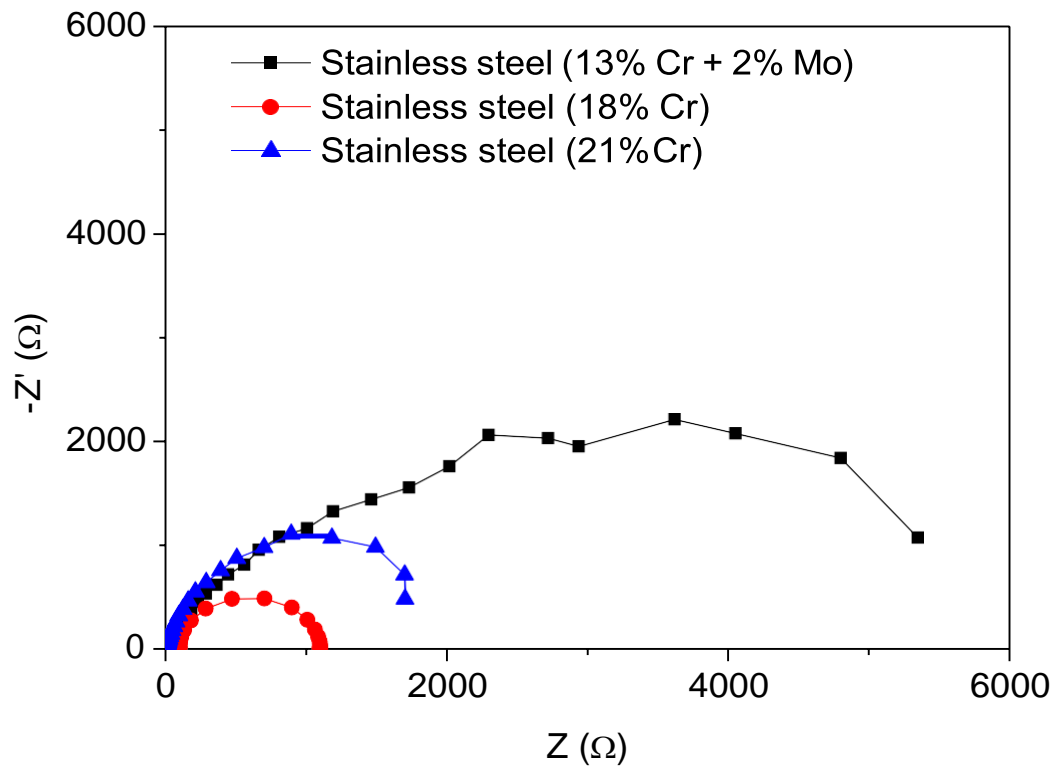


Figure 15: Nyquist diagram of stainless steels immersed in 3.5% mass solution of NaCl

The loop growth for stainless steel (13% Cr + 2% Mo) is bigger than the loop growth for the other 2 stainless steels. While loop growth of stainless steel (21%Cr) is bigger than the loop growth of stainless (18% Cr).

Table 2: Electrochemical parameters obtained by the technique of electrochemical impedance spectroscopy (EIS) of the metal/solution interface of steels in a NaCl solution (3.5% mass)

Steel type	$R_e$ ( $\Omega/\text{cm}^2$ )	$R_{TC}$ ( $\Omega/\text{cm}^2$ )	$R_p$ ( $\Omega/\text{cm}^2$ )	$C$ ( $\text{mF}/\text{cm}^2$ )
13 % Cr	02.092	6476.3	6478.8	$0.181 * 10^{-3}$
18 % Cr	99.189	990.74	1098.5	$1.010 * 10^{-3}$
21 % Cr	48.970	1790.9	1839.9	$0.938 * 10^{-3}$

### III.1.3. Polarization curves

Figure 16 shows Polarization curves of the different types of the stainless steels immersed in a solution of NaCl (3.5% mass). The polarization resistance of 3 stainless steels is obtained as a result.

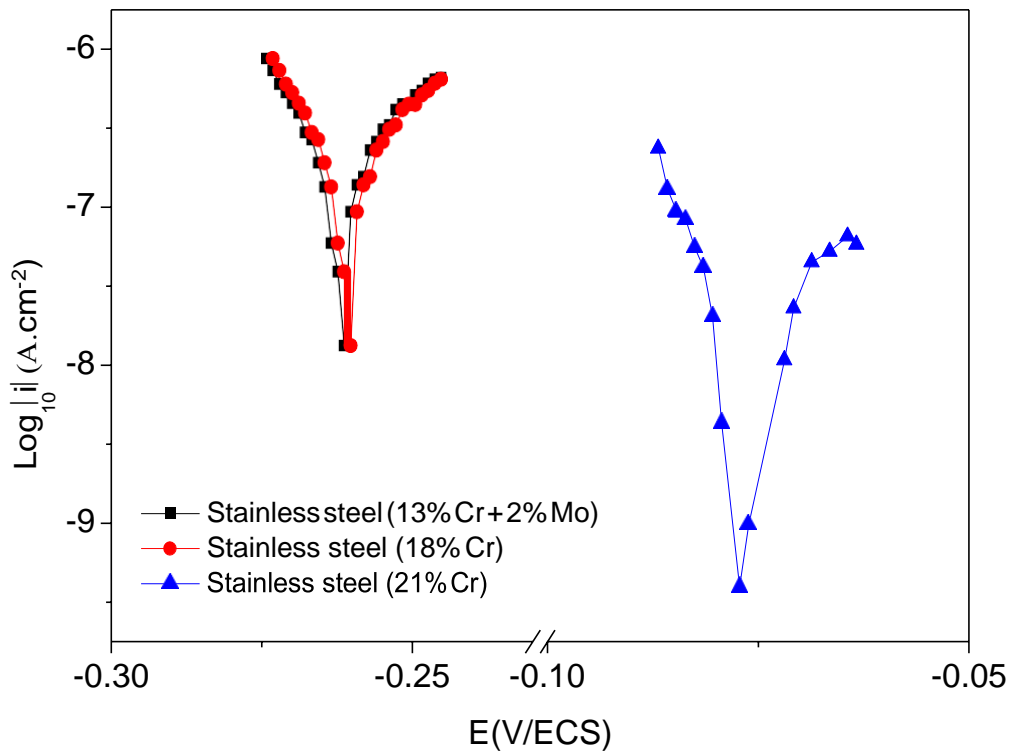


Figure 16: Polarization curves recorded on stainless steel electrodes immersed in 3.5% mass solution of NaCl

From figure 17, we can see that polarization resistance of stainless steel 21% Cr is lower than the polarization resistance of stainless steels 13% + 2%Mo and 18%Cr. While the polarization resistance of those two steels is almost same with a slight difference between them.

Table 3: The electrochemical parameters extracted from the Rp polarization curves of the steels in a NaCl solution (3.5% mass)

Steel type	$i_{\text{corr}}$ (A/cm <sup>2</sup> )	$E_{\text{corr}}$ (V/ECS)	$V_{\text{corr}}$ (mm/ans)	$R_p$ ( $\Omega$ )
13 % Cr	$1.0644 \cdot 10^{-7}$	-0.21300	$1.236 \cdot 10^{-3}$	29558
18 % Cr	$8.4899 \cdot 10^{-8}$	-0.26150	$9.86 \cdot 10^{-4}$	28690
21 % Cr	$1.3912 \cdot 10^{-8}$	-0.07728	$1.6 \cdot 10^{-4}$	186570

### III.1.4. Tafel curves

Figure 17 gives Tafel curves recorded on the three types of stainless steels in a solution of NaCl with a mass of 3.5%.

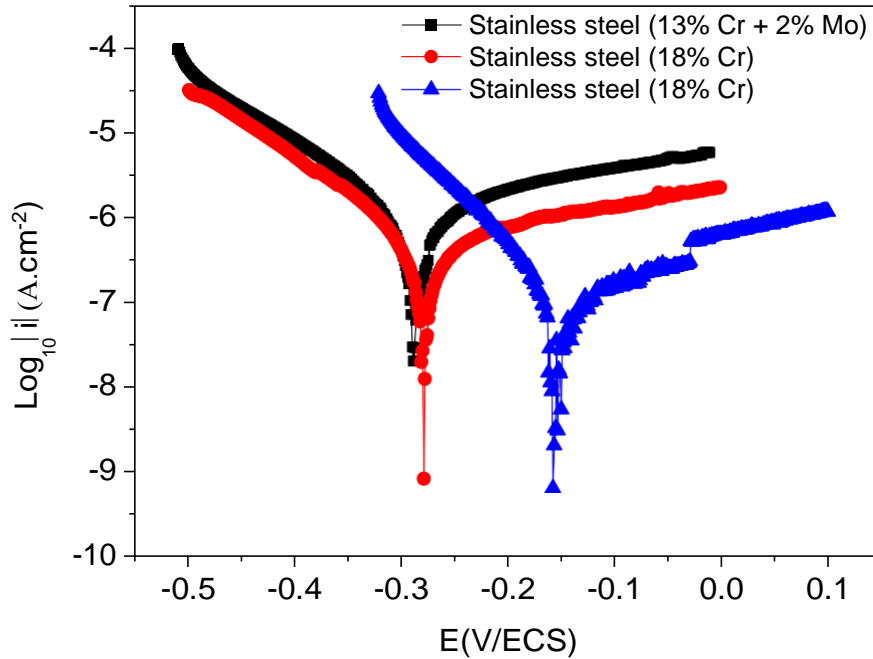


Figure 17: Tafel curves recorded on stainless steel electrodes immersed in 3.5% mass solution of NaCl.

From the tables below we see that there is a change in the  $R_p$  in solution of NaCl of 3.5% of the three steels which mean that the resistance of steel represented in blue is much higher than the other 2 while the one in red higher than the 13%Cr + 2% Mo.

Table 4: The electrochemical parameters extracted from the Tafel curves of the steels in a NaCl solution (3.5% mass)

Steel type	$i_{corr}$ (A/cm <sup>2</sup> )	$E_{corr}$ (V/ECS)	$V_{corr}$ (mm/ans)	$R_p$ ( $\Omega$ )
13 % Cr	$4.5941 \cdot 10^{-7}$	-0.24364	$5.338 \cdot 10^{-3}$	62473
18 % Cr	$1.026 \cdot 10^{-6}$	-0.28765	$1.1920 \cdot 10^{-2}$	34842
21 % Cr	$8.6809 \cdot 10^{-8}$	-0.15886	$1.008 \cdot 10^{-3}$	273120

### III. 2. Comparison between mediums:

#### III.2.1. Open-circuit potential

Figure 18 gives us the change of potential of stainless steels immersed in 3.5% mass NaCl solution and Albanian water by the change of time. For the stainless steel 21% Cr in both solutions we can see clearly that potential in open water keeps on rising with time and it is much higher than the potential in the other solution of NaCl. While the potential we got at the solution of NaCl, 3.5% mass stays almost constant by the change of time.

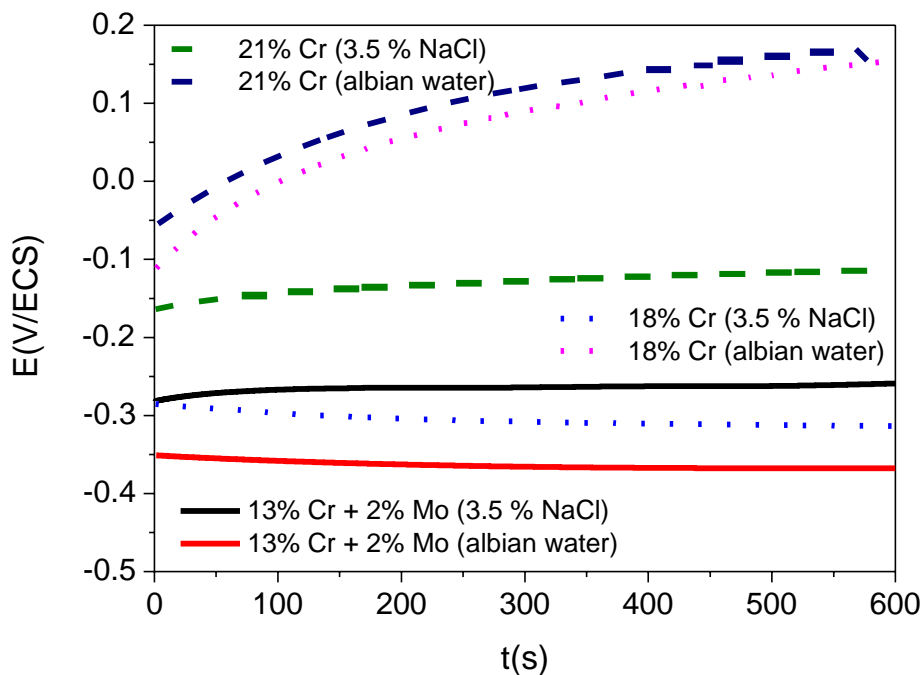


Figure 18: **Monitoring of open-circuit potential of stainless steels immersed in 3.5% mass NaCl solution and Albanian water**

For the stainless steel 18% Cr we see the opposite of what we got before. At this time the potential of stainless steel 18% Cr in solution of 3.5% mass NaCl were higher, while it rises with the change of time. While we see the potential of this type of stainless steel in solution of albanian water stay almost stable with the change of time.

In both solutions of NaCl, 3.5% mass and albanian water the potential of the stainless-steel 13%Cr +2%Mo was almost stable during the change of time.

### III.2. 2. Impedance spectroscopy:

Figure 19 shows Nyquist diagram of stainless steels where we see the radius of the capacitive loop for the stainless-steel 21%Cr high while the radius of the stainless steel 18% Cr and 13% Cr + %Mo identical. Experiment was performed in a solution of albian water.

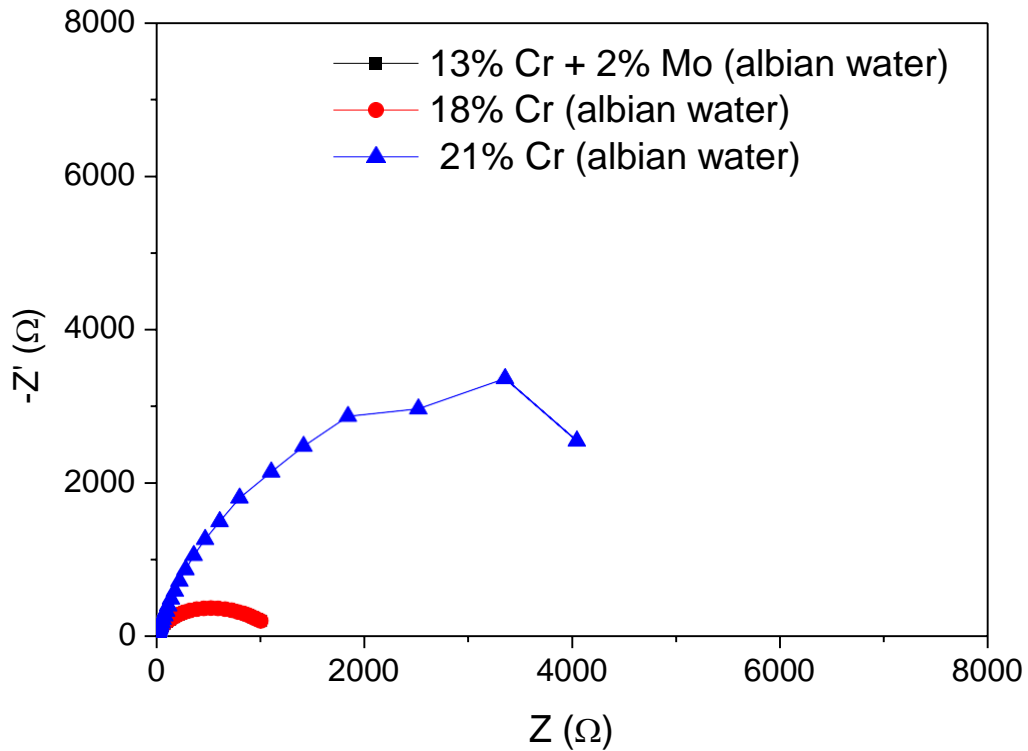


Figure 19: Diagram of Nyquist of stainless steels immersed in Albian water

Table 5: Electrochemical parameters obtained by the EIS technique of the metal/solution interface of steels in albian water

Steel type	$R_e$ ( $\Omega/\text{cm}^2$ )	$R_{TC}$ ( $\Omega/\text{cm}^2$ )	$R_p$ ( $\Omega/\text{cm}^2$ )	$C$ ( $\text{mF}/\text{cm}^2$ )
13 % Cr	12.11	1114.43	1126.4	$0.1 * 10^{-3}$
18 % Cr	12.82	23967	23980	$0.19 * 10^{-3}$
21 % Cr	3.275	22790	22794	$0.26 * 10^{-3}$

### III.2. 3. Polarization curves

Figure 20 shows the polarization curves of stainless steel 13% + 2%Mo in two different solutions of NaCl, 3.5% and albian water. From the analysis of Tafel setting we got in tables (4 and 7). That allows to see that the  $E_{corr}$  in solution of NaCl is higher than the  $E_{corr}$  that we got in the albian water.

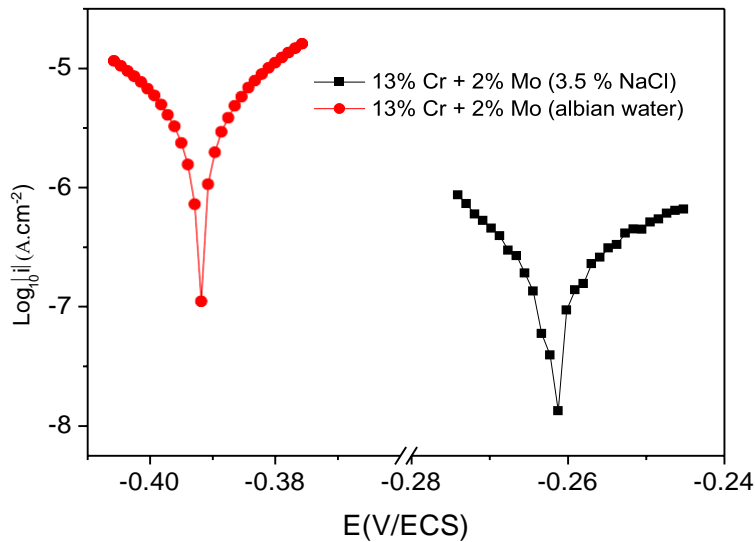


Figure 20: **Polarization curves recorded on a stainless-steel electrode (13% Cr + 2% Mo) immersed in a 3.5% mass solution of NaCl and albian water**

Figure 21 shows polarization curves of stainless steel 18% Cr in two different solutions albian water and NaCl, 3.5 mass. From the the  $R_p$  polarization tables (3 and 6) of both solutions we see that the  $R_p$  of the stainless steel (18% Cr) in NaCl is lower than  $R_p$  in the albian water. And the the  $V_{corr}$  in NaCl is faster than the  $V_{corr}$  in the solution of albian water.

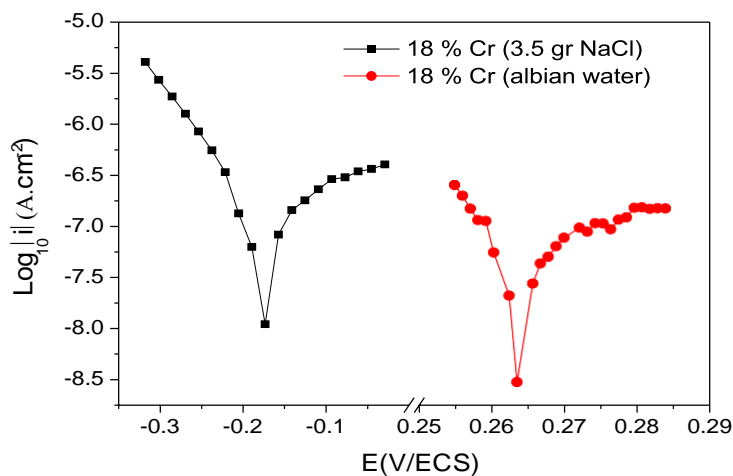


Figure 21: **Polarization curves recorded on a stainless-steel electrode (18% Cr) immersed in a 5% mass solution of NaCl and albian water**

Figure 22 shows polarization curves of the stainless steel in our solutions (NaCl 3.5% mass and albian water). From the the Rp polarization tables of both solutions we see that the Rp of the stainless steel (21% Cr) we see that Rp of stainless steel 21% Cr in NaCl solution a lot higher than the Rp in albian water solution.

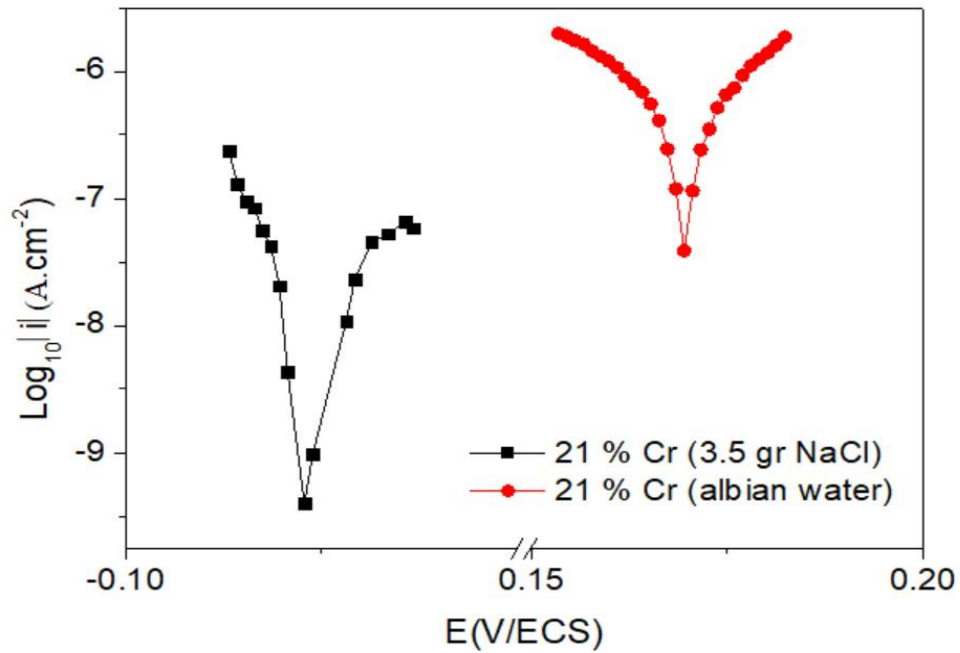


Figure 22: Polarization curves recorded on a stainless-steel electrode (21% Cr) immersed in a 3.5% mass solution of NaCl and albian water

Table 6: Electrochemical parameters extracted from Rp polarization curves of steels in albian water

Steel type	$i_{corr}$ (A/cm <sup>2</sup> )	$E_{corr}$ (V/ECS)	$V_{corr}$ (mm/ans)	Rp ( $\Omega$ )
13 % Cr	$1.768 \cdot 10^{-6}$	-0.39199	$2.05450 \cdot 10^{-2}$	1650.2
18 % Cr	$3.413 \cdot 10^{-8}$	0.1636	$3.966 \cdot 10^{-4}$	81750
21 % Cr	$6.5752 \cdot 10^{-8}$	0.16803	$7.640 \cdot 10^{-4}$	70952

### III.2.4. Curves of Tafel

Figure 23 gives us curves of Tafel of stainless steel 13% + 2%Mo registered from two deferent solutions (NaCl, 3.5 mass and albain water) from result we got in tables (4 and 7) of The electrochemical parameters extracted from the Tafel curves of the steels in both solutions we see that  $E_{corr}$  of the stainless steel (13% Cr+ 2%Mo) in solution of NaCl, 3.5% is higher than the  $E_{corr}$  in solution of albain water.

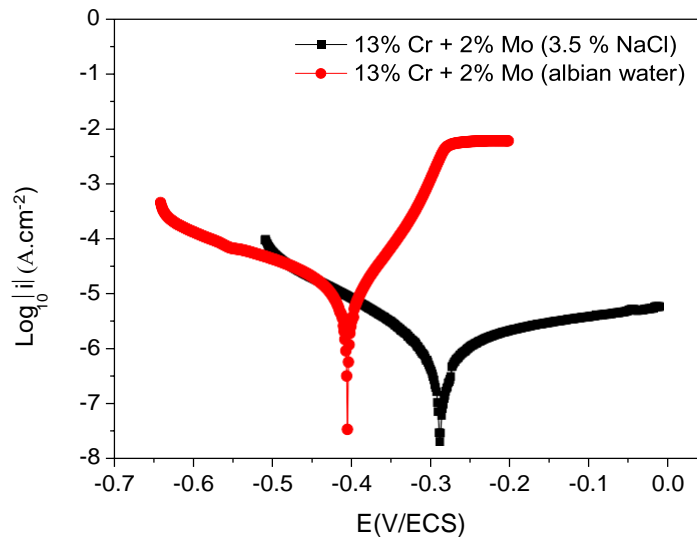


Figure 23 : Tafel curves recorded on a stainless-steel electrode (13% Cr+2% Mo) immersed in a 3.5% mass solution of NaCl and albain water

Figure 24 shows Tafel curves recorded on a stainless steel 18% Cr in both of solution of NaCl and albain water. From result we got in tables (4 and 7) of the electrochemical parameters extracted from the Tafel curves of the steels in both solutions we see that  $E_{corr}$  of the stainless steel (18%Cr) in albain water solution is higher than the  $E_{corr}$  in solution of NaCl, 3.5% mass.

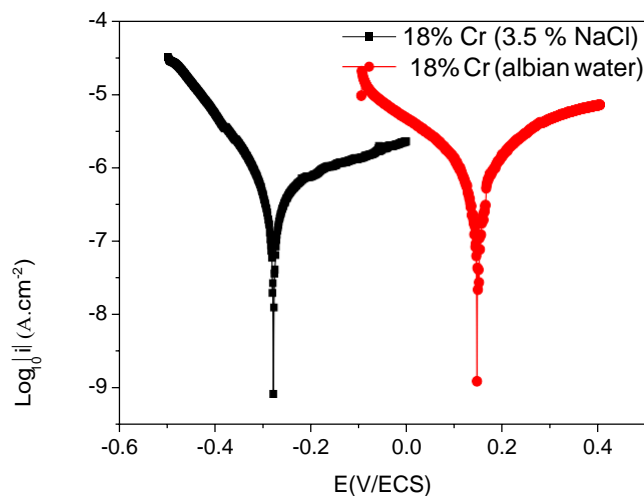


Figure 24 : Tafel curves recorded on a stainless-steel electrode (18% Cr) immersed in a 3.5% mass solution of NaCl and albain water

Figure 25 gives us tafel curves of a stainless steel electrode (21% Cr) in our solutions from result we got in tables (4 and 7) of The electrochemical parameters extracted from the Tafel curves of the steels in both solutions we see that  $E_{corr}$  of the stainless steel (21% Cr) in solution of NaCl, 3.5% is way higher than the  $E_{corr}$  in solution of albian water.

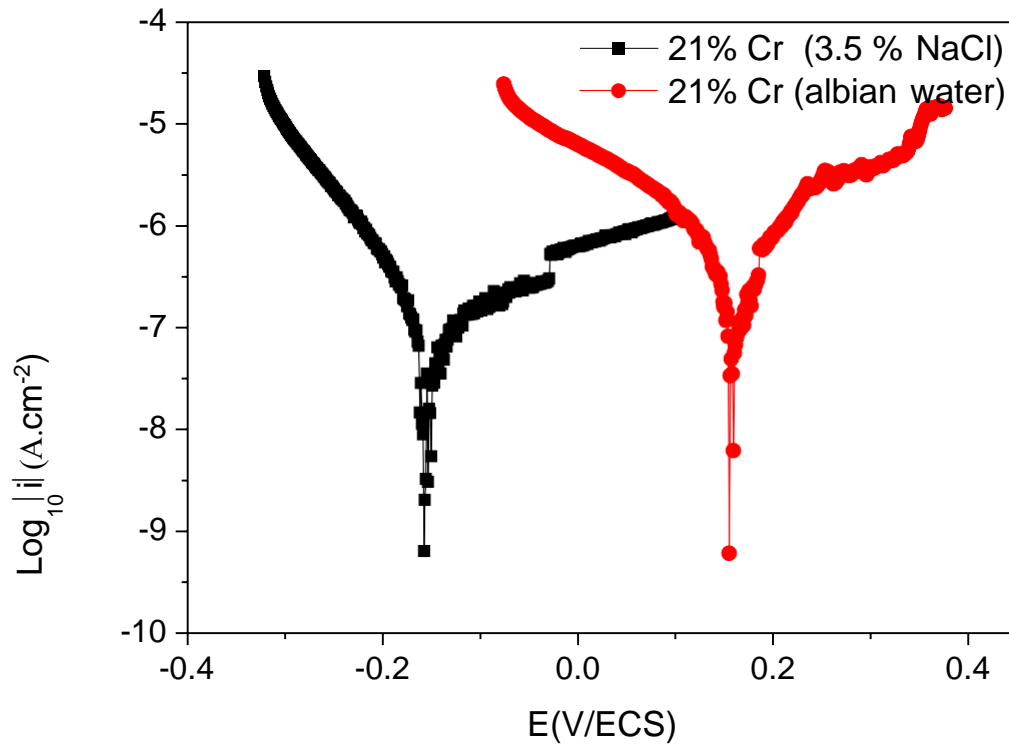


Figure 25: Tafel curves recorded on a stainless-steel electrode (21% Cr) immersed in a 3.5% mass solution of NaCl and albian water

Table 7: The electrochemical parameters extracted from the Tafel curves of steels in albian water

Steel type	$i_{corr}$ (A/cm <sup>2</sup> )	$E_{corr}$ (V/ECS)	$V_{corr}$ (mm/ans)	Rp ( $\Omega$ )
13 % Cr	$8.558 \cdot 10^{-6}$	-0.4048	$9.9448 \cdot 10^{-2}$	1846.8
18 % Cr	$6.948 \cdot 10^{-7}$	0.1466	$8.074 \cdot 10^{-3}$	51392
21 % Cr	$5.512 \cdot 10^{-7}$	0.1563	$6.408 \cdot 10^{-3}$	50685

**General conclusion**

## General conclusion

This work was a study of corrosion in the three types of stainless steel, which are 13% Cr + 2%Mo, 18%Cr and 21% Cr. To see which one of them is suitable and able to hold corrosion in the gas pipelines for a long time. As it is known that gas can be an aggressive field for the metals that contain it in the liquid state.

After the experiments that we did with the three types of stainless steels in two different solutions with all the results we got. The corrosion experiments were held in lab for the three types of the stainless steels (13% Cr + 2%Mo, 18%Cr and 21% Cr) by different methods. We can put a few points to help us distinguish between those three stainless steels we have in our hands.

- I. Each type of the stainless steels has its' own properties. In the same solutions and in the different solutions.
- II. We can detect corrosion by many ways some of those are tafel curves, polarizations curves and electrochemical impedance spectroscopy (EIS)
- III. Stainless steels corrosion resistance is based on the liquids they are in contact with.
- IV. Corrosion resistance of stainless steel 13% Cr was the lowest in solution of NaCl, 3.5% mass while the resistance of stainless steel 18%Cr was the highest.
- V. Corrosion resistance of stainless steel 21% Cr was the lowest in a solution of albian water. For the other 2 stainless steels they were almost with the same resistance in the albian water.
- VI. Polarization resistance of stainless steel 21% Cr in a solution of NaCl was higher than Polarization resistance of other stainless steels in both of tafel and polarization parameters.
- VII. Polarization resistance of stainless steel 18% Cr in a solution of albian water was higher than Polarization resistance of other stainless steels in both of tafel and polarization parameters.

- VIII. Corrosion speed of the stainless steel 21% Cr in solution of NaCl and albian water was lower than Corrosion speed of other stainless steels in both of tafel and polarization parameters.
- IX. Corrosion speed of the stainless steel 13% Cr + 2Mo in solutions of NaCl and albian water was higher than Corrosion speed of other stainless steels in both of tafel and polarization parameters.

In our life, corrosion is a threat that can lead to big problems even it can cost human lives if we didn't keep the Periodic monitoring in all the industries.

## Abstract:

This work is devoted to the study, effects of corrosion on the stainless steels, 13%Cr + 2%Mo, 18% Cr and 21%Cr, in two different aqueous solutions of NaCl, 3.5% mass and albian water. We used the electrochemical techniques of tafel curves, polarization curves and electrochemical impedance spectroscopy (EIS) with work electrodes of stainless steels 13%Cr + 2%Mo, 18% Cr and 21%Cr. To see which type of stainless steel can withstand corrosion in the solutions given. A chain of experiments were performed with the use of the electrochemical techniques we mentioned before. After pursuing and checking the results we could find ways to distinguish between the three types of stainless steels that we had in hands.

**Key words:** corrosion, stainless steel, pipelines, corrosion resistance.

## Résumé :

Ce travail est consacré à l'étude des effets de la corrosion sur les aciers inoxydables, 13% Cr + 2% Mo, 18% Cr et 21% Cr dans deux solutions aqueuses différentes de NaCl, 3,5% de masse et d'eau Albienne. Nous avons utilisé les techniques électrochimiques des courbes de tafel, des courbes de polarisation et de spectroscopie d'impédance électrochimique (EIS). Des électrodes de travail sont préparées à partir des nuances précédentes pour voir quel type d'acier inoxydable peut résister à la corrosion dans les solutions données. Une chaîne d'expériences a été réalisée avec l'utilisation des techniques électrochimiques que nous avons mentionnées précédemment. Après avoir analysé et vérifié les résultats, nous avons pu trouver des moyens de distinguer les trois types d'aciers inoxydables que nous avons entre les mains.

**Mots clés :** corrosion, acier inoxydable, pipelines, résistance à la corrosion.

## ملخص:

هذا العمل مخصص لدراسة آثار التآكل على الفولاذ المقاوم للصدأ مصنوعة من (13% كروم + 2% موليبدان، 18% كروم و 21% كروم) في محلولين مختلفين من كلوريد الصوديوم كتلته 3.5% والماء الأبيض. استخدمنا تقنيات الكهروكيميائية لمنحنيات تافل ومنحنيات الاستقطاب والتحليل الطيفي للمقاومة الكهروكيميائية (EIS) مع أقطاب من الفولاذ المقاوم للصدأ بالأنواع الثلاثة. لمعرفة أي نوع منها يمكنه مقاومة التآكل في محلولينا. تم إجراء سلسلة من تجارب باستخدام التقنيات الكهروكيميائية المذكورة. بعد متابعة النتائج والتحقق منها، تمكنا من إيجاد طرق للتمييز بين الأنواع الثلاثة من الفولاذ المقاوم للصدأ التي كانت بين أيدينا.

**الكلمات الرئيسية:** التآكل، الفولاذ المقاوم للصدأ، خطوط الأنابيب، مقاومة التآكل