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Faculty of Technology
Process Engineering Department

Corrosion in Oil and Gas Industry (Upstream, Midstream, and Downstream Production Operations): Sources, mechanisms, and mitigation For Petrochemical, Chemical Engineering, and Hydrocarbons Students

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Dedication

This work is dedicated to My late parents.

They have been the best models. Their constant prayers and encouragements made all these hard years enjoyable. (No words can explain how much I am thankful to them). My wife , and kids(Aboubaker, Saber, Mouataz, Razane, and Firas), for their patience, love, and their continual support of my work.

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Acknowledgement

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List of Figures

List of Tables

Table of Contents

Preface

The importance of materials reliability in society continues to grow, especially given the liability issues that arise when reliability is not guaranteed, safety is compromised, and failures occur. Despite the long history of university, college, and continuing education courses on corrosion, high-profile corrosion failures still happen. While corrosion education should not be deemed a complete failure, it has not succeeded in providing all engineers and technologists with a sufficient “literacy level” in corrosion to ensure reliability and prevent failures. Some organizations' senior management have adopted policies of "zero failures" or "no failures." To turn these policies into reality—where "zero" truly means "zero" and "no" truly means "no" engineers and others use a combination of well-established strategies, innovative methods, and experimental trials when necessary to manage corrosion. One aim of this edition is to offer students an updated overview of the key aspects of corrosion science and engineering that support the tools and technologies used to manage corrosion and prevent failures. Another objective is to actively engage students, encouraging them to participate in understanding corrosion and solving problems, rather than passively absorbing a wealth of information.

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General introduction

General Introduction

Corrosion is the destructive deterioration of a material due to its reaction with the environment [1] and represents a significant natural hazard in oil and gas production and transportation facilities [2]. Nearly any aqueous environment can cause corrosion, which can occur under various complex conditions in oil and gas production, processing, and pipeline systems [3]. This process involves three key elements: an anode, a cathode, and an electrolyte. The anode is where the metal corrodes, the electrolyte is the corrosive medium that facilitates the transfer of electrons from the anode to the cathode, and the cathode is the electrical conductor in the cell that remains unaffected by the corrosion process [4]. Crude oil and natural gas can contain various impurities that are inherently corrosive. In oil and gas wells and pipelines, highly corrosive substances such as carbon dioxide (CO_2), hydrogen sulfide (H_2S), and free water are often present [5]. The continuous extraction of CO_2, H_2S, and free water through oil and gas components can eventually lead to corrosion of their internal surfaces. The pipelines and fittings may undergo material degradation due to changes in fluid composition, well souring over time, and varying operating conditions of pressure and temperature. This degradation results in a loss of mechanical properties, such as strength, ductility, and impact resistance, leading to material loss, thickness reduction, and sometimes ultimate failure. Eventually, a point may be reached where a component completely fails, necessitating replacement and causing a halt in production. The severe consequences of corrosion have become a globally significant issue [1].

Corrosion remains one of the most significant and challenging issues facing modern industry. Industrial designs often must account for the impact of corrosion on equipment lifespan. Recent industrial disasters have shown that many industries have incurred losses of billions of dollars due to corrosion. Reports worldwide have confirmed that some oil companies have experienced pipeline ruptures due to corrosion, leading to oil spills, environmental pollution, costly clean-ups, and widespread ecological damage [6]. The potential for corrosion in industrial plants is a major concern for petroleum, chemical, and mechanical engineers, as well as chemists. It is now understood that corrosion can affect the chemistry of processes, and corrosion products can impact reaction outcomes and purity. Numerous catastrophic incidents resulting from corrosion failures have been documented.

The costs associated with corrosion damages are estimated to account for 3% to 5% of the gross national product of industrialized countries [7]. In the oil and gas production industry alone, the total annual cost of corrosion is estimated at $1.372 billion, which includes $589 million for surface pipeline and facility costs, $463 million for downhole tubing expenses, and $320 million in capital expenditures related to corrosion [8]. Overall, corrosion costs the oil and gas industry tens of billions of dollars in lost income and treatment expenses each year [3]. In the United States, corrosion costs industries an estimated $170 billion annually, with the oil and gas sector accounting for more than half of these expenses [9]. Internal corrosion in wells and pipelines is influenced by factors such as temperature, CO_2 and H_2S content, water chemistry, flow velocity, and the steel's surface condition [10]. Reducing the corrosion rate (measured in mm/year) can significantly extend the life of components, leading to reduced maintenance costs and other benefits. Addressing the problem of corrosion is a global challenge that requires urgent attention.

Corrosion Science and Corrosion Engineering:

As corrosion entails chemical transformations, students need a grasp of chemistry principles to comprehend corrosion reactions. Given that corrosion mechanisms predominantly involve electrochemical processes, an understanding of electrochemistry is equally crucial. Additionally, considering that the structure and composition of a metal significantly influence its corrosion tendencies, students should also acquaint themselves with the basics of physical metallurgy.

The corrosion scientist dedicates their research to investigating corrosion mechanisms with the aim of: (a) enhancing comprehension of the root causes of corrosion and, (b) devising strategies to prevent or mitigate the damage caused by corrosion. Conversely, the corrosion engineer employs scientific insights to manage corrosion actively. For instance, the corrosion engineer implements cathodic protection methods on a large scale to safeguard buried pipelines, conducts testing and development of novel and improved coatings, determines appropriate dosages of corrosion inhibitors, and recommends suitable coating applications. In contrast, the corrosion scientist contributes by refining criteria for effective cathodic protection, elucidating the molecular structure of chemical compounds with superior inhibitory properties, creating corrosion-resistant alloys, and suggesting optimal heat treatments and compositional adjustments to enhance alloy performance. Both scientific and engineering perspectives complement each other in diagnosing corrosion damage and prescribing solutions.

Importance of Corrosion:

The significance of corrosion stems from three primary reasons: economics, safety, and conservation. To mitigate the economic impact of corrosion, corrosion engineers, in collaboration with corrosion scientists, strive to minimize material losses and the associated financial losses resulting from corrosion damage to various structures such as piping, tanks, machinery components, ships, bridges, and marine structures.

Corrosion poses a threat to the safety of operational equipment, potentially leading to catastrophic failures of critical components such as pressure vessels, boilers, and containers for hazardous chemicals, turbine blades, bridges, aircraft parts, and automotive steering mechanisms. Safety considerations are particularly vital in the design of equipment for nuclear power plants and the management of nuclear waste disposal.

Furthermore, corrosion-related metal loss not only squanders the material itself but also wastes the energy, water, and human effort invested in the production and fabrication of these metal structures. Moreover, the restoration of corroded equipment necessitates further expenditure of these valuable resources—metal, energy, water, and human effort.

The economic aspect serves as a significant driving force behind much of the ongoing research in corrosion. Annual losses incurred by industries and governments worldwide amount to billions of dollars, with recent studies indicating approximately $276 billion in the United States alone, equivalent to 3.1% of the Gross Domestic Product (GDP) [11]. It has been estimated that a substantial portion, about 25-30% of this total, could be mitigated through the effective application of existing corrosion mitigation technologies [11].

Similar studies assessing the cost of corrosion have been conducted in Australia, Great Britain, Japan, and other nations. Findings consistently reveal that the cost of corrosion represents approximately 3-4% of the Gross National Product in each country examined [12].

Chapter I : Corrosion Control Overview

I) Corrosion Control overview

I-1) Terms Used in Corrosion and Electrochemistry:

&-Atomic Structure

The fundamental framework of all materials encountered or utilized daily follows a specific pattern known as the atomic structure of matter. Similar to constructing a building, builders adhere to precise steps from start to finish. The construction materials (such as steel girders, bricks, and cement), when arranged in the correct sequence and quantity, create a building. This idea of definite parts arranged in a specific order parallels the basic structure of all matter.

a) Matter:

Matter is anything that has mass and takes up space. It can exist in various forms, such as a liquid (like water), a gas (like oxygen), or a solid (like stone). Typically, matter has weight because it is influenced by Earth's gravitational force. Matter can consist of a single element or a combination of two or more elements.

b) Element:

An element is a substance that cannot be broken down or altered through chemical reactions. Elements are the fundamental building blocks of all matter. There are 92 naturally occurring elements, ranging from the lightest, hydrogen, to the heaviest, uranium. Iron, oxygen, and gold are examples of elements.

c) Compound:

A compound is a combination of two or more elements, forming a pure substance with a fixed composition. Examples of chemical compounds include:

- Carbon Dioxide (CO_2)
- Salt (NaCl)
- Water (H_2O)
- Ferric Oxide (Fe_2O_3)

d) Mixture:

A mixture is a combination of elements, compounds, or both, held together by physical rather than chemical forces. Unlike compounds, mixtures do not have a fixed composition. For example, air consists of approximately 20% oxygen and 78% nitrogen, along with other substances like argon (1%) and varying amounts of carbon dioxide and water vapor. Soil is another example of a mixture, comprising minerals formed from elements and compounds.

e) Atom:

The smallest particle into which an element can be divided while still retaining its original characteristics is the atom. The simplest atom is hydrogen, as illustrated in Figure below. This atom consists of a central body with one small body orbiting around it. The central body is called the nucleus, and the orbiting body is called an electron. The nucleus contains a positively charged particle known as a proton. The electron carries a negative charge, while the proton carries a positive charge. The term "unit particle" can be replaced with "charge."

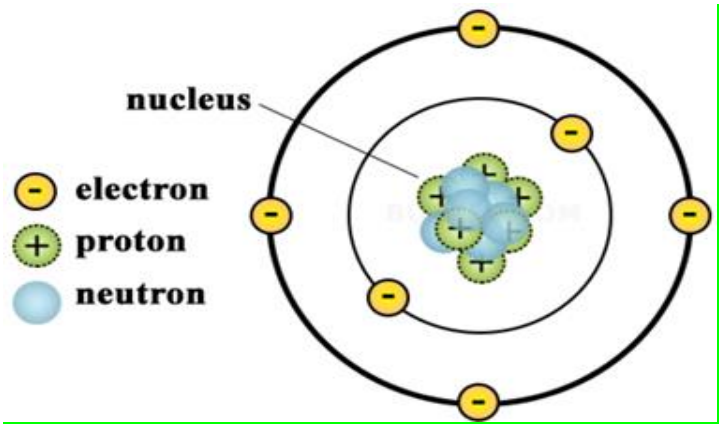


Figure I .1. Atom Particles.

&-Molecules:

The smallest particle of an element (H_2, Cl_2, O_2) or compound (H_2O, HCl, CH_4) that retains all the chemical properties of that element or compound is called a molecule.

&-Electrolytes

Electrolytes are chemical compounds, such as liquids or gels, that contain ions and can conduct electricity through the movement of these ions. Anions flow toward the anode, while cations flow toward the cathode. An electrolyte has an equal amount of positive and negative charges from the ions it contains. The conductivity of an electrolyte can vary; it can be highly conductive due to a high ion content (as in seawater) or only mildly conductive due to a low ion content (as in pure water).

&-Ions: An ion is a charged atom or molecule, which has either gained or lost electrons.

&-Cations: If an atom or molecule loses one or more electrons, it becomes positively charged and is called a cation.

&-Anions: If an atom or molecule gains one or more electrons, it becomes negatively charged and is called an anion.

Table. I-1. Characteristics of ions.

Anion	Cation
Negative ion	Positive ion
Net negative charge	Net Positive charge
Formed by addition of electrons	Formed by loss of electrons
Attracted to anode	Attracted to cathode

Table. I-2. Examples of ions.

Anion	Cation
Sulfate ion $(SO_4)^{-2}$	Ferrous ion (Fe^{++})
Chloride ion (Cl^-)	Ferric ion (Fe^{+++})
Hydroxyl ion (OH^-)	Hydrogen ion (H^+)

I.2) Chemical and Electro-chemical Reaction

The chemical reaction is the process that goes on during the conversion of reactants into products and does not include electron transfer.

An electrochemical reaction is a chemical process involving electron transfer, where electrons flow between a solid electrode and a substance, such as an electrolyte. Most corrosion reactions are electrochemical and are referred to as oxidation/reduction reactions. These reactions occur through the exchange of electrons at specific sites known as the cathode and anode. Oxidation takes place at the anode, while reduction occurs at the cathode. Electrons released at the anode travel through the metal to the cathode, where they are consumed in the reduction reaction. Corrosion reactions happen in an electrolyte that supplies the reactants for these processes.

Table. I-3. Characteristics of oxidation/reduction reaction.

Oxidation – Anodic reaction	Reduction – Cathodic reaction
Loss of electrons	Gain of electrons
Increase positive charge Or decrease negative charge	Increase negative charge Or decrease positive charge
Electrons remain in metal and transfer to cathodic area.	Electrons are consumed in the cathodic reaction at the metal/environment interface.

Table. I-4. Examples of oxidation and reduction.

Oxidation– Anodic reaction	Reduction– Cathodic reaction
$Fe^0 \rightarrow Fe^{++} + 2e^-$	$2H^+ + 2e^- \rightarrow H_2$
$Fe^0 \rightarrow Fe^{+++} + 3e^-$	$2H_2O + O_2 + 4e^- \rightarrow 4(OH^-)$
$Fe^{++} \rightarrow Fe^{+++} + e^-$	$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$

I-3) Physicochemical properties and corrosiveness of crude oils and natural gas:

In order to grasp the intricacies of corrosion challenges and remedies within the oil, gas, and refining sectors, we will delve into the physicochemical attributes of crude oils, natural gas, fuels, and their corrosive tendencies. Additionally, various other substances, including water (such as cooling water, boiler feed water, extinguishing water, and seawater), steam, different gases, and chemicals, can also contribute to the corrosion of equipment within oil, gas, and refining facilities.

Crude oil constitutes a blend of various liquid hydrocarbons, incorporating dissolved gases, water, and salts. It exists as emulsions, wherein drops of aqueous solution are dispersed within the continuous hydrocarbon phase. Interstitial or connate water is consistently found within crude oils, ranging from nearly freshwater to fully saturated aqueous solutions of salts, serving as the primary

contributor to the corrosive nature of crude. Furthermore, crude oils may contain sulfur, nitrogen, oxygen, and metal compounds alongside hydrocarbons. These contaminants can exist within crude oils as dissolved gases, liquids, solids, or distinct phases. Additionally, microorganisms may be present in crude oil, water, and fuels, either in an active or dormant state. While all crude oils comprise similar compounds, their proportions vary, resulting in differences in their corrosive characteristics.

Natural gas presents as a uniform gaseous blend of hydrocarbons, primarily, along with nitrogen (N_2), carbon dioxide (CO_2), hydrogen sulfide (H_2S), water vapor (H_2O), and traces of mercury, organic acids, and noble gases. Within these constituents, CO_2, H_2S, H_2O, mercury, and organic acids possess the potential to induce corrosion in metals at various stages of natural gas production, separation, handling, transportation, treatment, and storage. While water in crude oil wells may contain salts, it remains pure in natural gas wells. However, gases like CO_2 and H_2S dissolved in this pure water render it acidic and corrosive. Corrosion resulting from CO_2 exposure is termed "sweet corrosion," while corrosion due to H_2S is referred to as "sour corrosion." Additionally, oxygen-induced corrosion is known as "oxygen corrosion." The rate and severity of corrosion hinge upon the type and concentration (pressure) of aggressive components, temperature, flow regime, and velocity.

I-4) Sources of corrosion in oil/gas field:

Corrosion predominantly occurs in the water phase, except when water is trapped in the middle of the stream or surrounded by oil, in which case corrosion does not occur. The primary sources of corrosion in the oil industry include hydrochloric acid and its aqueous solutions, hydrogen sulfide, corrosion of steel at hydrocarbon-electrolyte interfaces and in emulsified two-phase environments, oxygen, naphthenic acids, carbon dioxide, and water cut. The sources and their respective roles are described below:

a) Hydrogen Sulfide:

Hydrogen sulfide is highly detrimental to the corrosion of metals or alloys, particularly in the oil and gas industry. It can cause sulfide stress corrosion cracking (SSCC) in pipelines. However, hydrogen sulfide is only corrosive when dissolved in water, where its solubility is higher than that

of carbon dioxide and oxygen. Additionally, hydrogen sulfide poses significant risks in sour oil and gas fields due to its prevalence in oil and production processes. The issues related to hydrogen sulfide corrosion are becoming more prominent as the sulfur content in crude oil increases with the decline of sweet oil reserves【13】.

The corrosion by hydrogen sulfide produces iron sulfide and hydrogen. Internal stresses caused by molecular hydrogen can lead to hydrogen cracking. The outcomes of hydrogen cracking are often unexpected and catastrophic, as there are no visible signs in the early stages【14】. Therefore, it is crucial to select the optimal materials for well completions, especially in fields containing sour oil and gas, to mitigate the risk of sulfide stress cracking (SSC) and potential equipment loss due to the presence of hydrogen sulfide and tensile strength.

b) Chloride:

Chloride, present in the mineralized water at the well bottom, is another critical substance that causes severe corrosion at high temperatures. This can lead to failures resulting from intergranular corrosion and chloride stress corrosion cracking (CSCC). The presence of both sulfide and chloride has been detected in deep sour gas production, which primarily consists of methane without liquid hydrocarbons, under high pressure【15】

c) Carbon Dioxide:

Carbon dioxide produced alongside oil and gas dissolves in water to form carbonic acid, resulting in a decrease in pH. Additionally, using injection methods for enhanced oil recovery can introduce more acid, further lowering the pH. This can lead to increased corrosion caused by CO_2, ultimately affecting both downhole and surface equipment. CO_2-based corrosion often results in pitting, characterized by deep, sharp-edged pits.

In the oil and gas industries, one of the most acidic environments is an aqueous system with high concentrations of carbon dioxide. Factors such as partial pressure, temperature, flow rate, and pH contribute to corrosion in the presence of carbon dioxide [16,17].

d) Oxygen

Oxygen is a critical corrosive agent in secondary recovery processes involving water flooding. Corrosion caused by dissolved oxygen can lead to pitting in drill pipes and propagate fatigue cracks due to stress. Additionally, oxygen can damage water injection equipment, such as pumps, pipes, and water storage tanks, and the corrosion byproducts might clog the formation.

The figure below compares the rusting rates of oxygen, hydrogen sulfide, and carbon dioxide on carbon steel in a water solution containing 2 to 5 g/L sodium chloride at 25°C. It shows that oxygen causes higher rusting rates at much lower concentrations compared to carbon dioxide and hydrogen sulfide. Rusting rates in pits can be several times higher, and the rusting rate of carbon dioxide is variable at low temperatures. Mixtures of oxygen with carbon dioxide or hydrogen sulfide create highly corrosive environments even at very low oxygen concentrations, such as 0.1 ppm【18】.

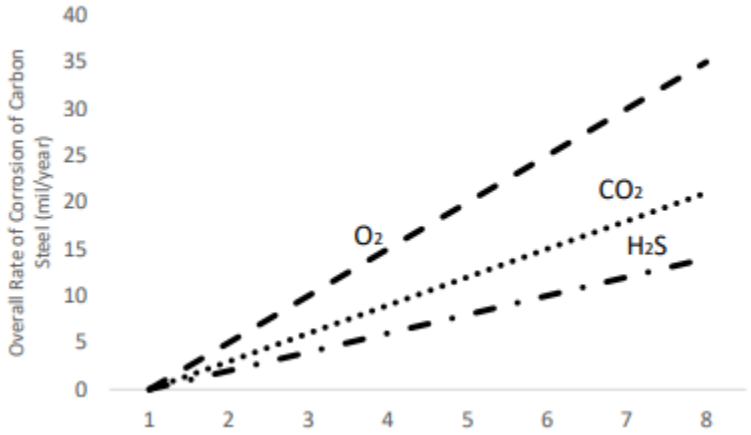


Figure.I.2. Comparison of rusting rates of three gases [19].

Bacteria:

Bacterial corrosion, driven by microorganism activity, can be particularly damaging in enhanced recovery processes. Sulfate-reducing and iron bacteria are among the most common types that contribute to this corrosion. Microbiologically-influenced corrosion (MIC) has been extensively studied from an industrial perspective to develop effective solutions for monitoring large water injection systems【20].

e) **Mercury:** Mercury although present in natural gas in minimal amounts, can pose several challenges [21, 22, 23]. Firstly, it constitutes a toxic element harmful to both humans and the environment. Secondly, at low temperatures within LNG (Liquid Natural Gas) units, mercury can induce corrosion in aluminum heat exchangers. Thirdly, it has the potential to contaminate catalysts. The corrosion mechanism attributed to mercury is distinct and termed "liquid metal embrittlement," a type of Stress Corrosion Cracking (SCC). Mercury's corrosive effects extend to various metals, including copper, nickel, zinc, iron, chromium, titanium, and zirconium. Effective measures for mitigating mercury-induced corrosion involve removing it from natural gas to concentrations lower than 0.01 milligrams per normal cubic meter ($mg.Nm^{-3}$) [21, 24-25].

Sediments found within natural gas systems comprise a mixture of sand, silicates, corrosion by-products (such as iron sulfides, oxides, hydroxides, and carbonates), sulfates, microorganisms, and their metabolic products. These solids can enter the system in two primary ways: either being carried along with the natural gas stream or forming through physicochemical processes, such as corrosion. Equipment including pipes, tanks, pumps, compressors, filters, steam lines, boilers, and reactors may suffer damage due to sediment accumulation. The presence of sediments can lead to various issues [26], including:

1-Under-deposit corrosion.

2-Blockages in pipes, pumps, filters, compressors, and heat exchangers.

3-Increased pressure drop, resulting in reduced flow rates.

4-Erosion of equipment.

5-Impaired heat exchange efficiency.

6-Unplanned shutdowns for sediment removal from equipment.

7-Contamination of natural gas and other products.

8-Safety hazards and environmental concerns.

Effective solutions involve maintaining proper process conditions and implementing regular maintenance practices, including periodic cleaning of equipment to remove sediments.

f) Water Cut:

The presence of oil is advantageous as it provides an inhibitory effect by forming a protective film on a steel surface, preventing water from wetting the metal. In contrast, gas and condensates do not offer any beneficial inhibition effects. For vertical tubing, an oil film on the steel surface remains stable with water cuts up to about 20%–40%. Using the de Waard and Milliams method, the corrosion rate for higher water volumes can be predicted, as the steel can be considered water-wet. In horizontal pipes, however, the volume of water is less significant.

Typically, water, being denser than oil, gas, and condensates, tends to settle at the lowest point of the pipe in a stratified flow. In this scenario, corrosion is expected to occur primarily on the water-wet surfaces. For stratified flow, corrosion is likely to happen at the highest point of the line due to the condensation of water droplets from the wet gas. In such cases, the inhibition effect is minimal, and the corrosion rate at the highest point of the line is expected to be about 10% of the rate projected for a completely immersed condition, regardless of the carbon dioxide content.

g) **Strong Acids**

In the oil and gas industry, acid stimulation is commonly used to boost production by enhancing formation permeability. Hydrofluoric acid is typically used for sandstone, while hydrochloric or acetic acids are used for carbonates. Without corrosion inhibitors, these acids can cause significant corrosion of production tubing, downhole tools, and casing【19].

h) Brines

Brines are often employed during the completion phase of oil and gas wells to assist with final operations before fluid production begins. Comprising zinc chlorides or calcium bromides, brines help regulate the well without harming the formation. However, they can be detrimental to downhole equipment due to the presence of dissolved oxygen.

I-5) Theory of Corrosion in the oil and gas industry:

The most common type of corrosion in the oil and gas industry occurs when steel is exposed to an aqueous environment, resulting in rust formation [27]. In this process, when metal is exposed to a

corrosive solution (the electrolyte), metal atoms at the anode lose electrons. These electrons are then absorbed by metal atoms at the cathode. The cathode, connected to the anode through the electrolyte, facilitates this electron exchange to balance positive and negative charges. Positively charged ions are released into the electrolyte, where they can bond with other negatively charged atomic groups. This anodic reaction in iron and steel is characterized by:

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

After the metal atoms at the anode site release electrons, there are four common cathode reactions [28]:

$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$ (oxygen reduction in acidic solution)

$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$ (oxygen reduction in neutral or basic solution)

$2H^+ + 2e^- \rightarrow H_2$ (Hydrogen evolution from acidic solution)

$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$ (Hydrogen evolution from neutral Water)

In the oil and gas industry, carbon dioxide (CO_2) and hydrogen sulfide (H_2S) are commonly present, with water acting as a catalyst for corrosion. When water interacts with CO_2 and H_2S, the following reactions occur [29]:

-**H_2CO_3 Reaction:**

$$H_2CO_3 + Fe \rightarrow FeCO_3 + H_2$$

-H_2S Reaction:

$$H_2S + Fe + H_2O \rightarrow FeS + 2H$$

If both gases are present, the two reactions described above can occur simultaneously. The resulting molecules may either attach to the cathode or be released into the electrolyte, allowing the corrosion process to continue. Classifying the types of corrosion in the oil and gas industry in a standardized way is challenging. Corrosion can be categorized based on the appearance of corrosion damage, the mechanism of attack, the industry sector, and the methods of prevention. There are numerous types and causes of corrosion, and the mechanisms in a given piping system depend on factors such as fluid composition, service location, geometry, and temperature. In all cases, an electrolyte must be present for corrosion to occur. In the oil and gas production industry, the main forms of corrosion include [30,31]: sweet corrosion, sour corrosion, oxygen corrosion, galvanic corrosion, crevice corrosion, erosion corrosion, microbiologically induced corrosion, and stress corrosion cracking.

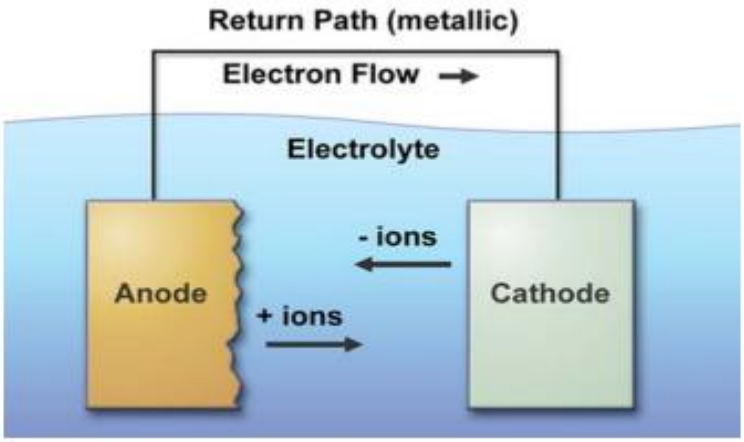


Figure.I.3. Basic corrosion cell (Source: NACE Corrosion Training Material)

The depicted reactions are known as cathodic reactions. The ions' movement through the electrolyte serves to close the electrical circuit. Normally, the iron ions react with water and/or oxygen, resulting in the formation of a corrosion deposit such as rust or another form of iron oxide. However, in certain instances, they may combine with carbon dioxide or hydrogen sulfide to produce iron carbonate or iron sulfide. The anode and cathode components of a corrosion cell can be positioned adjacent to each other or separated by considerable distances.

I-5-1) Thermodynamics:

Corrosion is described as the environmental deterioration of metals and alloys. From a thermodynamic perspective, it is the reverse of the ore refining process. The spontaneity of any chemical reaction can be predicted using Gibbs free energy, which represents the maximum amount of work a system can perform at constant temperature and pressure. A change in Gibbs free energy (ΔG) indicates the likelihood of a process occurring. Furthermore, the sign of ΔG reveals whether the process is spontaneous or requires external energy input.

When refining ore, energy, in the form of heat or electricity, is supplied to initiate the separation of pure metal from its compound form, analogous to pushing a large ball up a hill, as depicted in the figure below. This energy input corresponds to a positive ΔG, with a higher positive ΔG indicating greater energy required for metal extraction.

Once in its pure form, the metal remains stable at a high Gibbs free energy state until it encounters external factors such as oxygen, water, chlorides, or hydrogen ions. Upon interaction with these stimuli, the metal begins to form stable compounds, a process known as corrosion. This process is symbolized by the ball in the figure below rolling down the hill, reaching its lowest Gibbs free energy state. As a result, Gibbs free energy decreases, making ΔG negative for all corrosion processes.

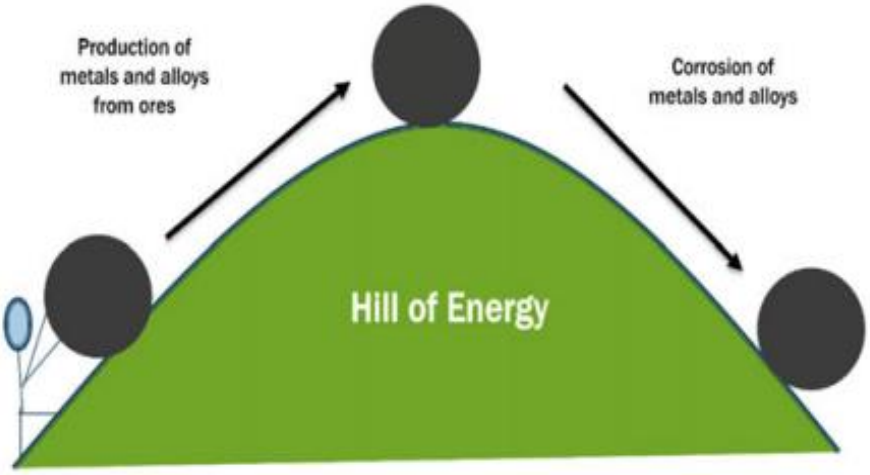


Figure I.4. Relationship between ore refining and corrosion

Electrochemically, Gibbs free energy represents the maximum capacity of temperature and pressure to drive the movement or electronic transfer of atoms. It also reflects the minimum work required to thermodynamically induce a chemical reaction. Therefore, when Gibbs free energy is negative, a chemical reaction occurs more readily. As a result, all corrosion processes are associated with negative Gibbs free energy. The equation to calculate Gibbs free energy from an electrochemical perspective is:

$$\Delta G = - nFE$$

where ΔG stands for Gibbs free energy change, n indicates the number of electrons, F is Faraday's constant, and E denotes the electrode potential for the electrochemical system.

The electrode potential E in the equation above represents the electromotive force of an electrochemical cell, which will be discussed later.

I-5-2) Electrochemistry

Since corrosion is an electrochemical process, the presence of an electrochemical cell is essential for it to occur. When a single, uniform electrode or material is immersed in an electrolyte, this setup is called a half-cell. A uniform electrode means that all atoms have an equal likelihood of interacting with the electrolyte. As illustrated in Figure below, when the electrode comes into contact with the electrolyte, some atoms release electrons and enter the electrolyte, while in other regions of the electrode, atoms accept electrons and return to the material. This behavior is also referred to as the escaping tendency.

Atoms that release electrons become ions and remain in the electrolyte near the electrode surface, while the released electrons form a similar layer on the electrode surface, rather than in the electrolyte. The movement of ions to and from the electrode takes place through this charged layer, known as the electrochemical double layer. As a result, the electrode immersed in the electrolyte reaches electrochemical equilibrium with the electrolyte. The potential at which this equilibrium is established is called the electrode potential. Each half-cell, therefore, has its own electrode potential, which is measured using reference electrodes.

Commonly, reference electrodes like the standard hydrogen electrode (SHE) are used to calculate standard electrode potentials, also known as standard reduction potentials, for various elements. These values are listed in a series known as the 'EMF' or 'electromotive force' series. This series, shown in Table I.5, provides the absolute values of electrode potentials relative to SHE and indicates the electrochemical behavior of elements in relation to the hydrogen equilibrium reaction

$$2H^{+} + 2e^{-} \leftrightarrow H_2$$

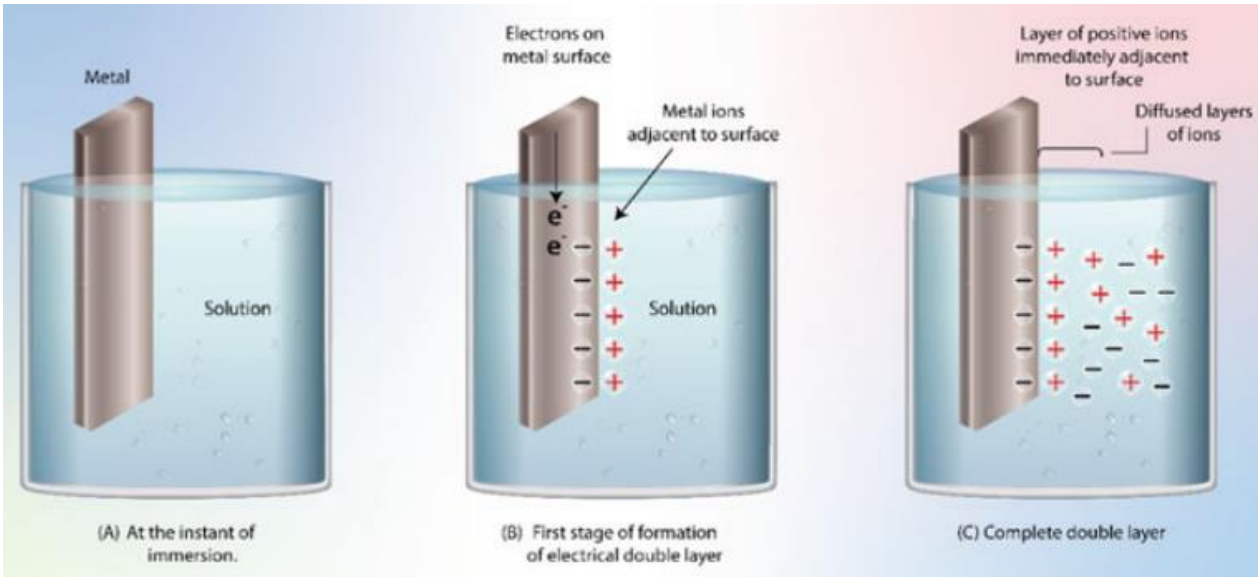


Figure.I.5. Stages of formation of an electrical double layer near the surface of the electrode in a half-cell [32]

The standard calomel electrode, silver-silver chloride electrode, and copper-copper sulfate electrode are some other reference electrodes commonly used to measure potentials in laboratories or field operations.

The standard electrode potential is influenced by various factors, including temperature, pressure, electrolyte concentration, the type of ions present in the electrolyte, and pH. Any alteration in these factors can lead to a change in the electrode potential of the system. This adjusted electrode potential can be calculated using the following Nernst equation:

$$\mathbf{E = E^0 - (RT\ /n\ F)\ ln\ Q}$$

where E denotes cell potential under polarized conditions (V), E^0 stands for cell potential under ideal conditions (V),R is the gas constant, T is the temperature (K), n indicates the number of moles of electrons transferred during the reaction, F is the Faraday's constant (96,500 coulombs/gram – equivalent), and Q is the reaction quotient, which is the equilibrium expression with ionic concentrations = activity of products/activity of reactants [32].

Any two half-cells can be connected both electrically and electrochemically. Electrically, they are connected by wires without the need for an external power source. The electrochemical connection is established using a salt bridge or by immersing both half-cells in the same electrolyte. This

configuration of two half-cells forms an electrochemical cell, which operates based on the flow of current through the electrical connection, driven by the chemical reactions occurring at the two electrodes immersed in the electrolyte.

Table I. 5. EMF series for standard redox potentials [33]

Electrode reaction	Standard potential at 25 °C (77 °F), V_{SHE}
$Au^{3+} + 3e^- \rightleftharpoons Au$	+1.50
$Pd^{2+} + 2e^- \rightleftharpoons Pd$	+0.987
$Hg^{2+} + 2e^- \rightleftharpoons Hg$	+0.854
$O_2 + 2H_2O + 4e^- \rightleftharpoons 4OH^-$	+0.82
$Ag^+ + e^- \rightleftharpoons Ag$	+0.800
$2Hg^{2+} + 2e^- \rightleftharpoons 2Hg$	+0.789
$Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$	+0.77
$Cu^+ + e^- \rightleftharpoons Cu$	+0.521
$Cu^{2+} + 2e^- \rightleftharpoons Cu$	+0.337
$2H^+ + 2e^- \rightleftharpoons H_2$ (Reference)	+0.000
$Pb^{2+} + 2e^- \rightleftharpoons Pb$	−0.126
$Sn^{2+} + 2e^- \rightleftharpoons Sn$	−0.136
$Ni^{2+} + 2e^- \rightleftharpoons Ni$	−0.250
$Co^{2+} + 2e^- \rightleftharpoons Co$	−0.277
$Ti^+ + e^- \rightleftharpoons Ti$	−0.336
$Cd^{2+} + 2e^- \rightleftharpoons Cd$	−0.403
$Fe^{2+} + 2e^- \rightleftharpoons Fe$	−0.440
$Cr^{3+} + 3e^- \rightleftharpoons Cr$	−0.74
$Cr^{2+} + 2e^- \rightleftharpoons Cr$	−0.91
$Zn^{2+} + 2e^- \rightleftharpoons Zn$	−0.763
$Mn^{2+} + 2e^- \rightleftharpoons Mn$	−1.18
$Zr^{4+} + 4e^- \rightleftharpoons Zr$	−1.53
$Ti^{2+} + 2e^- \rightleftharpoons Ti$	−1.63
$Al^{3+} + 3e^- \rightleftharpoons Al$	−1.66
$U^{3+} + 3e^- \rightleftharpoons U$	−1.80
$Mg^{2+} + 2e^- \rightleftharpoons Mg$	−2.37
$Na^+ + e^- \rightleftharpoons Na$	−2.71
$Ca^{2+} + 2e^- \rightleftharpoons Ca$	−2.87
$K^+ + e^- \rightleftharpoons K$	−2.93
$Li^+ + e^- \rightleftharpoons Li$	−3.05

The Daniell cell is a classic example of an electrochemical cell. It comprises a zinc half-cell and a copper half-cell. As depicted in the figure below, the zinc electrode is immersed in a $ZnSO_4$ solution, while the copper electrode is immersed in a $CuSO_4$ solution. The two half-cells are connected by a salt bridge containing a K_2SO_4 solution. Additionally, the two electrodes are

connected electrically through a voltmeter, which measures the resulting potential, also known as the cell potential.

Before being connected, the equilibrium reactions occurring at each electrode are:

Zn electrode in $ZnSO_4$: $Zn \rightleftharpoons Zn^{2+} + 2e^-$, $E^0_{Zn} = -762$ V_{SHE}

Cu electrode in $CuSO_4$: $Cu \rightleftharpoons Cu^{2+} + 2e^-$, $E^0_{Cu} = +0.34$ V_{SHE}

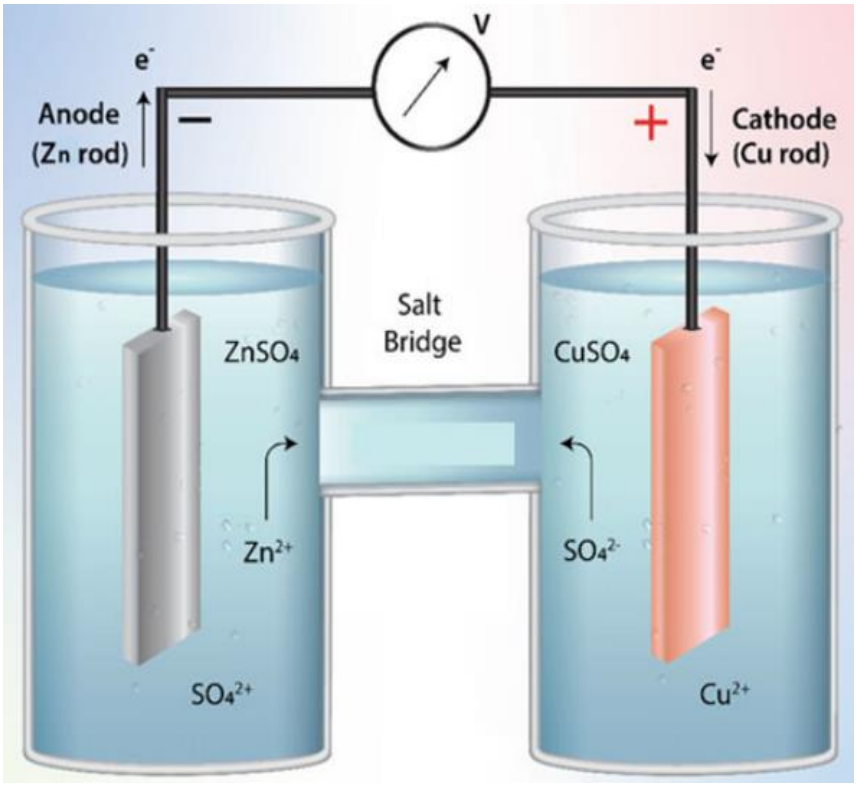


Figure I.6 . Example of electrochemical cell—Daniel cell [32]

In the EMF series shown in Table II.1, zinc is more electronegative than copper. As a result, when they are connected to form an electrochemical cell, zinc acts as the anode, and copper becomes the cathode. This leads to changes in the reactions occurring at the electrodes.

The Zn undergoes oxidation to produce Zn^{2+} ions:

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

The electrons are transported through the electrical connection to the Cu electrode. The Cu^{2+} ions in the $CuSO_4$ electrolyte accept these electrons to form Cu, which gets deposited on the electrode:

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

The cell potential thus generated due to the flow of current is calculated thus:

$$E_{Cell} = E^0_{cathode} - E^0_{anode}$$

$$E_{Cell} = E^0_{Cu} - E^0_{Zn}$$

$$E_{Cell} = +0.34 - (-0.762)$$

$$E_{Cell} = +1.102V_{SHE}$$

This process continues on its own until either the ions are entirely depleted or the resistivity of the electrolytes increases to a level that hinders the movement of ions.

I-5-3) Corrosion as Electrochemical Process:

Except for high-temperature corrosion, all corrosion reactions are electrochemical reactions occurring in an electrolyte.

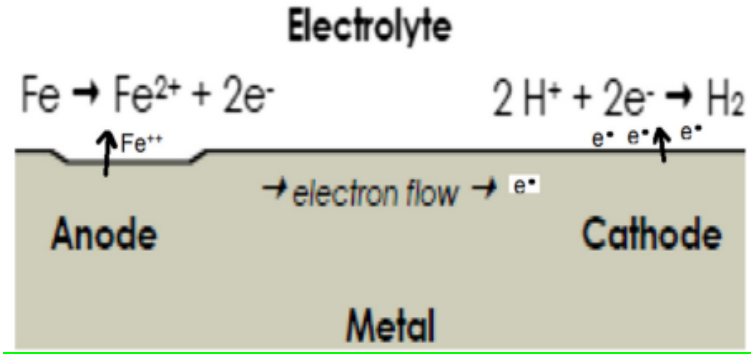


Figure I.7. Corrosion cell.

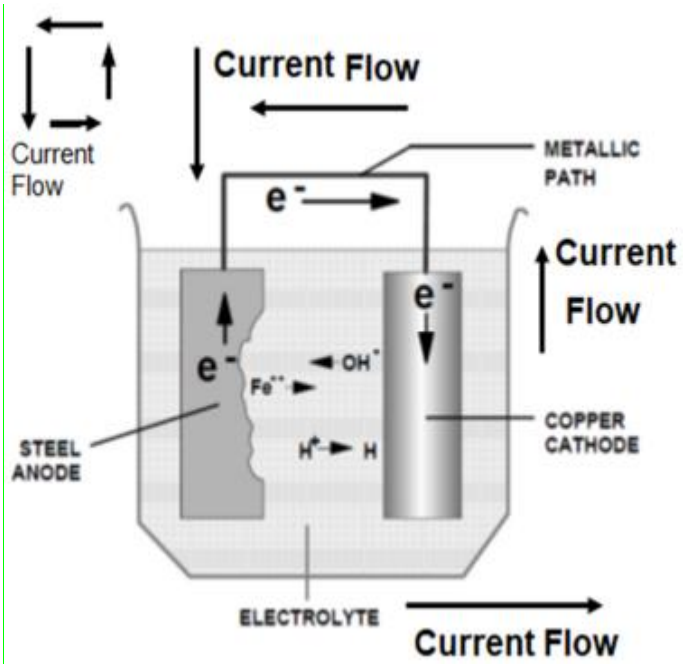


Figure. I.8 .Corrosion cell and current flow direction.

I-5-4) Corrosion Cell (The Complete Corrosion Circuit)

When an anodic reaction occurs, the electrons remain in the metal. If these electrons are not consumed in a reaction at the cathode, they will accumulate and potentially inhibit the corrosion reaction. The anodic reaction, which leads to the loss of metal, can only proceed as quickly as the electrons are consumed at the cathode. The buildup of reaction products can slow the rate of any chemical reaction. In this case, the products of the oxidation reaction are electrons that stay in the metal and metal ions that enter the solution. This type of reaction can be generically written as:

$$M^0 \rightarrow M^{n+} + ne^-$$

A buildup of metal ions in the electrolyte or reaction products in the metal will tend to reduce the reaction rate. In many corrosion reactions, the metal ions are consumed by reacting with other molecules or compounds in the electrolyte. These reactions decrease the dissolved metal ion content and allow the electrochemical oxidation reaction to proceed rapidly. The metal ions produced by oxidation at the anode combine with other substances in the electrolyte to form corrosion products. The formation of these corrosion products is a side reaction that can affect the rate of corrosion but is not directly involved in the primary electrochemical oxidation/reduction reactions.

A cathodic reaction consumes electrons. Table I-4 lists three of the most common cathodic reactions that consume electrons. Many other reactions are possible, depending on the chemical composition of the electrolyte and other conditions.

Metals are generally good conductors of electricity. Unlike electrolytes, which conduct electricity through the movement of ions, metals conduct electricity through the flow of electrons. In metals, electrons flow from areas of more negative charge (excess electrons) to areas of more positive charge (less negative charge or fewer electrons).

One source of confusion is the difference between current flow and electron flow. Conventional current flow in an electrical circuit is defined as opposite to electron flow (electron flow goes from more negative to more positive). Therefore, current flows from the more positive area in the circuit to the less positive (or from less negative to more negative) areas. The transfer of positive ions is also considered current flow, as it moves from more positive to less positive areas.

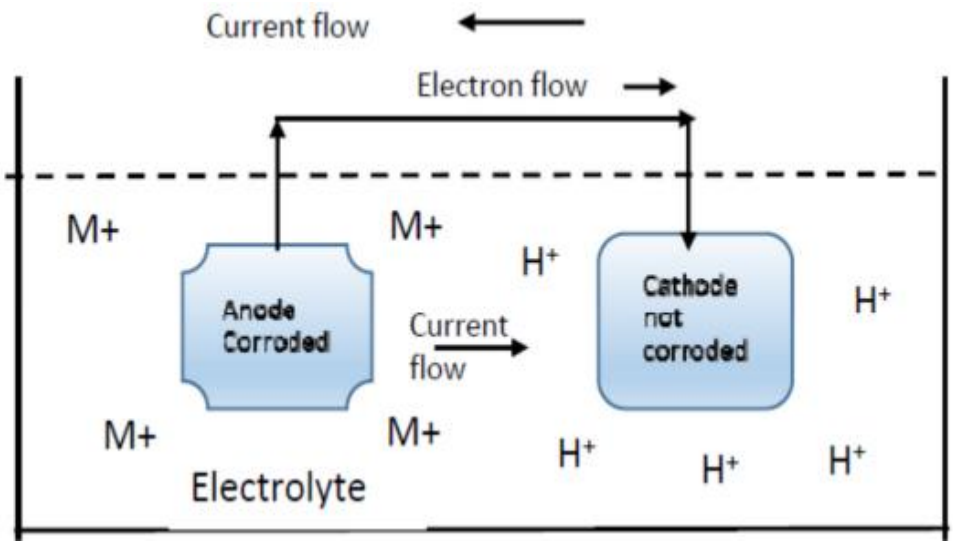
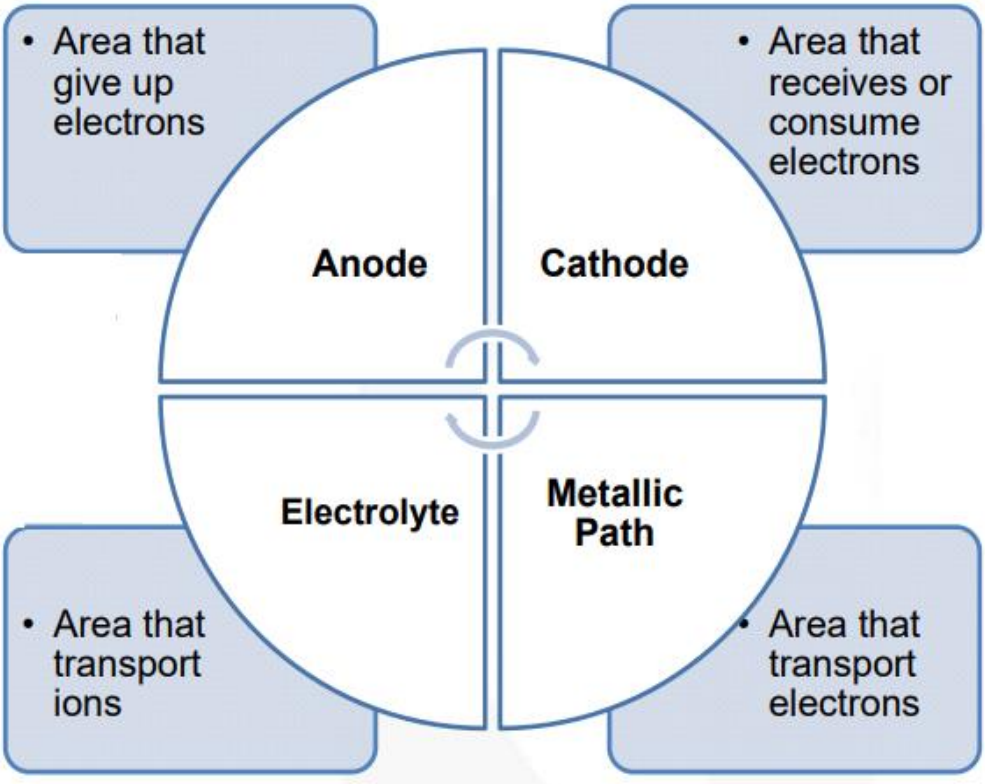


Figure. I-9. Corrosion cell and conventional current opposite to electrons flow.

In a corrosion cell, electrons flow through the metal from sites where anodic reactions occur to sites where they facilitate cathodic reactions. Electrical current also flows through the electrolyte to balance the electron flow in the metal. In this case, ions in the electrolyte carry the electrical current. Anions (negatively charged ions) move toward the anode, while cations (positively

charged ions) move toward the cathode. For the complete corrosion reaction to occur, all four components must be present and active. Therefore, the formation of a corrosion cell, which consists of the following four components, is essential for corrosion to take place:

1. Anode
2. Cathode
3. Electrolyte
4. Electrical connection between anode and cathode



1-Anode: The anode is the site where metal is lost and electrons are produced

Anodic reaction: (Oxidation): $M^0 \rightarrow Mn^+ + ne^-$

Anodic reaction is an oxidation reaction results in generation of electrons and increase of the positive charge of a metal.

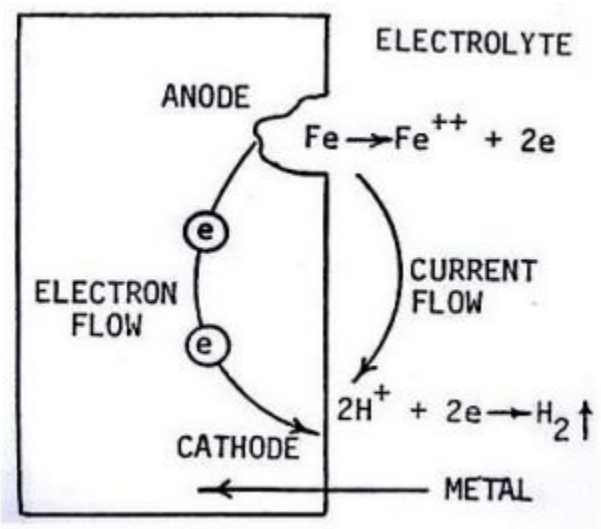
Example: $Fe^0 \rightarrow Fe^{++} + 2e^-$

2- Cathode: The cathode is the site where the electron produces at the anode are consumed. Cathodic reaction (Reduction) is any reaction consumes electrons.

Example: $2H^+ + 2e^- \rightarrow H_2$

3- Metallic path: The metallic pass conducts electrons from the anodic sites to the cathodic sites.

4- Electrolyte: The electrolyte provides reactants for the cathodic reactions and allow the flow of ions.



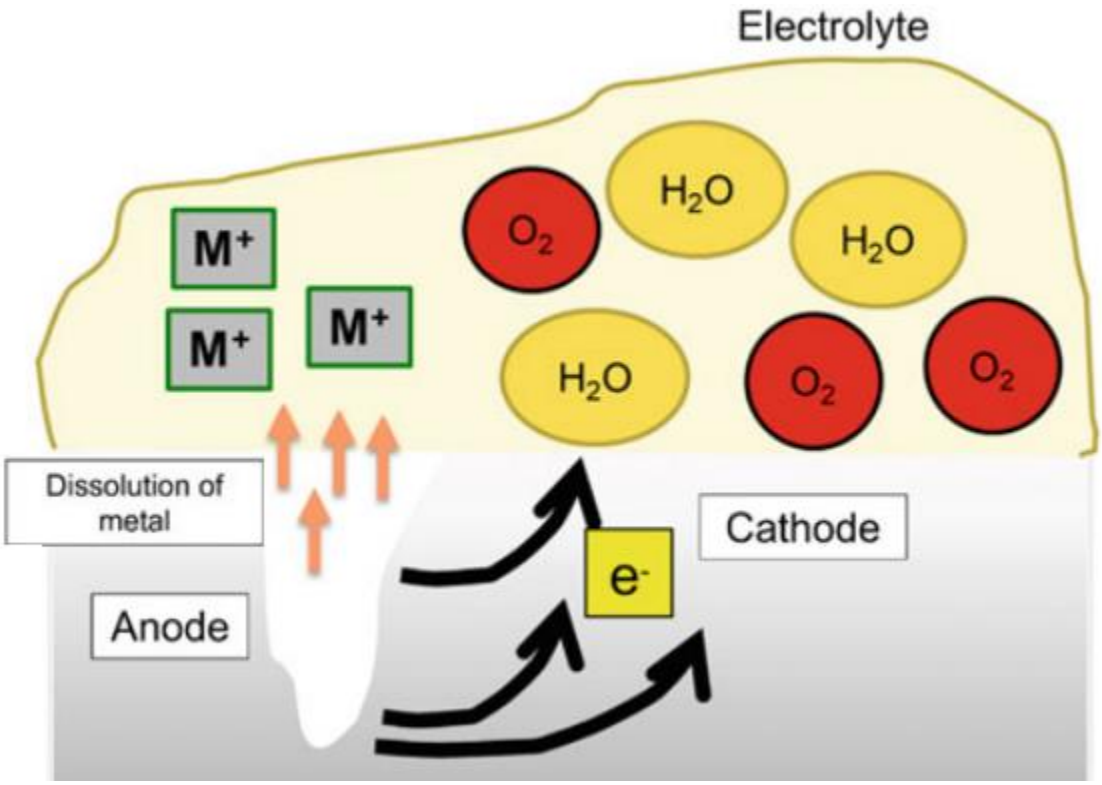


Figure. I-10.. Mechanism of Metal dissolution in Corrosion cell.

Generally, a higher potential difference increases the likelihood of corrosion. This holds true for systems where the anode and cathode are distinct. However, in practical scenarios, corrosion can occur on a single material without a separate cathode. When only one material is exposed to the environment, all the necessary elements for corrosion are present on that single material. The figure below illustrates a typical example of such a corrosion cell.

I-5-5) Corrosion rate expressions:

Corrosion rates can be assessed using various methods, including:

- ✓ Measurement of depth of penetration
- ✓ Determination of weight loss
- ✓ Evaluation of electrical current related to corrosion
- ✓ Analysis of time to failure

Among the methods for assessing corrosion, the most straightforward concept to grasp is depth of penetration, typically denoted in millimeters per year (mm/yr) or mils (thousandths of an inch) per

year (mpy). This metric, often measured by the loss of wall thickness, serves as a crucial indicator for determining the remaining lifespan of equipment or establishing safe operating pressures in piping systems, storage tanks, and similar structures. Table below outlines a widely used classification system for relative corrosion rates. The utilization of mpy in the U.S. Standard units simplifies comprehension due to the generation of small numerical values, making corrosion rates expressed in mpy a prevalent global standard, although alternative expressions are also utilized [34].

Table I-6. Relative Corrosion Resistance versus Annual Penetration Rates

Relative Corrosion Resistance	Corrosion Rate	
	mpy	mm/yr
Outstanding	< 1	<0.02
Excellent	1-5	0.02-0.1
Good	5-20	0.1-0.5
Fair	20-50	0.5-1
Poor	50-200	1-5
Unacceptable	200+	5+

Source: Adapted from M. Fontana. 1986. Corrosion Engineering. New York: McGraw - Hill.

Weight loss measurements are frequently employed in monitoring corrosion rates within oil and gas production through exposure samples. While converting these measurements into average depths of penetration is relatively straightforward, it can be misleading. This is because corrosion tends to occur in localized areas, and the average penetration rate often fails to accurately reflect the true condition of oilfield equipment.

The current generated from the anodic dissolution of a metal can serve as a basis for calculating the corrosion rate using Faraday's law. This computation of mass loss can then be translated into remaining thickness. It's important to note, however, that corrosion predominantly occurs in localized regions, and calculations assuming uniform cross-sectional loss can often lead to misleading conclusions.

On the other hand, the time until failure, regardless of its specific definition, remains the primary concern for equipment managers and operators. In certain corrosion testing scenarios, such as stress corrosion cracking assessments, the time until failure serves as a means to evaluate alloys, environmental conditions, or other pertinent variables.

I-5-6) Hydrogen Potential of Environment:

The acidity level within an environment stands as a pivotal determinant for the onset of corrosion, impacting the specific type of corrosion encountered as well.

$$pH = -Log[H^+]$$

where the $[H^+]$ expression shows the hydrogen ion activity of the environment.

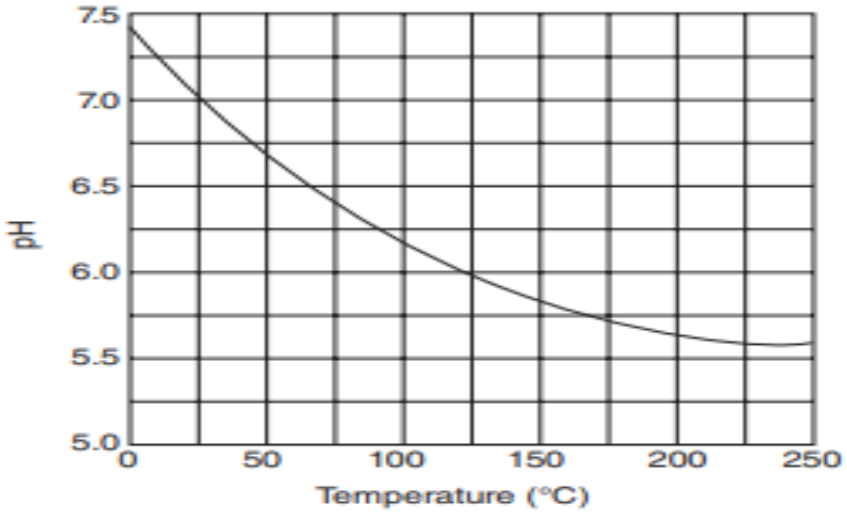


Figure I.11. pH values of pure water at various temperatures.[35]

The concentration of hydrogen ions ($[H^+]$) is contingent upon the ionization of water and fluctuates according to temperature. At the standard temperature of 25°C, the pH of neutral water is 7.00, yet neutrality varies with temperature, as depicted in Figure above. In oilfield environments, where temperatures are typically elevated, it is customary to compute the in situ pH of any fluids that may impact corrosion or scale deposition. Numerous software solutions are available for this purpose. Figure below illustrates how pH influences the corrosion rates of iron in water. At low pH levels, the metal surface is exposed to the surrounding environment, leading to corrosion rates controlled by acid reduction on the surface. For intermediate pH levels, a partially protective layer of iron oxide mitigates corrosion rates, while the diffusion of oxygen to cathodic sites on the metal surface takes precedence. As pH rises to higher values, the surface becomes coated with mineral scales, reducing corrosion.

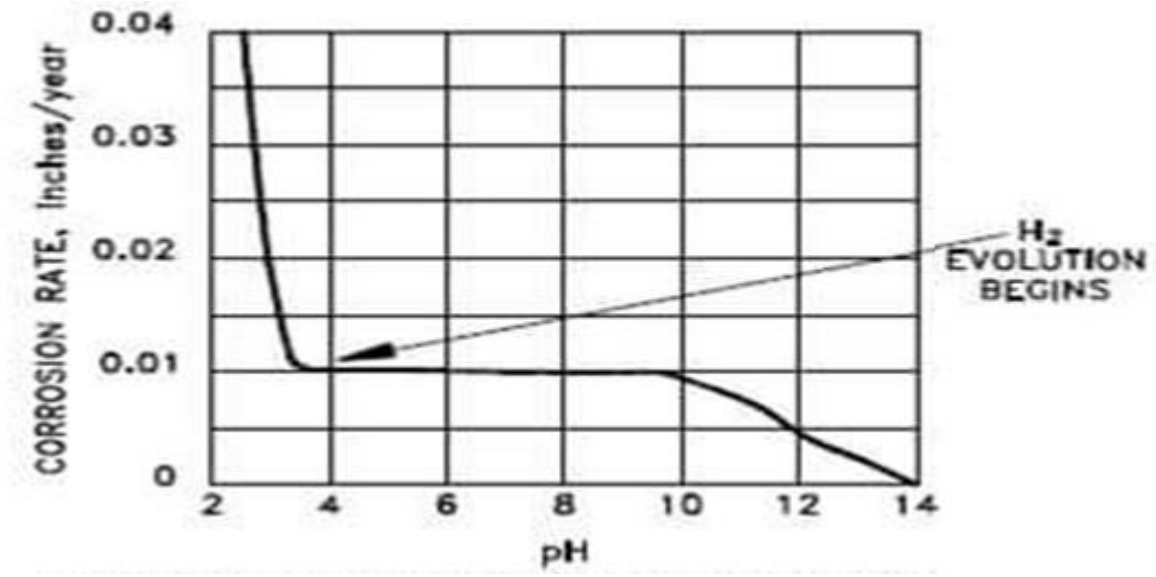


Figure.I.12. The effect of pH on the corrosion rate of iron in water at room temperature. Adapted from W. R. Revie and H. H. Uhlig, Corrosion and Corrosion Control , Wiley - Interscience, 2008.

I-5-7) Evans Diagram:

The Evans diagram, developed by scientist Ulick Richardson Evans in the early 1900s, illustrates the relationship between the potential and current density of an electrochemical system. This diagram can represent any redox reaction. The figure below displays the Evans diagram for iron (Fe) in an acidic environment. The primary redox reactions in this electrochemical system are:

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

$$2H^{+} + 2e^{-} \leftrightarrow H_2$$

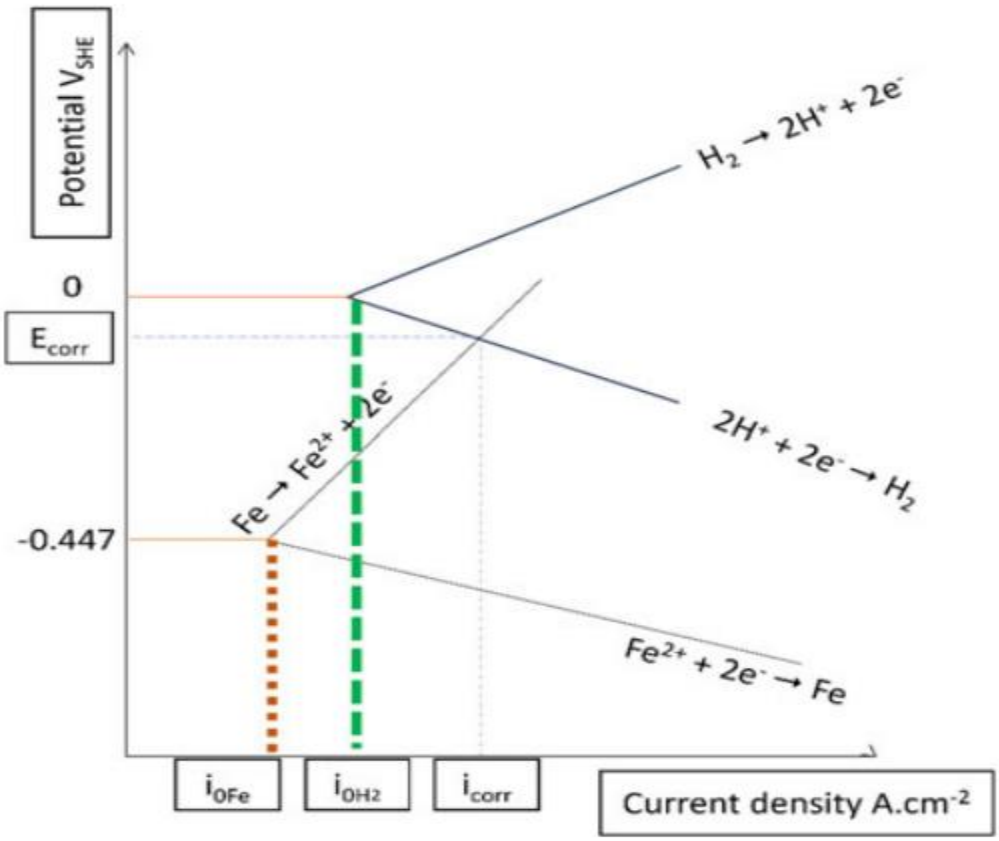


Figure I.13. Evans diagram for a Fe–H_2 system [32].

The Evans diagram plots the relationship between current density and potential for each of these reactions. As shown in the figure below, the X-axis represents current density, while the Y-axis denotes potential. The diagram features two sets of plots. The first set corresponds to $Fe|Fe^{2+}$. According to the EMF series, the standard electrode potential for Fe (E^0_{Fe}) is −0.447 V_{SHE}.

The current density I_0 at this point represents the exchange current density, which reflects the rate of ion exchange at the electrochemical double layer near the Fe surface in the electrolyte. From this point, two branches emerge: The branch extending to more negative potentials than E_0 Fe is the cathodic branch. When the system's potential shifts toward this branch, the reduction of Fe^{2+} ions to form Fe becomes more dominant. Conversely, if the potential moves to more positive values than −0.447 V, the oxidation of Fe to form Fe^{2+} ions becomes more prevalent. This inclined line represents anodic branch.

Similarly, the plot for $H_2|H^+$ also exhibits anodic and cathodic branches. The intersection of these branches occurs at a potential of 0V because the standard electrode potential for the $H_2|H^+$ redox reaction is zero in the EMF series. The current density I_0 for $H_2|H^+$ represents the exchange current density for this reaction. Like the Fe redox reaction, the anodic branch signifies a predominant formation of H^+ ions, while the reduction of H^+ ions and the evolution of H_2 are favored at potentials in the cathodic branch.

Additionally, the cathodic branch of $H_2|H^+$ intersects with the anodic branch of $Fe|Fe^{2+}$. At the intersection point, the reactions of Fe oxidation and H^+ reduction occur at the same current density and potential. This intersection indicates the corrosion of Fe in an acidic environment. The current density at this point is termed the corrosion current density (i_{corr}), and the potential is referred to as the corrosion potential (E_{corr}). This approach to analyzing corrosion kinetics is known as the 'mixed potential theory' [36].

This Evans diagram is particularly useful when multiple cathodic species are involved, as illustrated in Figure below.

The plot for $Fe|Fe^{2+}$ is positioned at the bottom of the diagram at the standard electrode potential E^0_{Fe}=−0.447 V_{SHE} and represents the following redox reaction:

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

Above this, there are two cathodic species: $H_2|H^+$ and $O_2–H_2O|OH^-$, with standard electrode potentials E^0_{H2}=0 V_{SHE} and $E^0_{O2–H2O}$ = +0.82 , respectively. Their redox reactions are:

$$2H^+ + 2e^- \leftrightarrow H_2$$

$$O_2 + 2H_2O + 4e^- \leftrightarrow 4OH^-$$

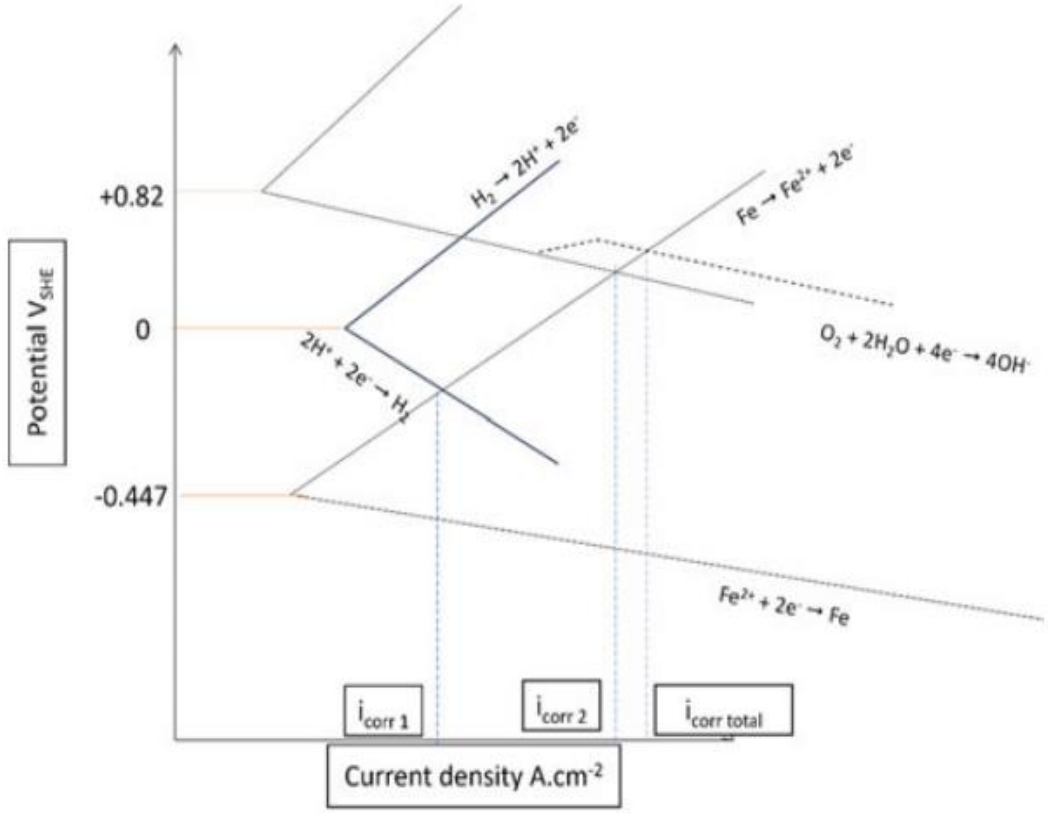


Figure I.14. Evans diagrams for a Fe–H_2–O_2/H_2O system [32]

In the plot for O_2–H_2O|OH^-, at potentials along the cathodic branch, O_2 and H_2O accept electrons and react to form OH^-, while along the anodic branch, OH^- releases electrons to produce O_2 and H_2O. This plot is positioned above the H_2|H^+ plot.

Additionally, the cathodic branches for both H_2 reduction and O_2–H_2O reduction intersect with the anodic branch of Fe oxidation. As a result, Fe experiences oxidation due to the combined effect of these cathodic reactions.

The dotted line represents the combined rates of anodic and cathodic reactions. The corrosion potential (E_{corr}) and corrosion current density (I_{corr}) are determined from the intersection point of the synergistic cathodic branch with the anodic branch of the metal. Therefore, when a system involves multiple cathodic or anodic reactions, the Evans diagram can be employed to plot each individual branch and assess the combined effects of the species. This approach is particularly

useful in complex environments, such as dilute acidic conditions where both hydrogen ions and O_2, as well as H_2O, act as cathodic species.

I-5-8) Potential - pH (Pourbaix) Diagrams:

Marcel Pourbaix introduced a method for elucidating the thermodynamic aspects of corrosion systems through the creation of potential-pH (Pourbaix) diagrams. These diagrams illustrate the regions of thermodynamic stability for metals and their reactions at various potential and pH levels [37-38]. The regions depicted on a Pourbaix diagram can be characterized as follows:

- ✓ **Immunity:** In this region, the metal is incapable of undergoing oxidation or corrosion, although it may still be susceptible to hydrogen embrittlement.
- ✓ **Corrosion**: Metals in this zone have ions that are thermodynamically stable, leading to corrosion of the metal.
- ✓ **Passivity:** Compounds of the metal and environmental chemicals reach thermodynamic stability in this region. The metal may be shielded from corrosion if a protective and adherent passive film forms.

The ultimate point often overlooked by many users of Pourbaix diagrams is that thermodynamics alone cannot determine whether passive films will provide effective protection or not.

In Figure below, the Pourbaix diagram for iron is overlaid onto the water diagram. Comparable diagrams are accessible for the majority of structural metals with available thermodynamic data [39-40]. These diagrams highlight several significant points that are valuable for corrosion control in oilfield applications.

These diagrams convey several crucial insights relevant to corrosion control in oilfield operations:

- ✓ The stability of water is limited to a potential range slightly exceeding one volt. This fact bears significant importance in the context of cathodic protection strategies.
- ✓ Iron (specifically carbon steel) typically forms passive oxide layers in most aqueous environments. Regrettably, these passive films often fail to provide adequate protection, necessitating alternative corrosion prevention methods.
- ✓ The protective potentials for iron (carbon steel) against corrosion do not align with the immunity regions depicted on the Pourbaix diagram.

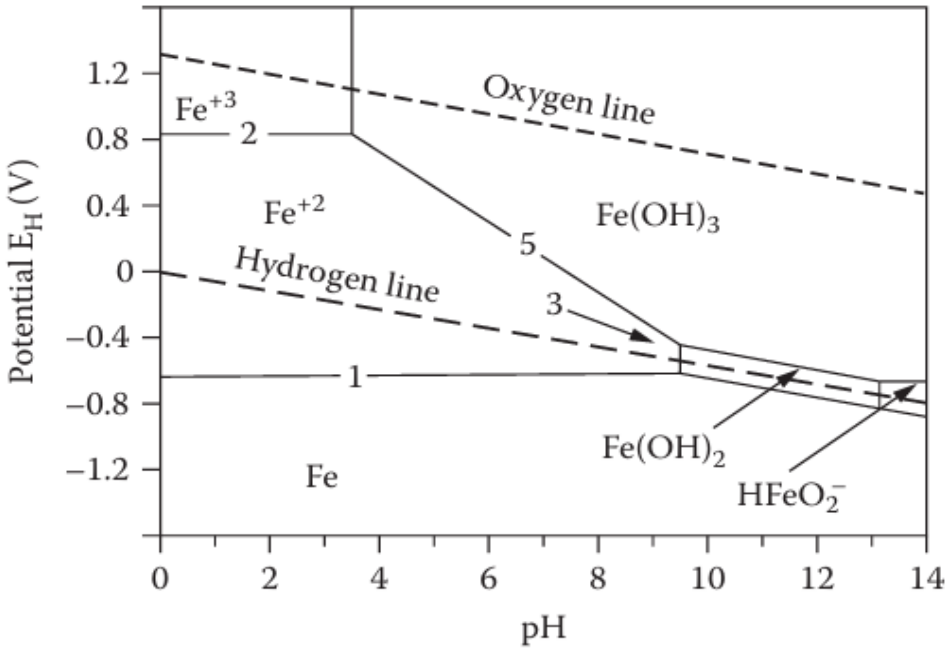


Figure I.15. Potential–pH (Pourbaix) diagram for Fe–H2 O system..[41]

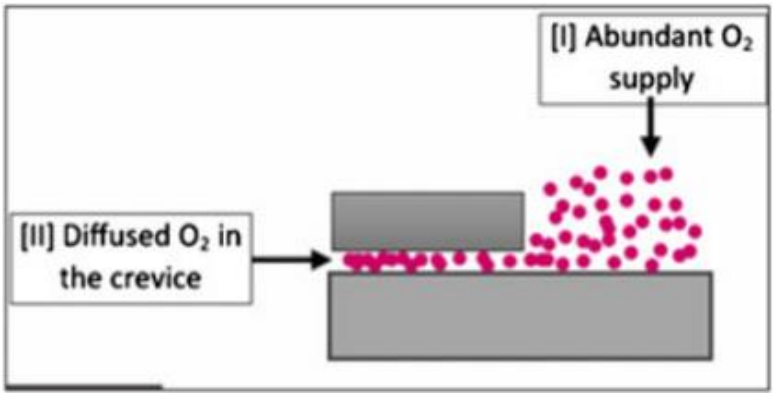
The Pourbaix diagrams for zinc, aluminum, and cadmium, often known as the amphoteric coating metals, exhibit passive regions in neutral environments. These metals also demonstrate lower corrosion rates in neutral conditions compared to acidic or basic environments.

In addition to the challenge of thermodynamics in predicting the effectiveness of passive films, Pourbaix diagrams have further limitations. One limitation is that they are typically applicable only to alloys, although there have been reports of experimental Pourbaix diagrams[38-42].

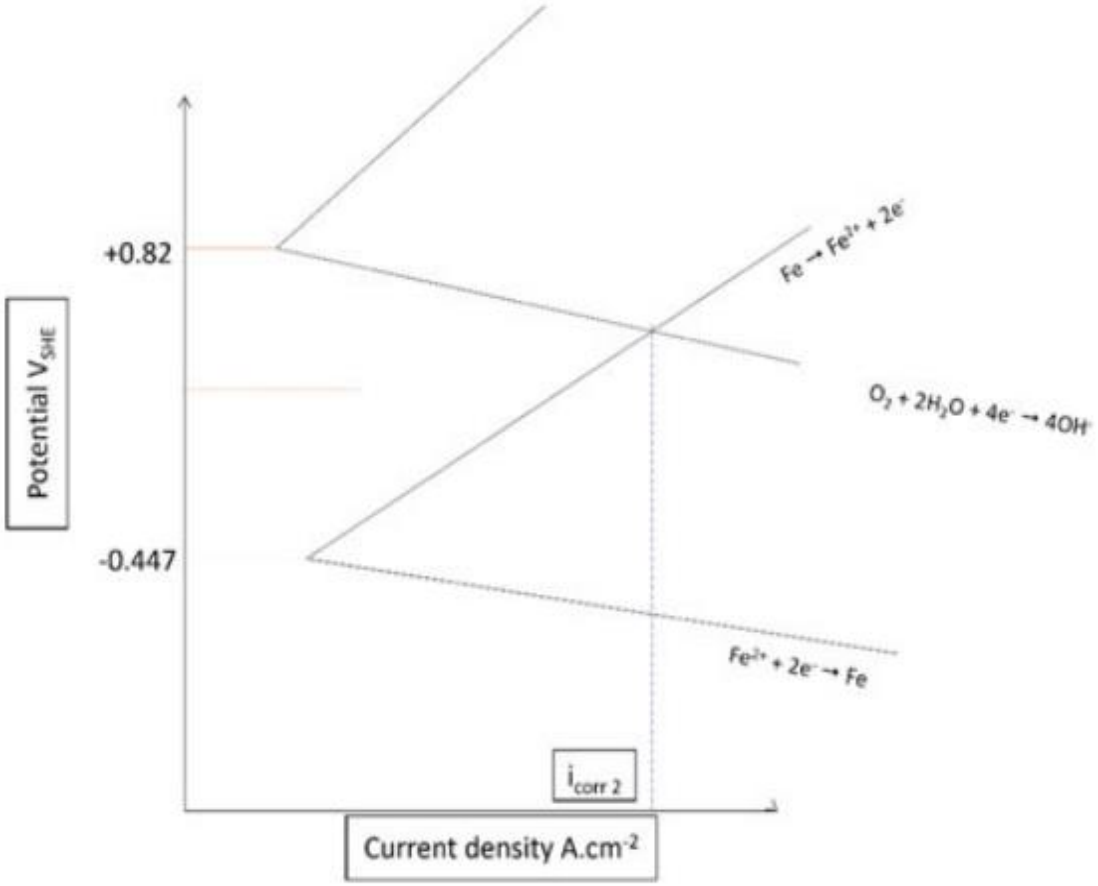
I-5-9) Polarization:

When the cathodic and anodic species are well dispersed in the liquid electrolyte, the system undergoes active corrosion, similar to the behavior depicted in the Evans diagram shown earlier. However, if the cathodic species is a gaseous substance, such as O_2, the cathodic branch of the reduction reaction may alter, as illustrated in Figure.I.16. The factors influencing the cathodic branch of a gaseous substance include its concentration, diffusion coefficient, temperature, pressure, or pH. These factors can cause a shift in the potential of the cathodic reaction. This shift

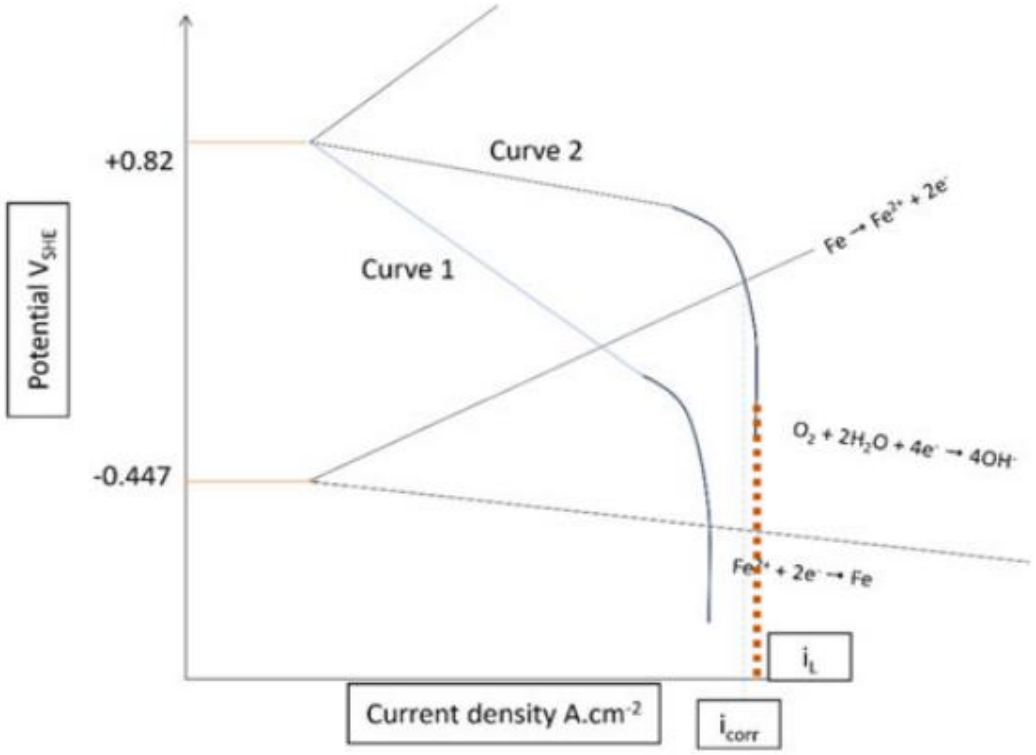
in potential due to these factors is known as polarization, and the extent of this shift is referred to as overpotential or overvoltage.



(a) Pictorial representation of concentration cells in a crevice



(b) Activation polarization



(c) Concentration polarization

Figure. I.16 . Types of polarization, inset pictorial representation of difference in the O_2 concentration in a crevice and on open surface [32]

Figure I.16a: illustrates a crevice with O_2 concentration cells. The region outside the crevice is exposed to a plentiful supply of O_2 from the atmosphere, resulting in a high O_2 concentration. If polarization occurs due to species that promote active corrosion, allowing efficient contact between anions and cations, this process is termed active polarization. However, if the movement and reaction of anions depend on the concentration of the cathodic species, the resulting change in potential, or polarization, is known as concentration polarization. Activation polarization is described by the Tafel equation, as shown below.

$$\eta_a = \pm\beta \log \frac{i}{i_o},$$

where η_a is the overvoltage, β is the slope of the active anodic or cathodic branch, i is the current density causing the overvoltage, and i_0 is the exchange current density when η_a is zero.

Meanwhile, the concentration of O_2 within the crevice is low due to its limited availability, leading to the development of concentration polarization. This type of polarization depends on the concentration and diffusion of the species. As illustrated in Figure. I.16c, curve 1, which represents activation polarization, shifts to become curve 2 when the O_2 concentration decreases due to insufficient diffusion within the crevice. The curve becomes vertical and intersects the X-axis at a point known as the limiting current density, i_L, which is defined as the constant current density that results from a steady concentration of the species. This scenario is particularly relevant for components with crevices, gaps, or enclosed areas, such as boilers, where the amount of O_2 is limited. The formula used to calculate concentration polarization is as follows:

$$\eta_c = 2.3\frac{RT}{nF}\log\left(1 - \frac{i}{i_L}\right),$$

where η_c is the concentration overvoltage, i is the current density causing the over voltage, i_L is the limiting current density, R is the gas constant, T is the temperature (K), n indicates the number of moles of electrons transferred during the reaction, and F is the Faraday's constant.

The limiting current density, i_L, needed for this formula is determined based on the diffusion coefficient. The concentration and the area between the spaces where O_2 can diffuse are calculated as shown below:

$$i_L = \frac{DnFC_B}{x},$$

where D is the diffusion coefficient, n indicates the number of moles of electrons transferred during the reaction, F is the Faraday's constant, C_B = concentration of the diffusing species, and x is the width of the crevice.

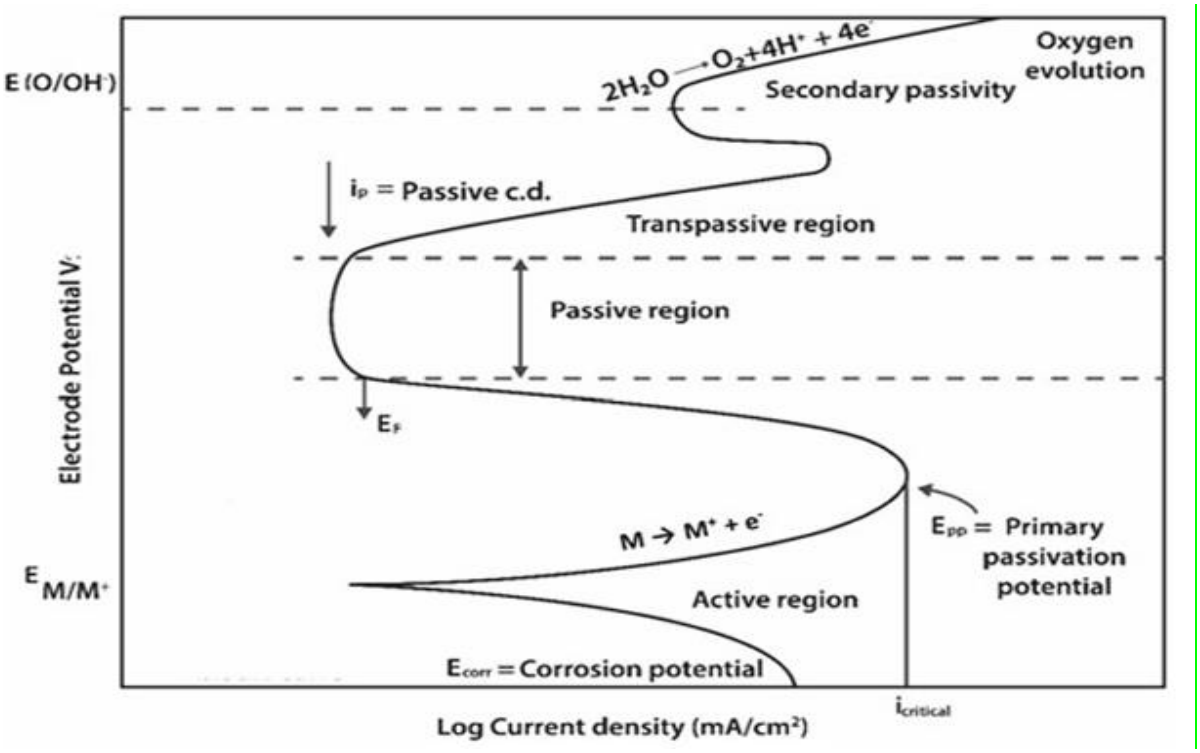


Figure. I.17. Evans diagram for an active–passive metal—adapted from [43]

All the Evans diagrams above show active corrosion only when equilibrium is reached, and corrosion occurs at a steady, constant rate at the corrosion potential and corrosion current density. However, when the material contains an oxide, it tends to form an oxide film. The Evans diagram exhibits some additional characteristics, which are detailed below in figure 9.

As shown in Figure. I.17, the active region consists of both anodic and cathodic branches. However, at a specific potential known as the primary passivation potential, or E_p , the current density begins to decrease as the potential increases. This decline in current density suggests that some areas of the surface have developed an oxide film, making them unavailable for further corrosion. As the passive film forms across the entire surface, the amount of corrosion decreases. When the current density reaches a certain lower value, the corresponding potential is referred to as the flared potential, indicating a transition from active to passive corrosion behavior [43]. Passivation continues in the passive region, where the passive film is constantly breaking and reforming.

However, this occurs at a constant current density, even as the applied potential continues to increase. Beyond a certain point, the passive film cannot withstand additional potential, causing it to break down and fail to reform, leading the material into the transpassive region. The current

density at which the passive film is maintained is known as the passive current density. In the transpassive region, the alloy may experience continuous corrosion and might form a transitional passive film, but this film is not durable because it lacks sufficient compactness. As a result, the film easily breaks, leading to a secondary transpassive region known as secondary passivity. Beyond this stage, the alloy is unable to regain its passive state, and pitting corrosion continues without interruption.

Stainless steels, aluminum alloys, magnesium alloys, Inconel alloys, chromium alloys, and titanium alloys are common examples of materials that exhibit active–passive behavior. These alloys form an oxide film when exposed to the atmosphere.

I-6) Types of corrosion in Oil and Gas Industry:

Corrosion is an electrochemical process that occurs wherever metal is exposed to an environment. This process involves the deterioration of the metal through an oxidation-reduction reaction, where the metal acts as the anode and is oxidized by releasing electrons to the surrounding environment. Corrosion has significantly affected metallic structures in the oil and gas industry. It is an inevitable process primarily due to two factors: working conditions and environmental exposure. Corrosion can be categorized into two types: internal and external.

Internal corrosion typically occurs within tanks, pipelines, boilers, and similar equipment, and is associated with the transport of fluids and hydrocarbons within these containers and pressure vessels. The primary causes of internal corrosion are corrosive components present in the fluids and hydrocarbons. On the other hand, external corrosion is related to exposure to corrosive elements in the external environment, such as seawater, temperature, humidity, rain, microorganisms, and external stresses, which can impact the surface of the metal.

In the oil and gas sector, carbon dioxide (CO_2) and hydrogen sulfide (H_2S) are frequently encountered, with water acting as a catalyst for corrosion. When water interacts with CO_2 and H_2S, it initiates the following reactions [44]:

H_2CO_3 Reaction : $Fe + H_2CO_3 \rightarrow FeCO_3 + H_2$

H_2S Reaction : $Fe + H_2S + H_2O \rightarrow FeS + 2H$

If both gases are present, a combination of the aforementioned reactions may occur. The resulting molecules can either adhere to the cathode or be released into the electrolyte, thereby perpetuating the corrosion process.

Classifying the various types of corrosion in the oil and gas sector uniformly presents a significant challenge. Corrosion can be categorized based on the appearance of the damage, the attack mechanism, the industry sector, and preventive measures. There exists a multitude of corrosion types and causes. The mechanisms at play in a particular piping system depend on factors such as fluid composition, service conditions, geometry, temperature, and more. Regardless of the specific type, electrolytes must be present for corrosion reactions to take place.

I-6-1) Sweet corrosion (CO_2 corrosion):

CO_2 corrosion has posed a persistent challenge in oil and gas production and transportation facilities for numerous years [45]. Among the primary corrosive agents in these systems, CO_2 stands out prominently [46]. While dry CO_2 gas lacks corrosive properties at the temperatures typical of oil and gas production systems, it becomes corrosive upon dissolving in an aqueous phase. In this state, it facilitates an electrochemical reaction between steel and the surrounding aqueous phase. Upon mixing with water, CO_2 forms carbonic acid, thereby acidifying the fluid. The occurrence of CO_2 corrosion is influenced by various factors including temperature, pH level, aqueous stream composition, presence of non-aqueous phases, flow conditions, and metal characteristics [46,47]. This type of corrosion represents the predominant form of attack encountered in oil and gas production [48]. Additionally, at elevated temperatures, an iron carbide scale may form on the surface of oil and gas pipes, initially serving as a protective barrier; however, corrosion still proceeds under these conditions. CO_2 corrosion typically manifests in two primary forms: pitting, characterized by localized and rapid metal penetration at specific areas [49], and mesa attack, occurring under medium-flow conditions [50]. Figure I.18 illustrate pitting corrosion and mesa attack, respectively.

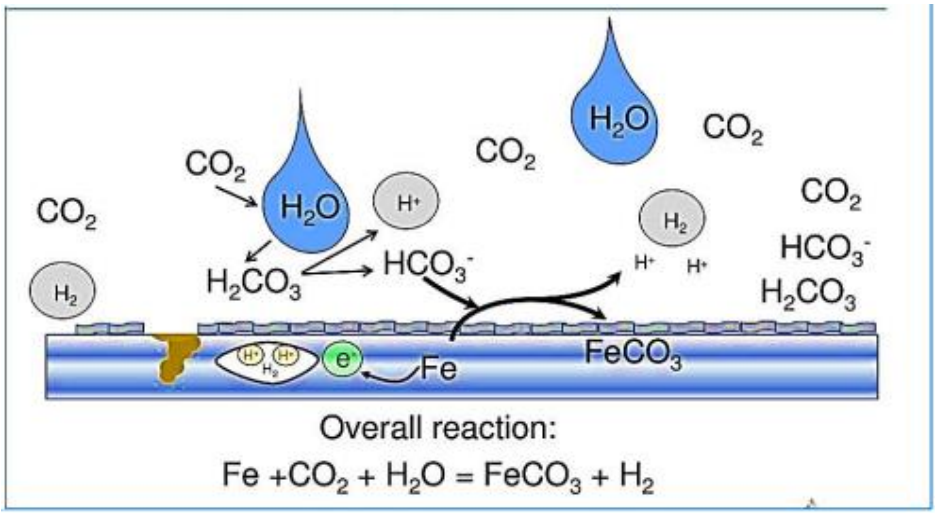


Figure I.18. Mechanism of Sweet Corrosion

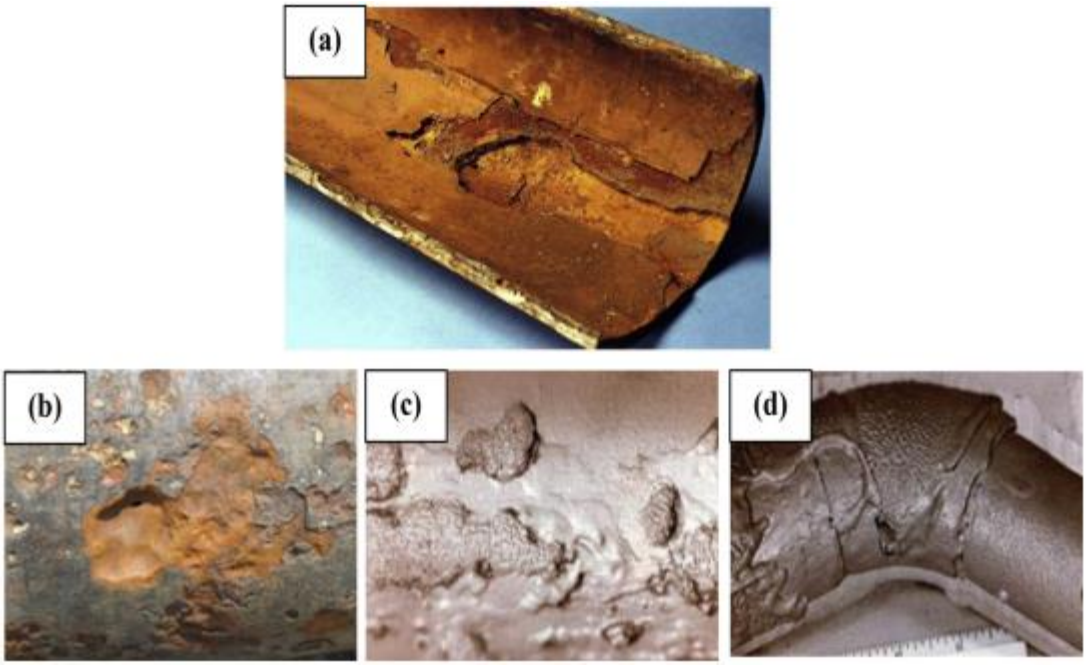


Figure I.19: Corrosion induced by CO_2. (a) general corrosion, (b) pitting, (c) mesa attack, and (d) flow induced localized [51]

Sweet corrosion can lead to various forms of corrosion in metallic structures, with pitting corrosion, mesa corrosion, and flow-induced localized corrosion being the most common.

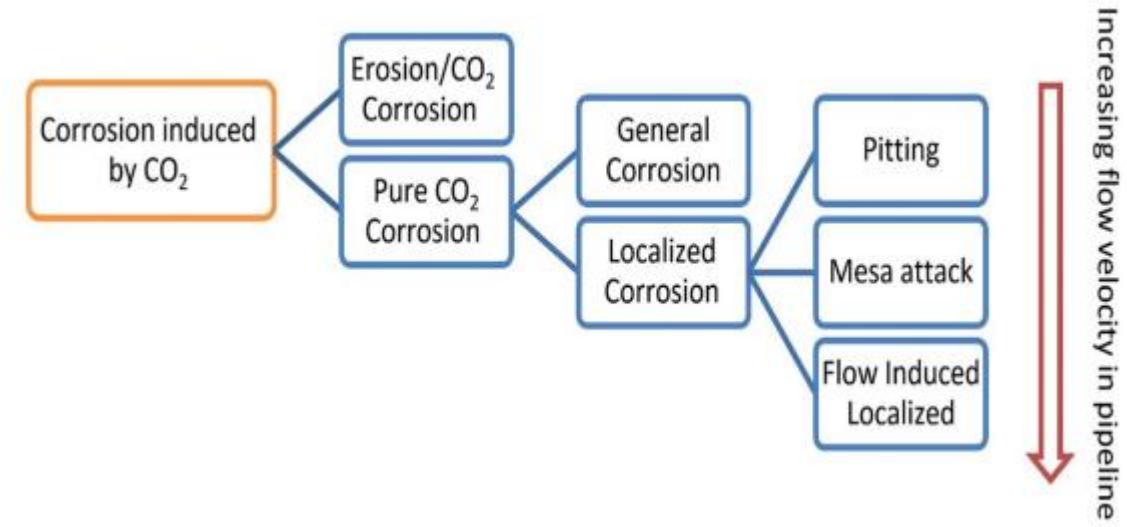


Figure.I.20. Corrosion induced by CO_2

-Factors influence CO_2 corrosion

The severity of CO_2 corrosion depends on a number of factors that affect the formation and properties of the carbonate film. These factors include [52]:

- ✓ Temperature;
- ✓ Partial pressure of CO_2;
- ✓ pH;
- ✓ water content and chemistry of water;
- ✓ flow type and its velocity;
- ✓ The presence of oxygen, organic acids and H_2S.

The severity of corrosion has been found to increase with higher flow velocity, elevated partial pressure of CO_2, increased water content, and lower pH levels. Several studies [53–54] have investigated the factors affecting the rate of CO_2 (sweet) corrosion in oil and gas facilities.

I-6-2) Sour corrosion (H_2S corrosion):

Sour corrosion, also known as H_2S corrosion, refers to the degradation of metal resulting from exposure to hydrogen sulfide (H_2S) and moisture, posing significant damage to drill pipes. Although H_2S does not exhibit corrosive properties on its own, its interaction with water transforms it into a highly corrosive agent, leading to the embrittlement of pipelines [55]. When hydrogen sulfide dissolves in water, it acts as a weak acid, releasing hydrogen ions and thereby contributing

to corrosion. The corrosion byproducts primarily consist of iron sulfides (FeS_x) and hydrogen. Iron sulfide can form a protective scale that, at lower temperatures, acts as a barrier to impede corrosion [56]. Sour corrosion can manifest in various forms, including uniform corrosion, pitting corrosion, and stepwise cracking.

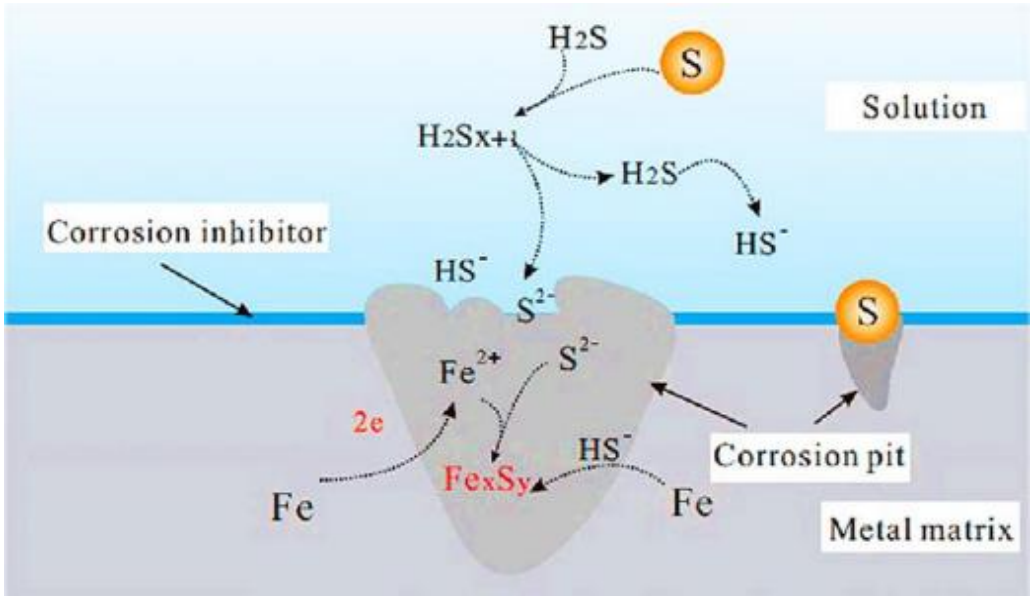


Figure. I.21. Mechanism of Sour Corrosion

Figure.I.22. Oil and gas pipeline under sour corrosion

Factors influence H_2S corrosion:

Several factors have been reported to affect the rate and behavior of H_2S corrosion in the oil and gas environment [57,58]. These factors include flow velocity, temperature, H_2S partial pressure,

exposure time, concentrations of dissolved salts and organic acids (such as NaCl and CH_3COOH), the concentration and dissociation of H_2S, steel composition, the nature of deposits on the metal surface (such as corrosion products, scales, and wax), the presence of oxygen, and fluid chemistry (such as pH, water cut, phase ratios, organic acids, and oil wettability). Since these factors are interconnected and influence H_2S corrosion, it is challenging to isolate the impact of a single factor. However, H_2S corrosion has been extensively studied in the oil and gas industry [57,59].

I-6-3) Microbiologically induced corrosion

This corrosion type is instigated by bacterial activity within the pipeline. These bacteria generate byproducts such as CO_2, H_2S, and organic acids, which heighten the corrosive nature of the fluid flowing through the pipes [60]. Microbial colonies tend to form in conducive environments, accelerating corrosion within these colonies. The development of such colonies is facilitated by neutral water conditions, particularly in stagnant areas [61]. Various studies have reported the presence of microbes in reservoirs [62-63]. Lazar et al. [64] identified a diverse microbial flora indigenous to oil field formation waters, including species such as Bacillus, Pseudomonas, Micrococcus, Mycobacterium, Clostridium, and Escherichia. Escherichia, known to contain hydrogenase enzymes that utilize molecular hydrogen, may contribute to cathodic hydrogen depolarization, thereby inducing corrosion in steel casings and pipes within oil fields [65]. Bacteria capable of producing slime, such as Achromobacter sp., Flavobacterium sp., and Desulfuricans sp., aggregate to form large masses and adhere to pore walls, leading to significant plugging issues in injection wells [63]. The occurrence of microbiologically induced corrosion (MIC) is evident from the presence of black slimy waste material or nodules on the pipe surface, along with pitting of the pipe wall beneath these deposits.

Figure.I.23: Pipeline affected by MIC corrosion

I-7) Forms of Corrosion:

Numerous systems exist for classifying corrosion, yet the most prevalent categories adhere to a framework introduced by M. Fontana. He popularized this pattern through a series of articles in Chemical and Engineering News during the 1940s and later in a textbook he authored while serving as a professor at Ohio State University [34].

According to Fontana [34], there are eight forms of corrosion: • Uniform • Galvanic • Pitting • Crevice • Intergranular • Selective leaching • Stress corrosion cracking • Erosion corrosion

A benefit of this type of corrosion classification is its potential for confirmation through visual inspection, facilitating the identification of potential remedial actions without the need for laboratory analysis[34]. The widespread adoption of the terminology for various forms of corrosion listed above is attributed to its alignment with suitable methods of corrosion control. These forms of attack are prevalent in the chemical process industry, where Fontana initiated his career. Additionally, they necessitate water in some capacity as part of the environment. All of the above forms are commonly encountered in oilfield applications:

a) **General Corrosion :** General corrosion manifests as a uniform attack and is the most frequently encountered type. It involves a chemical or electrochemical reaction that uniformly progresses across the entire exposed surface area. As a result, the metal gradually thins out and eventually fails.

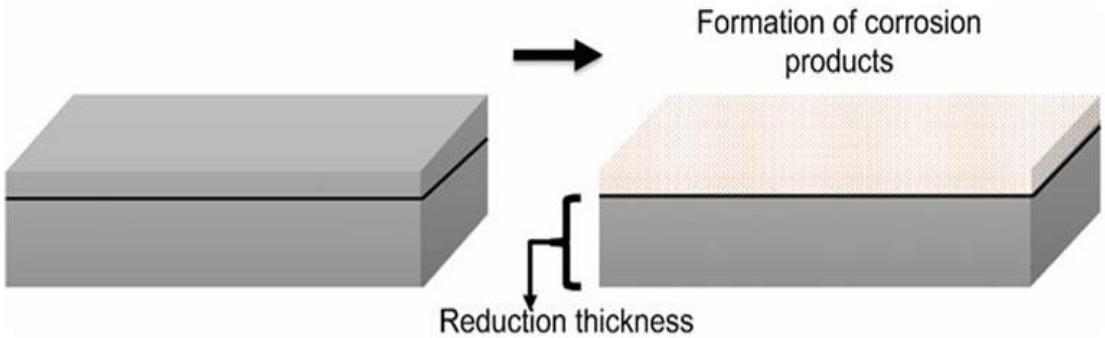


Figure. I.24. Uniform corrosion resulting in thickness reduction [32]

Mechanism: When corrosion cells develop across the entire surface of a material exposed to a corrosive environment, corrosion occurs uniformly across the surface. This results in material loss in all areas of the surface, leading to a reduction in wall thickness, as illustrated in Figure I. 24. This process is also accompanied by the formation of a corrosion

product layer, where the dissolved material reacts with anions in the electrolyte to form compounds. Uniform corrosion can be calculated using the following formula:

$$CR = \frac{W}{A \times t \times d},$$

where CR is the corrosion rate, A is the area exposed to the corrosive medium, t is the time of exposure, and d is the density.

The corrosion rate can be expressed in units of mils(1000 mils= 1 Inch) per year or millimeters per year, depending on the units of the individual measurements. Factors such as temperature and the concentration of the corrosive medium typically influence the rate of uniform corrosion. An increase in temperature raises the corrosion rate. Additionally, if the concentration of the corrosive medium or the number of different cathodic species within the medium increases, the corrosion rate also accelerates.

Occurrence: • Pipelines • Tanks • Marine equipment • Rigs • Piers • Boilers • Heat exchangers • Copper structures

b) **Galvanic Corrosion:** Galvanic corrosion is a form of general attack that occurs when dissimilar metals come in close contact.

Mechanism: When two alloys with a significant potential difference are connected, they create a macro corrosion cell, where the more electronegative alloy acts as the anode and the more electropositive alloy serves as the cathode. The potential difference between these alloys can be determined from the standard potentials listed in the galvanic series. This series is similar to the EMF series but differs primarily in that it includes a range of alloys rather than metallic reduction reactions, as shown in Figure I.25.

The more electropositive alloys are positioned at the top of the series, becoming increasingly less electropositive and more electronegative as you move downward. The contact interface between these alloys forms the metallic path. When exposed to a corrosive environment, the corrosion cell becomes complete. The cathode then facilitates reduction reactions, while the anode undergoes corrosion (see Figure. I.26). Galvanic corrosion is influenced by three main factors: environment, distance, and area, which are discussed below.

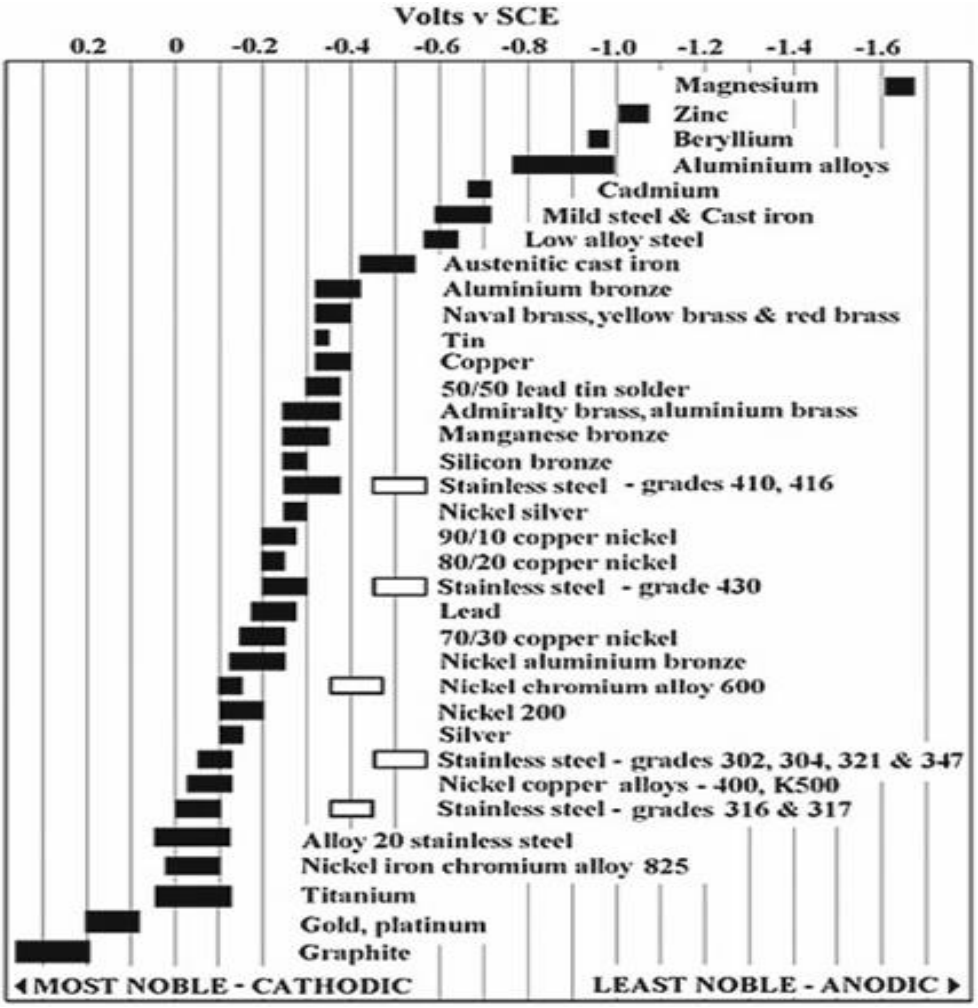


Figure. I.25. Galvanic series. Source Tugsataydin, CC BY-SA 4.0, via Wikimedia Commons

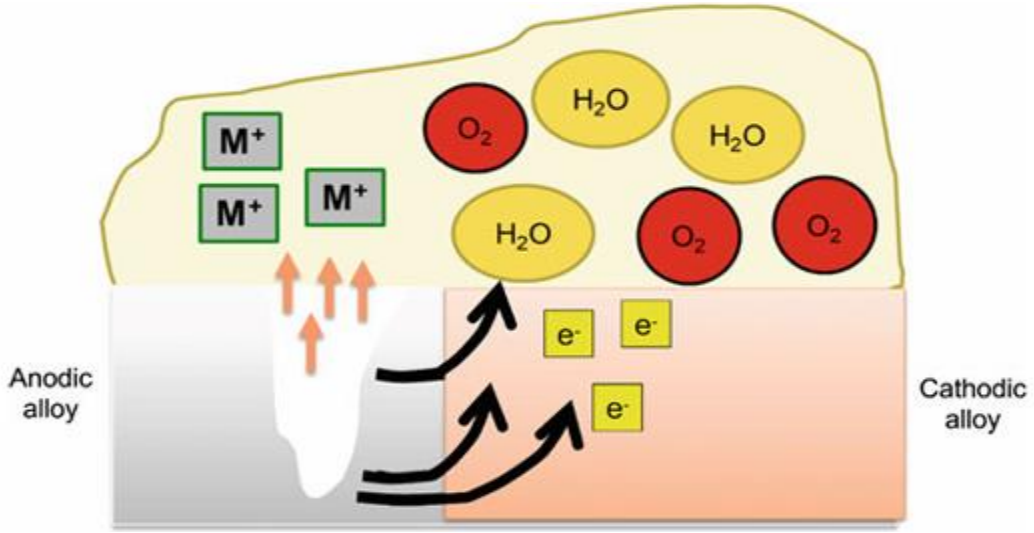


Figure.I.26. Galvanic Corrosion

Environment Effect:

The environmental effect occurs when the characteristics of the anode and cathode are reversed. For instance, at room temperature, when Zn and Fe are connected, Zn acts as the anode and Fe as the cathode (see Figure. I.27). However, at temperatures above 80 °C, an oxide film forms on Zn, inhibiting further dissolution of Zn ions. As a result, Zn begins to support cathodic reactions, while Fe becomes the anode. This phenomenon is known as the environmental effect.

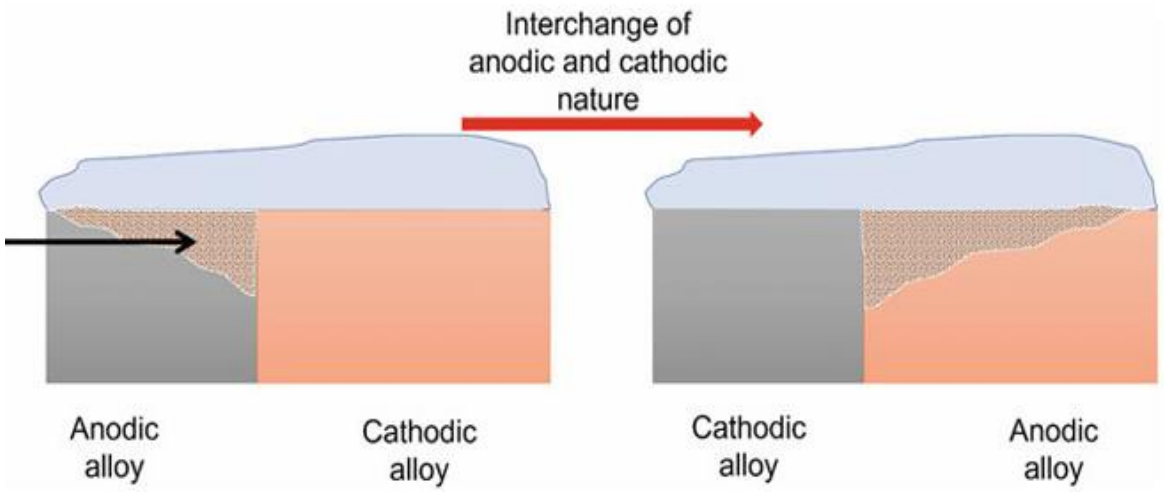


Figure. I.27 Environment effect in galvanic corrosion [32]

Area Effect:

For a galvanic couple, the anodic and cathodic currents are equal.

$$I_{cathode} = I_{anode}$$

However, the areas exposed to the corrosive medium may differ. As a result, the currents can be broken down into current density and electrode area as follows:

$$i_{cathode} \times Area_{cathode} = i_{anode} \times Area_{anode}$$

If the cathode area is smaller than the anode area, the current density at the cathode will be lower than at the anode. As a result, the cathode facilitates numerous cathodic reactions but remains intact since it does not dissolve. In contrast, the anode will experience dissolution, albeit at a slower rate due to its lower current density.

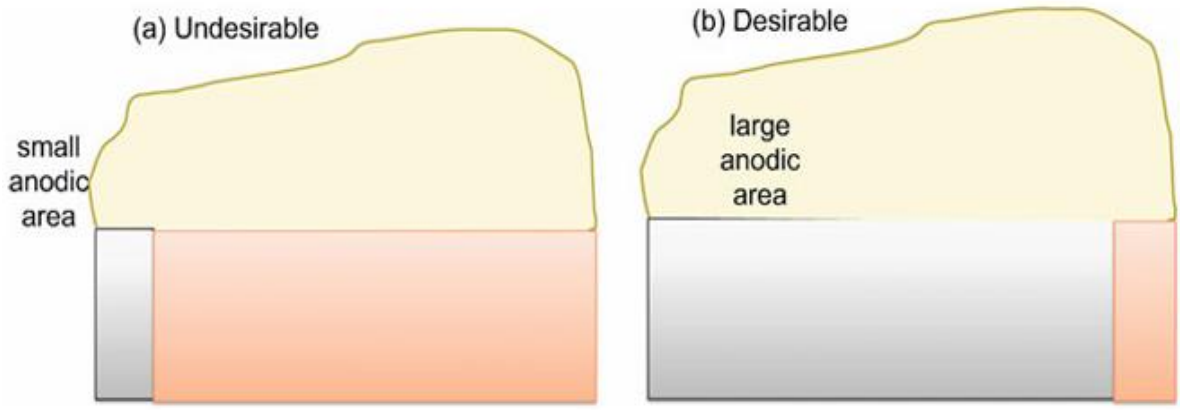


Figure. I.28. Area effect in galvanic corrosion [32]

Conversely, if the anode area is larger than the cathode area, the anodic current density will increase significantly, resulting in accelerated dissolution of the anode when exposed to the corrosive medium. The cathode will remain unaffected, continuing to facilitate the cathodic reactions. This phenomenon is known as the area effect. It is a critical factor in component design, as a small anode area can lead to rapid failure in practical applications.

Distance Effect:

The distance effect refers to the decrease in corrosion of the anode as the distance from the anode/cathode interface increases. Maximum anode dissolution occurs at the interface because the anode area near the interface can more readily transfer electrons to the cathode, form ions, and dissolve. In contrast, the anode area further from the interface experiences less corrosion due to the increased difficulty in directly transferring electrons to the cathode.

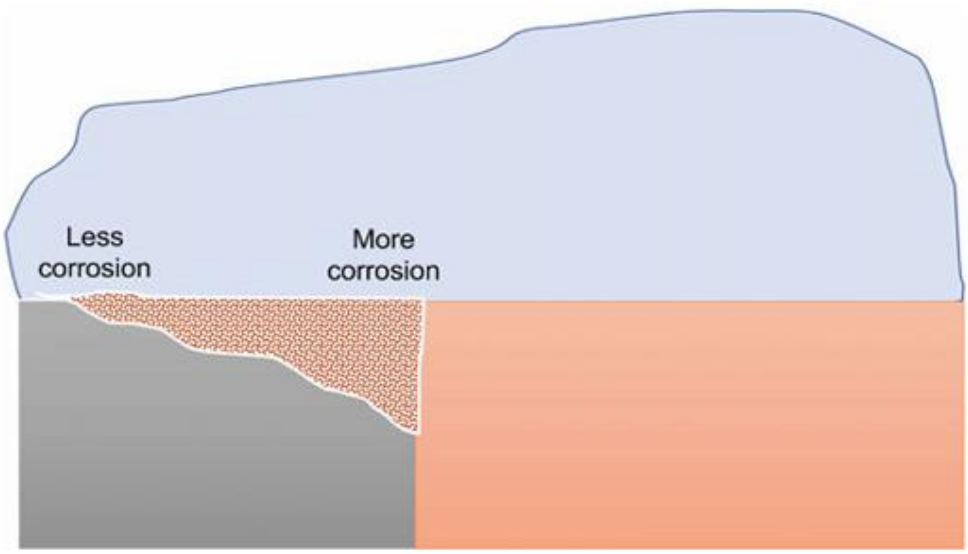


Figure. I.29. Distance effect of galvanic corrosion[32]

Occurrence: • Joints in automotives • Pipeline flanges • Fixtures with bolts • Brass caps on steel pipes • Dissimilar pipe parts in water plumbing • Steel manifold with aluminum couplings

c) **Pitting Corrosion :** Pitting corrosion is localized corrosion where the material loss occurs only in certain sites.

Mechanism:

The location of pitting sites is influenced by metallurgical factors such as phase differences, coarse and fine intermetallics, oxide films, coatings, and corrosion product layers. The three conditions most likely to initiate pitting corrosion, as shown in Figure.I.30. are :

- **Intermetallics and Phases:** A galvanic couple may form between intermetallics and the surrounding matrix, or between different phases.
- **Oxide Film:** The oxide film may be compromised by ions such as chloride ions, exposing the underlying substrate to the environment and creating a corrosion cell.
- **Coating:** Coatings, particularly organic ones, may have large pores or suffer mechanical damage like scratches, allowing electrolytes to penetrate and reach the substrate.

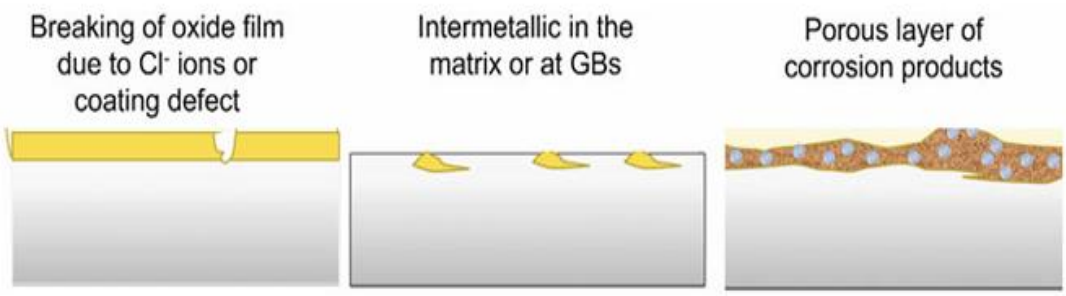


Figure. I.30. Conditions that enable pit initiation [32]

These conditions lead to the formation of electrolyte pockets on the surface. Pitting then begins and spreads according to the following mechanism:

- **Pit Initiation:** As depicted in Figure. 17a, electrolyte pockets create localized corrosion cells. The anodic region experiences material loss, with the reaction occurring as follows:

$$M = M^{+} + e^{-}$$

The cathodic reaction depends on the cathodic species, which are typically O_2 and H_2O:

$$O_2 + 2H_2O + 4e^{-} = 4OH^{-}$$

- **Generation of Positive Charge:** As oxidation continues at the anode, cations (M^{+}) are produced and accumulate in the pit, creating an area with an excess positive charge, as shown in Figure. I.28 b. This leads to the attraction of negatively charged Cl^{-} ions toward the pit. The Cl^{-} ions diffuse into the pit and react with the cations to form chlorides.

$$M^{+} + Cl^{-} \rightarrow MCl$$

- **Hydrolysis and Acid Generation:** The metal chloride that forms undergoes hydrolysis, resulting in the production of metal hydroxide and hydrochloric acid:

$$MCl + H_2O \rightarrow MOH + HCl$$

The HCl further dissociates to form hydrogen ions and chloride ions:

$$HCl \rightarrow H^{+} + Cl^{-}$$

These H^+ ions act as a second cathodic species and promote additional dissolution of the metal in the pit:

$$2H^+ + 2e^- \rightarrow H_2 \quad \text{(Cathodic reaction)}$$

$$M \rightarrow M^{2+} + 2e^- \quad \text{(Anodic reaction)}$$

In this situation, the metal within the pit is exposed to two cathodic species instead of just one, which accelerates its dissolution and leads to rapid pit growth. The resulting metal cations further increase the positive charge within the pit, attracting more Cl^- ions, thus perpetuating the cycle. This ongoing pit growth driven by the local acidic environment within the pit is known as 'Autocatalysis.' As a result, once a pit starts and develops in a material, it will continue to expand even if the material is removed from the corrosive medium, as the local acidic environment inside the pit will remain unless the surface is polished thoroughly to eliminate the pit.

Occurrence : • Swimming pool facilities • Refinery components • Pipelines • Aluminum plates • Bridges • Piers

d) **Crevice Corrosion**: Crevice corrosion is localized corrosion that occurs in areas where a gap or crevice is formed between two surfaces, leading to accumulation and stagnation of fluid. The surfaces can be metal–metal or metal–non-metal

Mechanism:

As per the Fontana and Greene model [34], crevice corrosion occurs in the following four distinct steps

. • **Corrosion initiation:** Initially, the concentration of O_2 is uniform both inside and outside the crevice, as depicted in Figure. I.31.a–b. Consequently, corrosion begins inside and outside the crevice through the standard anodic and cathodic reactions:

$$M = M^+ + e^-$$

$$O_2 + 2H_2O + 4e^- = 4OH^-$$

- **O_2 Consumption Inside the Crevice:** Over time, the O_2 inside the crevice gets depleted due to the cathodic reaction. The narrow gap of the crevice restricts the diffusion of

sufficient O_2 to replace what is consumed. As a result, the cathodic reactions within the crevice diminish, leaving only the anodic reactions to continue, as shown in Figure I.31c.

- **Generation of Excess Positive Charge:** As the anodic reactions accelerate, a large number of cations are produced, creating an excess positive charge within the crevice. This leads to the attraction of anions, such as OH^- and Cl^-, towards the crevice.
- **Hydrolysis:**

Inside the crevice, the Cl− ions react with the cations to form metal chlorides:

$$M^+ + Cl^- \rightarrow MCl$$

The metal chloride reacts with H_2O to form metal hydroxide and hydrochloric acid:

$$MCl + H_2O \rightarrow MOH + HCl$$

The HCl then dissociates into hydrogen ions and chloride ions:

$$HCl \rightarrow H^+ + Cl^-$$

The H^+ ions act as a second cathodic species and promote further dissolution of the metal in the pit:

$$2H^+ + 2e^- \rightarrow H_2 \quad \text{(Cathodic reaction)}$$

$$M \rightarrow M^+ + e^- \quad \text{(Anodic reaction)}$$

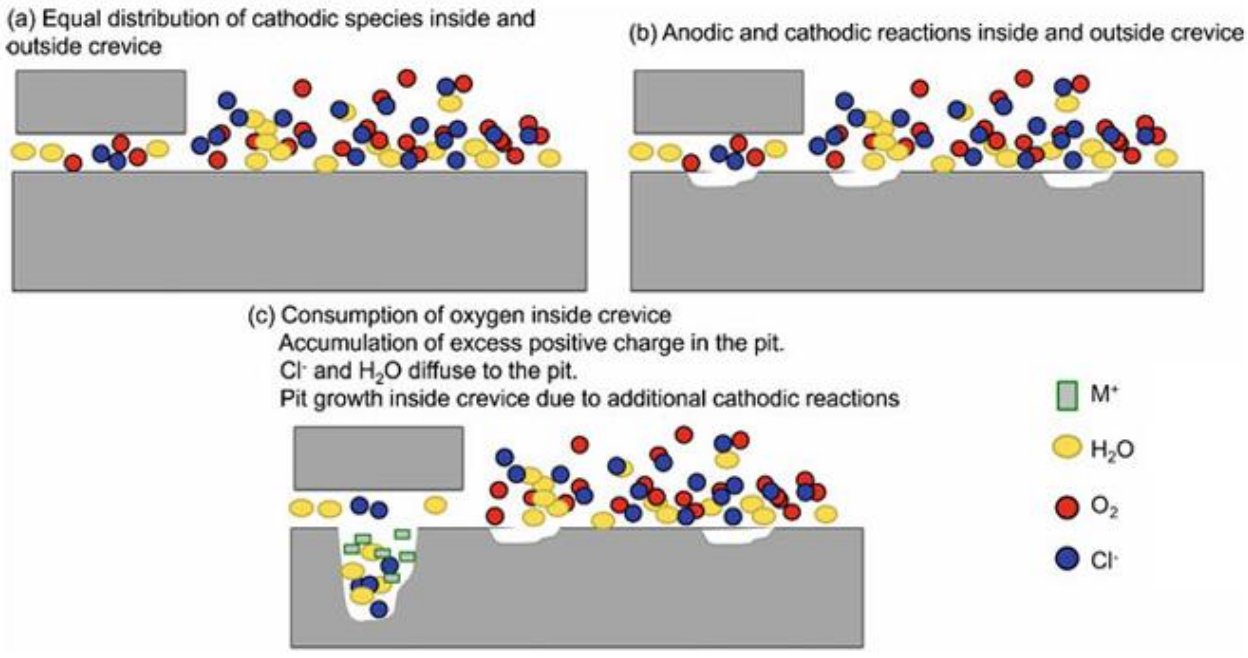


Figure. I.31: Mechanism of crevice corrosion

e) **Filiform Corrosion:**

This type of crevice corrosion occurs specifically in thin organic coatings and is influenced by the humidity of the environment. All organic coatings contain pores. As shown in Figure. I.32 a, when exposed to a humid environment, moisture and dissolved O_2 penetrate these pores and reach the underlying substrate. This creates a corrosion cell beneath the coating, where the following reactions take place:

$$Fe \rightarrow Fe^{2+} + 2e^{-} \quad \text{(Anodic reaction)}$$
$$O_2 + 2H_2O + 4e^{-} \rightarrow 4OH^{-} \quad \text{(Cathodic reaction)}$$
$$Fe^{2+} + 3OH^{-} \rightarrow Fe(OH)_3$$

The accumulation of $Fe(OH)_3$ causes the coating to lift. This exposes the underlying surface to additional O_2. As illustrated in Figure I.32 b and c, a concentration cell forms with lower O_2 concentration at the inner edge of the delaminated coating and higher O_2 at the outer edge. A distinctive feature of filiform corrosion is that even at the inner edge of the delaminated coating, moisture and O_2 can still penetrate. Despite this, filiform corrosion progresses with the continued formation of $Fe(OH)_3$ beneath the delaminated coating. As the corrosion product builds up, it pushes the coating upward, resulting in thin, worm-like filaments of delaminated coating.

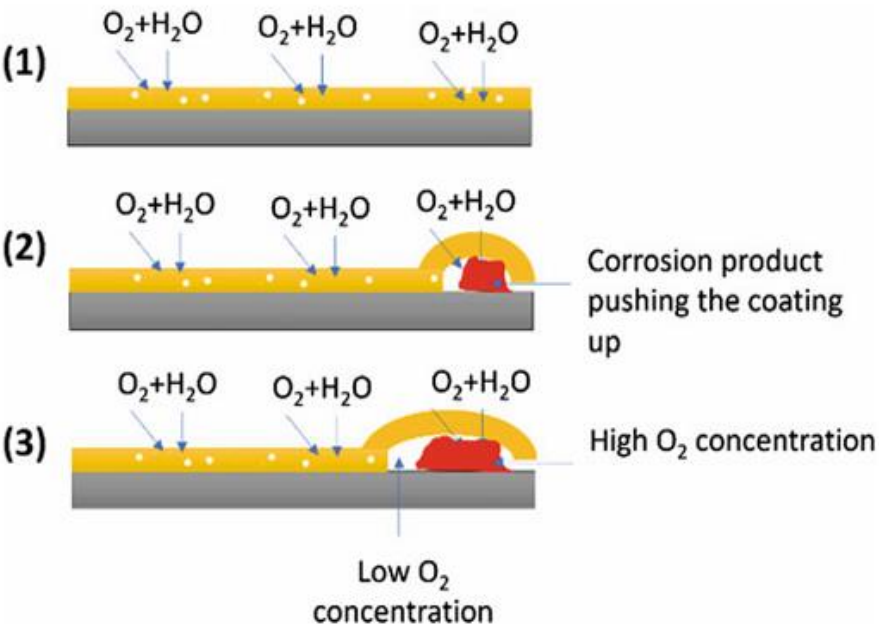


Figure. I.32 : Filiform corrosion [32]

Occurrence: • Gaskets • Couplings • Joints • Overlapping plates • Valves • Taps • Rivets • Bolts

f) **Intergranular Corrosion:** Intergranular corrosion (IGC) is the metal dissolution that occurs at or near the grain boundaries.

Mechanism:

Intergranular corrosion (IGC) occurs due to certain metallurgical changes at elevated temperatures. Stainless steel is resistant to corrosion in various environments because of the passive film of chromium oxide (Cr_2O_3) that forms on its surface. To maintain a good, compact passive film, a minimum chromium content of 11.5% is required. Therefore, all commercial stainless steel alloys contain at least 12% chromium, while higher grades contain up to 22% chromium. In stainless steel, chromium is present as a solid solution [32].

As illustrated in Figue.I.33, when stainless steel is exposed to temperatures between 500 and 780 °C, chromium atoms diffuse from the surrounding areas to the grain boundaries. At these boundaries, chromium atoms combine with carbon atoms to form chromium carbide ($Cr_{23}C_7$), a process known as sensitization [32].

In this sensitized condition, both the grain boundaries and the grains themselves have a chromium content greater than 11.5%, allowing the Cr_2O_3 film in these regions to be adequately protective. However, the areas adjacent to the grain boundaries have a chromium content below 11.5%, resulting in an insufficient and patchy Cr_2O_3 film [32].

When exposed to a corrosive environment, the regions near the grain boundaries begin to corrode. The corrosion is localized near the grain boundaries but can spread into the cross-sectional areas. Therefore, IGC starts as a surface phenomenon but evolves into a three-dimensional material loss.

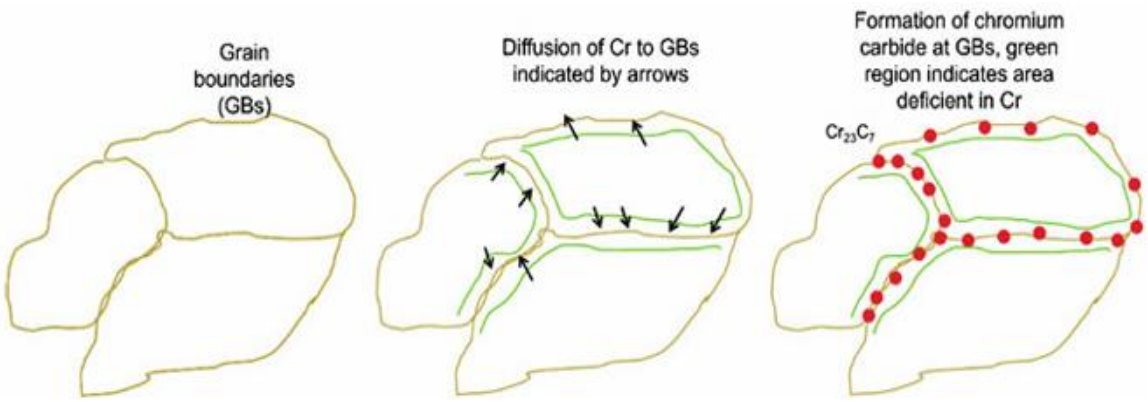


Figure.I.33. Mechanism of intergranular corrosion

Weld Decay:

Weld decay occurs in the base material of stainless steel. During welding, the weld zone reaches its maximum temperature as it is in a molten state. However, the temperature of the base metal decreases with increasing distance from the weld zone. In a specific region near the weld, the temperature falls within the range of 500 to 780 °C, causing the stainless steel in this area to undergo sensitization. As a result, when exposed to a corrosive environment, this zone becomes susceptible to intergranular corrosion (IGC), a phenomenon known as weld decay

Knife Line Attack:

Certain stainless steel (SS) alloys with low carbon content and added elements like titanium (Ti) and cobalt (Co) are used to reduce the likelihood of sensitization. These alloys are known as stabilized stainless steels. In these alloys, carbon reacts with Ti and Co to form their respective carbides, preventing the formation of chromium carbide ($Cr_{23}C_7$). These carbides are soluble in the temperature range of 500–780 °C, preventing sensitization during the operation of the components [32].

However, in welded areas, regions very close to the weld can reach higher temperatures, between 780–1230 °C. Within this temperature range, Ti and Co carbides precipitate at the grain boundaries, leading to the sensitization of stabilized SS. When exposed to a corrosive environment, the area adjacent to the weld zone becomes susceptible to corrosion. Because this affected zone is very narrow, this phenomenon is known as a knife line attack (KLA).

Exfoliation:

Exfoliation corrosion is a type of intergranular corrosion that results in the delamination of material layers. This form of corrosion is most commonly observed in rolled aluminum alloy sheets, which have an elongated grain structure.

Aluminum alloys typically contain a primary alloying element, such as zinc (Zn) in the AA 7XXX series, magnesium (Mg) in the AA 5XXX series, or manganese (Mn) in the AA 3XXX series. These elements are present as nanostructures at the grain boundaries, known as fine intermetallics. When a rolled aluminum alloy sheet undergoes aging, the atoms of the main alloying element diffuse to the grain boundaries, forming additional intermetallics. This process creates a galvanic couple between the fine intermetallics and the precipitate-free zones near the grain boundaries [32].

In the case of the 7XXX series alloys, the intermetallic compound formed is Zn, which is cathodic relative to the aluminum matrix. This leads to anodic dissolution of the matrix near the grain boundaries. The corrosion progresses along the regions adjacent to the grain boundaries, eventually linking with corrosion occurring at other grain boundaries. As a result, layers of elongated grains lift off together, causing the material to delaminate.

Occurrence: • Airplane wings

g) **Selective Leaching:**

Selective leaching is the dissolution of only one phase or alloying element from an alloy in the presence of a corrosive medium. It is also known as parting or dezincification.

Mechanism:

In alloys like brass, the primary alloying element, zinc (Zn), exists as a separate phase from the copper (Cu) phase. When exposed to a corrosive environment, these two phases create a galvanic couple, with Zn acting as the anode and Cu as the cathode. As a result, Zn undergoes dissolution and leaches out of the alloy, leaving behind a copper network, as illustrated in Figure.I.34 .

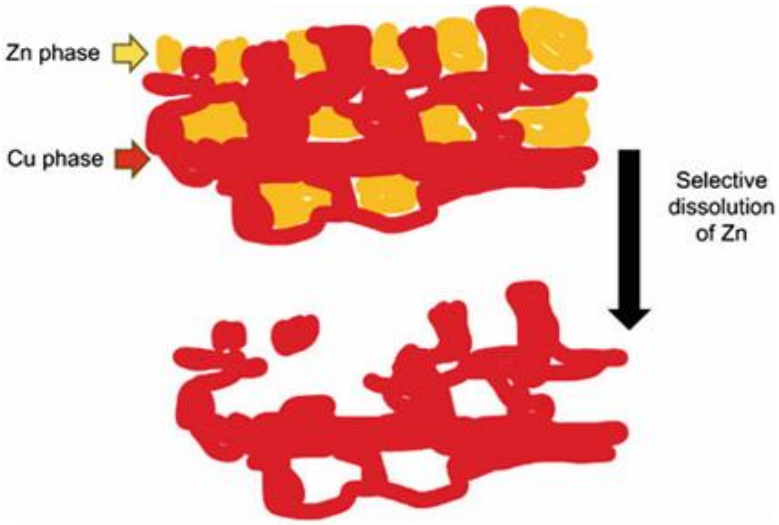


Figure. I.34. Mechanism of selective leaching[32]

The copper (Cu) matrix remains intact, and the pits formed due to the dissolution of zinc (Zn) allow more electrolyte to infiltrate the alloy, leading to the dissolution of Zn in the internal regions of the component as well. This selective leaching of Zn from brass is known as dezincification.

In cast iron, the iron matrix is anodic relative to the graphite particles, leading to the selective dissolution of iron and leaving behind the graphite particles. This type of corrosion is referred to as graphitic corrosion.

A similar selective leaching process occurs with nickel and chromium in stainless steel and copper alloys, known as de-nickelification. In aluminum bronzes, de-aluminification occurs, where aluminum (Al), being anodic to copper (Cu), preferentially dissolves and leaches out.

Occurrence: • Brass valves • Drain lines

h) **Stress Corrosion Cracking** : Stress corrosion cracking (SCC) refers to the initiation and propagation of cracks that occur in a corroded material in the presence of a constant tensile load.

Mechanism:

Stress corrosion cracking (SCC) occurs through two primary mechanisms: anodic dissolution and hydrogen embrittlement.

Anodic Dissolution:

Alloys like carbon steel and active-passive metals with an oxide film are prone to pitting. Pits form due to the anodic dissolution of the substrate, and the tip of the pit serves as a stress concentration point. Under constant tensile loading, a crack can develop at the pit tip at a stress level lower than the yield strength of the material.

Hydrogen Embrittlement:

In materials such as carbon steel, pitting can occur due to corrosion products or phase differences within the matrix. Environmental factors, such as acid formation within the pit, highly negative cathodic protection, the composition of the stored fluid, the presence of hydrogen sulfide, and water production (as often seen in crude oil transport), can lead to the generation of nascent hydrogen atoms in localized areas.

$$Fe + H_2S \rightarrow FeS + 2H_{ads}$$

Anodic and cathodic reactions occur as follows:

$$Fe \rightarrow Fe^{2+} + 2e^- \qquad \text{(Anode)}$$

$$2H^+ + 2e^- \rightarrow 2H_{ads} \qquad \text{(Cathode)}$$

These nascent hydrogen atoms are adsorbed onto the surface of the pit. Due to their small size, they can easily diffuse into the material's matrix, reaching voids and intermetallics.

$$H_{ads} \rightarrow H_{abs}$$

If the intermetallics are sulfides like MnS, the hydrogen atoms react with them as follows:

$$2H_{ads} + MnS \rightarrow Mn + H_2S$$

If the intermetallics are oxides, or the hydrogen atoms reach a void, they combine to form hydrogen gas:

$$H_{ads} + H_{ads} \rightarrow H_2$$

Both hydrogen sulfide (H_2S) and hydrogen (H_2) gases generate internal pressure within the alloy. As a result, the alloy loses its mechanical integrity and becomes brittle, leading to cracking failure under a load significantly lower than the tensile strength of the alloy (as shown in Figure. I.35).

Corrosion Fatigue:

Corrosion fatigue is a type of corrosion that involves both applied stress and material dissolution. Unlike static loading, the applied load in corrosion fatigue is cyclic. When subjected to tensile loading, cracking occurs in a manner similar to stress corrosion cracking (SCC). During the subsequent compression loading, the cracked areas may move closer together but do not fuse. In the next tensile cycle, the existing crack propagates, and new cracks can form at stress concentration points created by corrosion on the surface.

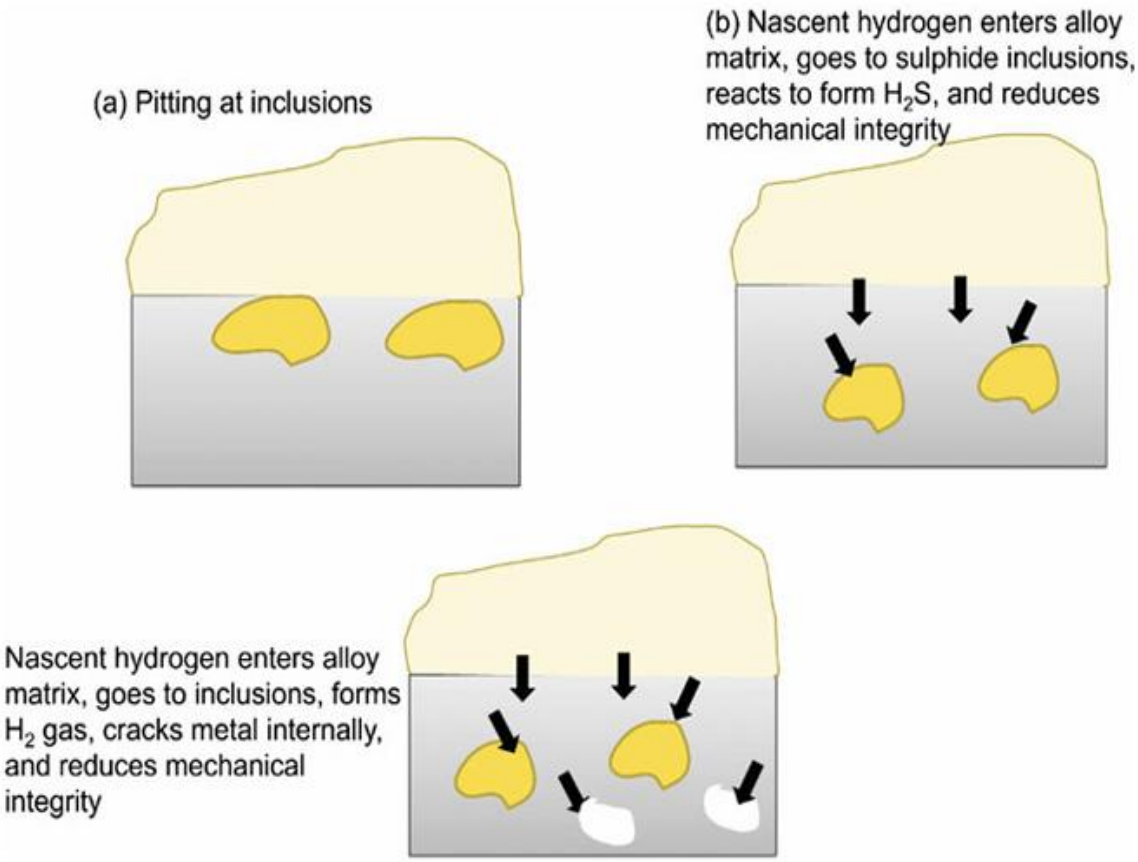


Figure. I.35: Mechanism of hydrogen embrittlement

Occurrence: • Pipelines • Defense equipment and vehicles • Oil and gas extraction and distribution equipment • Refineries and chemical production • Nuclear energy infrastructure

i) **Erosion Corrosion** : Erosion corrosion refers to the corrosion of alloys that occurs when solid particles, such as dust, sand, or corrosion products, or the influence of fluid flow, interact with a corrosive medium. [66].

Mechanism:

The mechanism of erosion corrosion is illustrated in Figure.I.36. As fluids and particles move through components like pipelines, they carry significant kinetic energy. The turbulent flow causes these fluids and particles to strike the walls, applying mechanical force to the substrate. This force causes the material on the substrate to loosen and detach from the wall. Once exposed, the bare substrate interacts with oxygen (O_2), water (H_2O), hydrogen sulfide, and other cathodic species present in the fluid, initiating and advancing corrosion.

Cavitation corrosion

primarily affects impeller and rotor blades. Unlike other types of corrosion, it does not involve solid particles causing material loss. The mechanism of cavitation corrosion is illustrated in Figure. I.37. Impeller blades are typically made from high-grade alloys with a passive oxide film on their surface. As water (H_2O) rotates within the impeller, bubbles form on the blade surfaces, as shown in step (1). These bubbles experience continuous stress due to the rotating liquid. As a result, they implode, exerting mechanical force on the oxide films, causing them to break and exposing the bare substrate to the corrosive medium.

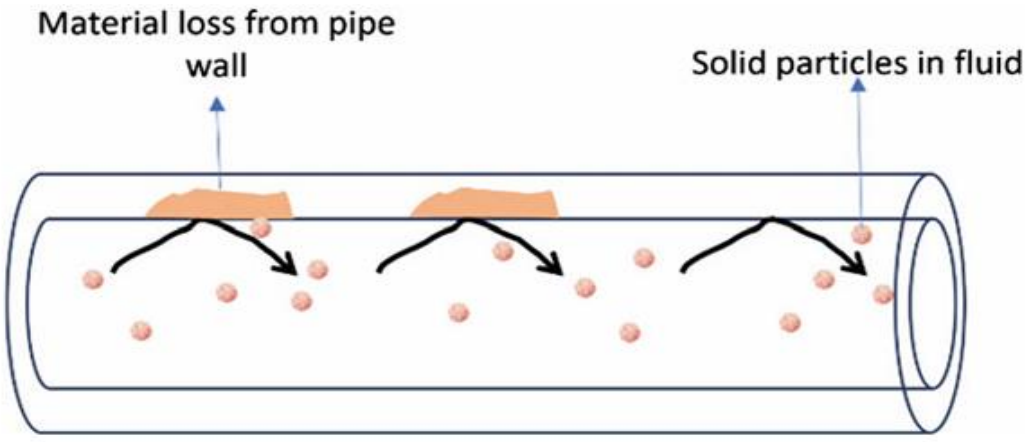


Figure. I.36. Mechanism of erosion corrosion [32]

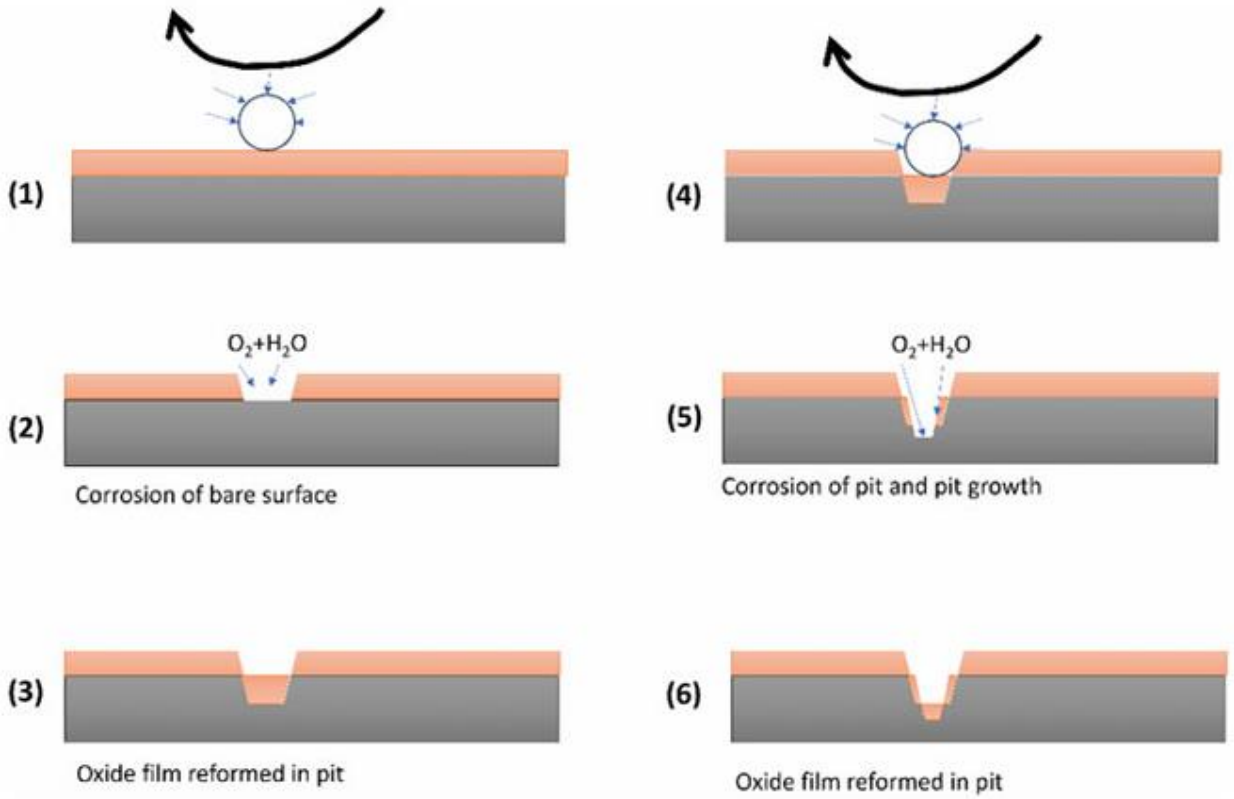


Figure.I.37: Mechanism of cavitation corrosion [32]

Oxygen (O_2) and water (H_2O) initiate corrosion on the exposed surface, leading to the formation of a pit, as shown in step (2).

At this stage, the oxide film reforms over the pit, maintaining its shape, as depicted in step (3). Subsequently, bubbles redeposit on the oxide film within the pit, as illustrated in step (4). The cycle then repeats, with bubbles imploding and breaking the oxide film in steps (5) and (6), causing further corrosion and deepening the pit. This process continues until the pit completely perforates the blade, unless detected and addressed earlier.

Fretting Corrosion

Fretting corrosion is a localized form of corrosion that arises from the combined effects of friction, such as local temperature increases and moisture entrapment. It occurs when two surfaces move against each other with sufficient friction, as illustrated in Figure.I.38. When both materials have

an oxide film, the friction causes the oxide films to abrade and damage each other, exposing the bare metal underneath. This frictional movement can also lead to localized temperature rises and moisture accumulation at the exposed metal surface, making it susceptible to corrosion in the affected areas.

In the second scenario shown in Figure I.39, fretting corrosion occurs in regions with a cold weld. The frictional movement can cause the cold weld to break, exposing the underlying surface to high temperatures and moisture, which accelerates the corrosion of the exposed metal.

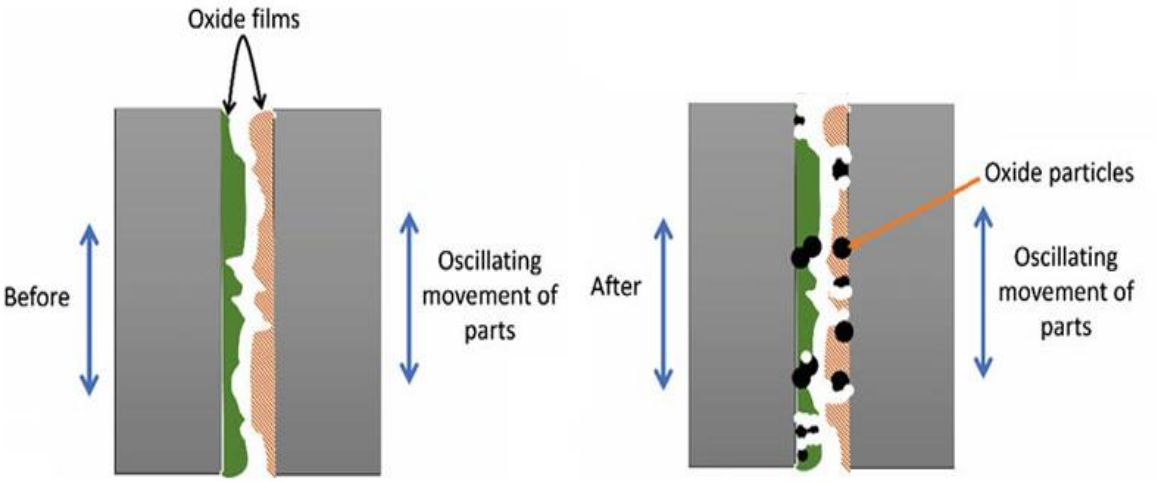


Figure.I.38. Mechanism of fretting corrosion: type 1

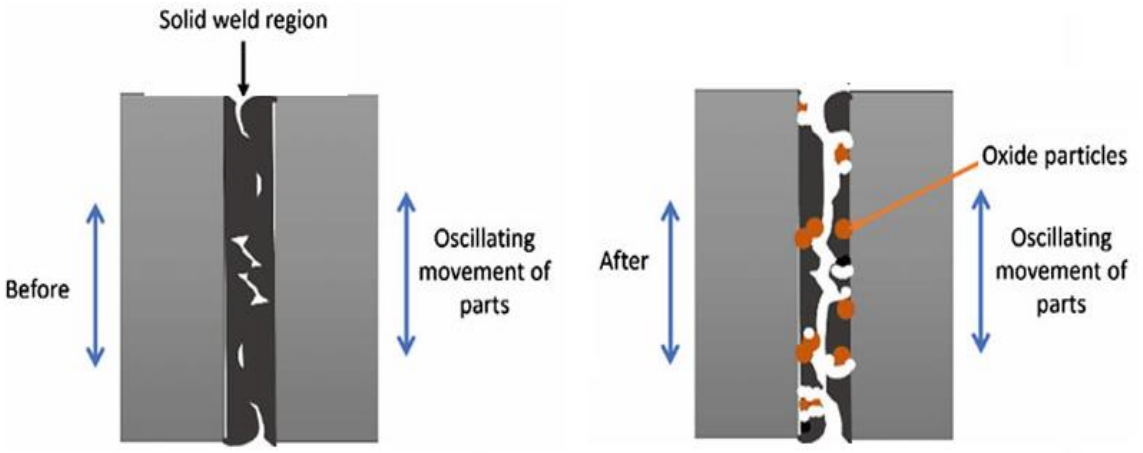


Figure. I.39 Mechanism of fretting corrosion: type 2

Occurrence: • Propellers, impellers • Stirrers • Stirred vessels • Pumps • Heat exchangers • Turbine blades • Nozzles • Pipe bends and tees• Copper alloys

I-8) Corrosion Mitigation Methods:

In a harsh environment, it is essential to protect metallic equipment from corrosion by employing mitigation techniques such as applying coatings or injecting corrosion inhibitors. These mitigation strategies should be integrated into the engineering design. Figure I.40 illustrates the latest advanced corrosion protection methods used in the industrial sector.

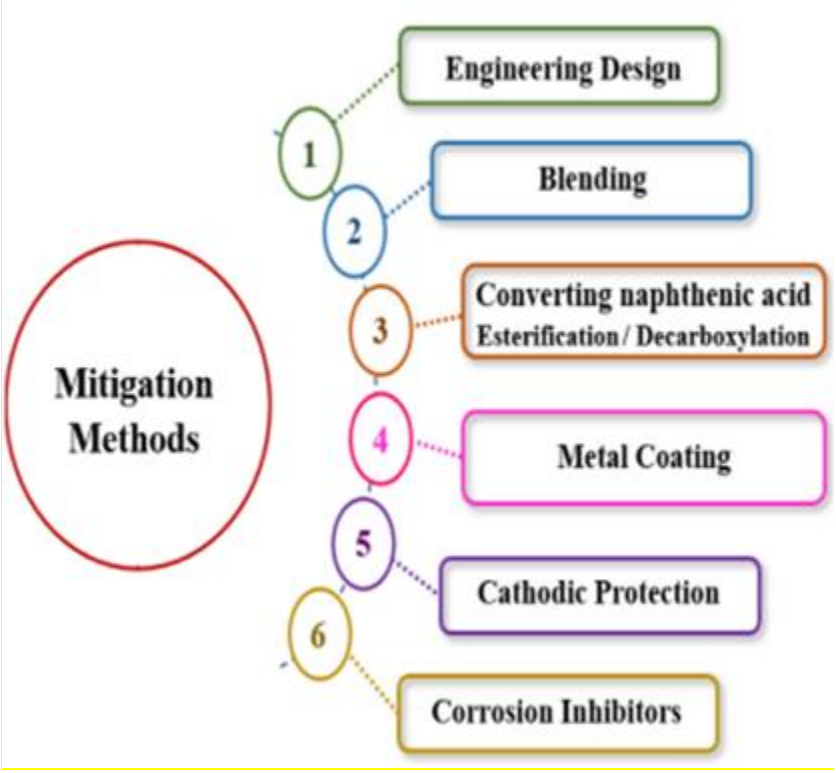


Figure.I.40. Mitigation methods currently implemented in Oil and gas industries.

I-8-1) Engineering design:

When designing a plant, it is important to consider factors that could contribute to corrosion. For instance, by taking into account the equipment's geometry, fluid velocity can be controlled, and areas where sour water might accumulate can be avoided, thereby minimizing erosion-corrosion issues [67]. Selecting a construction material appropriate for the refinery's harsh environment is also crucial. It is essential to recognize that no single material is resistant to all types of media

under all conditions. Corrosion in refineries can be categorized into low-temperature and high-temperature corrosion [68].

Carbon steel can be used in areas where low-temperature corrosion occurs, except where aqueous corrosion caused by inorganic contaminants is present [68]. For instance, corrosion from HCl or H_2S requires a more resistant alloy. Effective removal of corrosive contaminants using processing units, such as desalters and hydrotreaters, is important for mitigating low-temperature corrosion issues. In areas exposed to high-temperature corrosion, more durable metals, such as stainless steel, nickel alloys, and copper alloys, are required [69].

In the petroleum industry, polymeric materials and composites play a significant role. These materials are known for their high chemical resistance to various gases and solvents. However, compared to metals, polymers are generally considered to have lower temperature resistance and inferior mechanical properties. In petroleum refinery systems, polymeric materials are used for gaskets, seals, sumps, rings, pipes, and tanks that are exposed to water, cooling water, seawater, firefighting water, acid and alkali solutions, soil, and atmospheric conditions. Polymeric materials are characterized by their thermal, electrical, mechanical, and chemical resistance. Temperature greatly affects the properties of polymers; excessive heat can cause chemical degradation, while cooling can make them brittle. Therefore, the selection of polymeric materials and composites depends on their intended use in refinery operations [70].

I-8-2). Blending:

With the increasing use of opportunity crude oil, managing high acid content remains a significant corrosion control challenge for refineries. Blending is one approach to handling high TAN (Total Acid Number) crude oil. Mixing heavy and light crude oils effectively reduces the acid concentration in the feed, thereby lowering the corrosion rate [71]. However, the composition and properties of crude oils vary, leading to different levels of compatibility in crude oil blends. Some oils are naturally incompatible due to the insolubility of asphaltene in more paraffinic light crude oils [68]. It is important to note that blending does not remove acids from high-acid crude but simply reduces the acid concentration. The naphthenic acids (NA) remain in the blended product and can react with the catalyst, potentially causing catalyst deactivation. Additionally, Dettman et al. [72] reported that blending may introduce further issues during refining if the crude being blended contains high levels of sulfur compounds or other corrosive substances.

I-8-3). Conversion of naphthenic acid:

High-TAN crude oil contains cyclopentane, cyclohexane, and naphthenic acids (NAs), which are saturated linear hydrocarbons with either a terminal carboxylic group or unsaturated aromatic rings. Refineries employ various methods to transform NAs, such as neutralization, esterification, and catalytic decarboxylation. However, each of these methods has its own set of challenges and limitations. For instance, caustic treatment to neutralize acidic components can lead to the formation of insoluble emulsions, product loss, and pollution [73]. Research on the esterification and decarboxylation of NAs using catalysts aims to develop more efficient catalysts that offer lower treatment costs and pose fewer environmental risks.

I-8-3-1) Esterification

The conversion of carboxylic acids to esters in the presence of heat and alcohol is known as catalytic esterification [74]. A study [75] utilized catalytic esterification with a SnO/Al_2O_3 catalyst system to remove naphthenic acids from diesel fuel. The study examined variables such as reaction temperature, methanol/oil ratio, and space velocity. The data indicated that esterification is favored by a high reaction temperature, a high methanol/oil ratio, and a low space velocity. Quiroga-Becerra et al. [76] investigated the impact of esterification of naphthenic acids on the corrosion of ASTM A106 Gr.B steel, finding a 91% reduction in the corrosion rate after esterification. Wang et al. [77] also used catalytic esterification with alcohol and a SnO/Al_2O_3 catalyst, achieving a reduction in TAN (Total Acid Number) by over 85%, from 2.8 mg KOH/mg to 0.5 mg KOH/mg. However, there has been limited research on using catalytic esterification to lower the TAN of heavy crude oil [73]. In an earlier study, Wang et al. [78] found that naphthenic acids with lower molecular weights and boiling points are more reactive during esterification. The Exxon Research and Engineering Company experimented with batch reactor systems to reduce crude oil acidity without using a catalyst, but this method was not adopted in refineries due to the long reaction times required [73].

I-8-3-2) Decarboxylation

Decarboxylation is a chemical reaction that removes the carboxyl group from naphthenic acids (NAs) and is used in refineries to treat high-acidity crudes [79]. Thermal decarboxylation can occur in the refinery's distillation column, where temperatures can reach up to 400°C [9]. Recent research has focused on developing catalysts that maximize the reaction rate while operating at

lower temperatures. The effectiveness of calcium oxide (CaO) and magnesium oxide (MgO) catalysts in converting carboxylic compounds has been evaluated based on CO_2 formation. Using MgO on crude oil has resulted in a lower Total Acid Number (TAN) due to significant NA removal, with most reactions occurring between 150 and 300°C. The effectiveness of catalysts such as ZnO, Ag_2O, ZrO_2, Cu-based catalysts, and zeolite catalysts in catalytic decarboxylation for NA removal has also been studied, showing promising results. However, many of these studies are limited to catalysts that are sensitive and have low thermal stability [80–81]. Additionally, using Cu-based catalysts to upgrade crude oil is impractical because they are easily poisoned by sulfur compounds in the oil [80,82].

I-8-4) Metal Coating

Metal coating is a technique used to reduce the rate of corrosion by applying a thin layer of a protective substance to the metal surface. This coating prevents corrosion by either controlling the electrochemical reactions or creating a barrier between the metal and its hostile environment [82]. Metal coatings can provide resistance to heat, erosion, pitting, and general wear [83].

The effectiveness of a coating in enhancing a metal's corrosion resistance depends on several properties, including its ability to resist water, chemicals, abrasion, weather, bacteria and fungi, and extreme temperatures. Coatings can be classified into three main categories based on the base material: organic, inorganic, and metallic [84]. Figure I.41 illustrates these coating types with examples. In refineries, all three types are used to protect tanks, pipes, columns, and other equipment from exposure to natural gas, water, and environmental conditions [84].

In recent years, many coatings have been developed to meet the diverse and demanding needs of the oil and gas industry. These coatings not only improve operational safety but also enhance the efficiency of various industrial processes. The most commonly used external anti-corrosion coating systems are fusion-bonded epoxy (FBE) and three-layer polyolefin (3LPO), which can be made from either polyethylene (PE) or polypropylene (PP). Single-layer FBE is widely used in North America, Saudi Arabia, and the United Kingdom. In contrast, dual-layer FBE coatings are more popular in Australia, while 3LPO coatings dominate the pipe coating market in other parts of the world [85].

The high-performance composite coating system (HPCC) represents the latest advancement in anti-corrosion coating technology. The HPCC is a single-layer, powder-coated, multi-component system consisting of an FBE base coat, a medium-density polyethylene outer coat, and a tie layer with chemically modified polyethylene adhesive. All three components are applied using an electrostatic powder coating process. The tie layer is a blend of adhesive and FBE with a gradient of FBE concentration. The HPCC system offers excellent adhesion to pipe surfaces, inherent shear resistance, flexibility at low temperatures, resistance to impact and cathodic disbondment, and very low moisture permeability [86]. Figure I.42. shows the FBE, 3LPO, and HPCC coating systems that protect oil and gas pipelines from corrosion.

Numerous studies on different types of coatings have demonstrated their effectiveness in protecting various types of steels in crude oil environments [86].

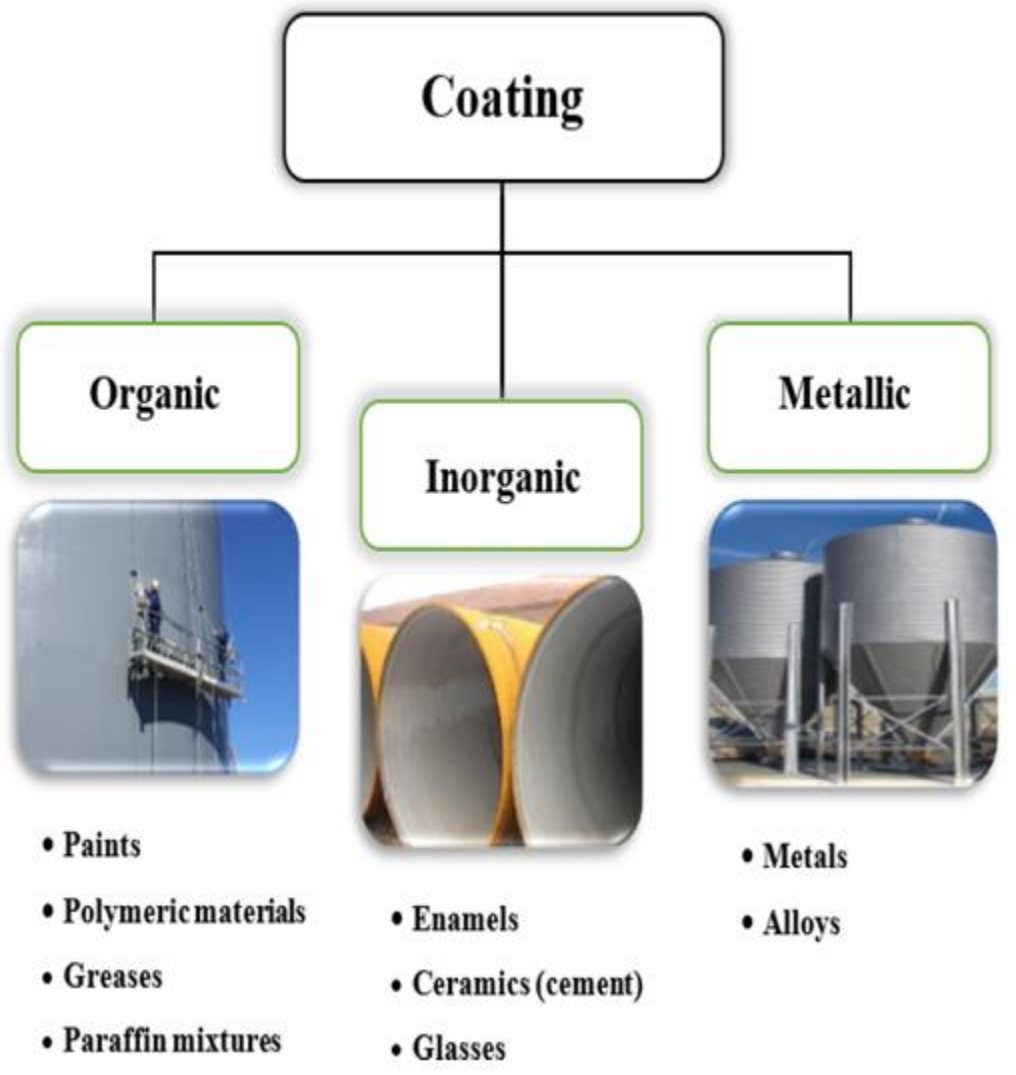


Figure.I.41. Different types of coating used in oil and gas industry .

Figure. I.42: FBE, 3LPO, and HPCC coating system that protect oil and gas pipelines from corrosion.

I-8-5) Electrochemical protection:

Cathodic protection (CP) is a corrosion-control method that involves converting a metal surface into the cathode of an electrochemical cell [69]. This technique can sometimes help prevent stress corrosion cracking and is commonly used in oil and gas industry to protect buried pipelines and storage tanks. The principle behind CP is that while organic coatings are the primary method for controlling corrosion, cathodic protection is employed along side them to address defects that may occur during application and service [84]. Combining CP with coatings is often the most cost-effective solution.

CP is applied to both the inner and outer surfaces of aboveground storage tanks used in petroleum sector (for oil products and/or water). Although pure hydrocarbon fluids are typically non-corrosive, internal corrosion may still occur in aboveground tanks due to exposure to sediments, water, and other contaminants [87].

For CP to be effective, all four basic components must be present: anode, cathode, electrolyte, and a complete electrical circuit. If any of these components is missing, the cathodic protection process will not function. It is important to note that while CP significantly reduces the corrosion rate of metal structures, it does not eliminate it entirely. However, the corrosion rate remains extremely low and manageable. CP can effectively protect various metals and alloys, including carbon steel, ductile iron, cast iron, stainless steel, aluminum, and brass [84].

There are two main types of CP systems [84,69]:

1. **Sacrificial Anode Cathodic Protection (SACP)**: In this method, an active metal such as aluminum (Al), zinc (Zn), or magnesium (Mg) is attached to the metal structure. The active metal corrodes, releasing current to the structure being protected. The corrosion occurs on the anode, which sacrifices itself to prevent corrosion of the protected metal structure.
2. **Impressed Current Cathodic Protection (ICCP)**: This method involves using an anode connected to a direct current (DC) power source. The anode, which can be made of materials such as graphite, mixed metal oxides, or high silicon cast iron, is either inert or has a low consumption rate. It can be surrounded by carbonaceous backfill to enhance efficiency and reduce costs [84,,85]. Figure I.43. illustrates the differences between the two CP methods.

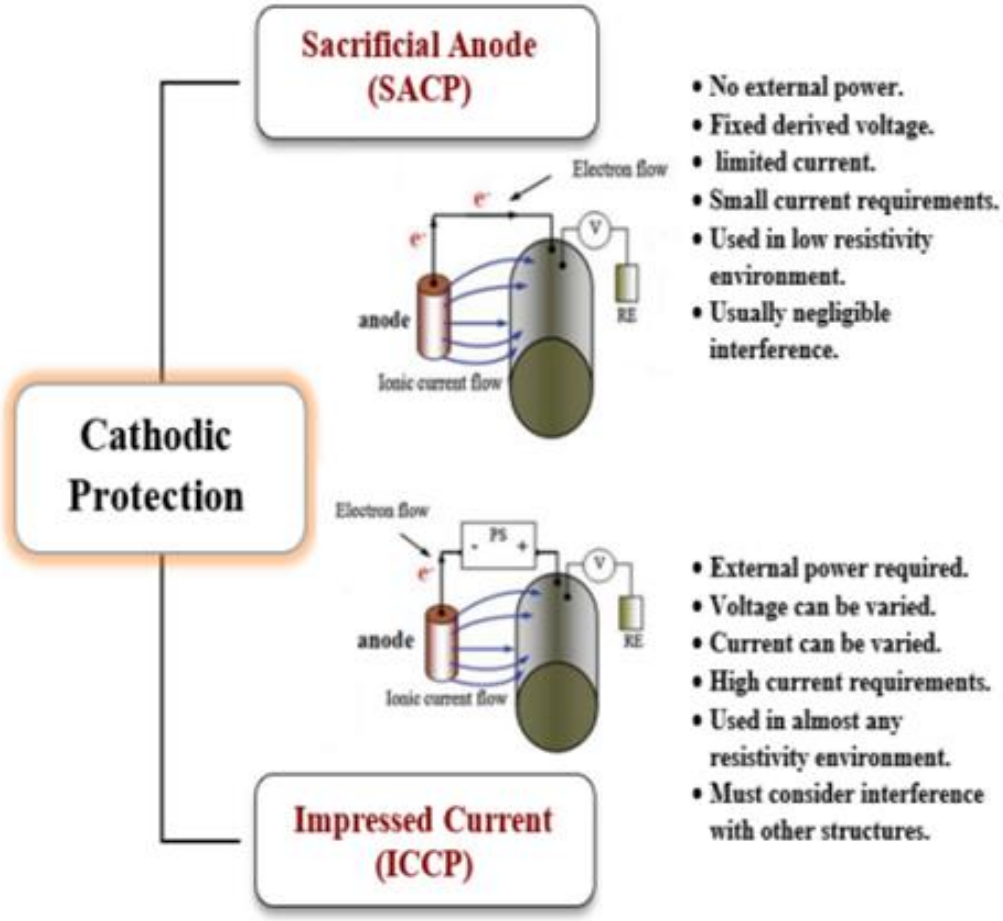


Figure.I.43. Cathodic protection (CP) systems used to protect metal structures from corrosion in Oil and gas industry.

I-8-6) Corrosion Inhibitors

Internal corrosion is one of the most challenging and hazardous types of corrosion in oil and gas industry due to the difficulty and cost of maintaining and inspecting internal surfaces. To avoid expensive alloy upgrades, an economically viable solution is to use corrosion inhibitors. These substances, when applied at low concentrations to a corrosive medium, reduce the rate of corrosion by forming a protective film that prevents the corrosive agents from contacting the exposed metal surface [88]. Although there is no universal classification for corrosion inhibitors, they can be categorized based on their composition and mechanism of action, as shown in Figure below. Literature [89,90] provides detailed insights into various types of inhibitors used in oil and gas facilities based on these classifications.

Potential corrosion inhibitors in the oil and gas industry should possess the following physical and chemical properties [91]:

- ✓ Stability
- ✓ Non-precipitation in the form of residue
- ✓ Non-formation of emulsions
- ✓ Sufficient solubility in hydrocarbons

Choosing an appropriate corrosion inhibitor for specific industrial applications is a complex process . The effectiveness of an inhibitor depends on several factors [91]:

- ✓ The type of material it interacts with
- ✓ The aggressiveness of the environment (e.g., presence of redox species, pH level)
- ✓ The application location (e.g., refinery, drilling equipment, gas and oil pipelines)
- ✓ The type of fuel being transferred or stored

Various organic compounds containing elements such as nitrogen (N), sulfur (S), oxygen (O), phosphorus (P), and silicon (Si) are used as corrosion inhibitors. In oil and gas industry, nitrogen-containing compounds like amines, ammonium salts, quaternary ammonium salts, imidazoline, and their derivatives are commonly employed [91].

Given the wide range of corrosion inhibitors available, selecting the appropriate one depends on the specific corrosive media and operating environment. Some organic inhibitors are effective at temperatures above 200°C. For acidic corrosion, inhibitors such as alkyl phenols, organic polysulfides, fatty acid amines, thiazolidines, and thiophosphates have shown effectiveness inoil and gas industry. While these high-temperature acidic corrosion inhibitors have proven successful, they can sometimes cause catalyst deactivation. To mitigate high-temperature corrosion, a low concentration of inhibitor is continuously injected into the process stream [79]. In refineries, phosphate ester-based corrosion inhibitors are used at critical locations in the overhead distillation process to combat NA corrosion. However, because these inhibitors are highly corrosive to alloy and even stainless steels, they are dosed using injection quills [69].

Inorganic corrosion inhibitors, such as salts of copper, zinc, arsenic, nickel, and other metals, are commonly used, with arsenic compounds being particularly prevalent. These inhibitors have the advantage of being effective at high temperatures for extended periods and are generally less

expensive than organic inhibitors. However, they may lose effectiveness in strong acid solutions (stronger than 17% HCl) and can release toxic arsine gas as a byproduct of corrosion [92].

Research is increasingly focusing on polymeric materials, both naturally occurring and synthetic, as potential alternatives to inorganic inhibitors. Polymers consist of long chains of monomers with various structures, including linear chains, branched chains, hyperbranched structures, rotaxanes, comb-like formations, and dendrimeric cross-links. Compared to traditional small molecule inhibitors, polymers offer better film-forming capabilities, multifunctionality, solubility, flexible viscosity, increased attachment points to metal surfaces, cost-effectiveness, and eco-friendliness [93,94]. Examples of polymers used as corrosion inhibitors in the oil and gas industry include polyvinylamide derivatives, polyamino acids, polyanilines, polycarboxylates/polycarboxylic acids, polysulfides, and polysaccharides (such as hydroxyethyl cellulose, carboxymethyl cellulose, guar gum, and polygalactomannans) [94]. These polymers can also be modified for use as corrosion inhibitors in refineries.

The trend towards "green" corrosion inhibitors is gaining traction. Although there is no universally accepted definition, "green" inhibitors are generally characterized by their low toxicity (preferably non-toxic), biodegradability, and absence of harmful elements or substances. Current corrosion inhibitors must comply with safety and risk requirements, as well as reliability and quality assurance standards [95].

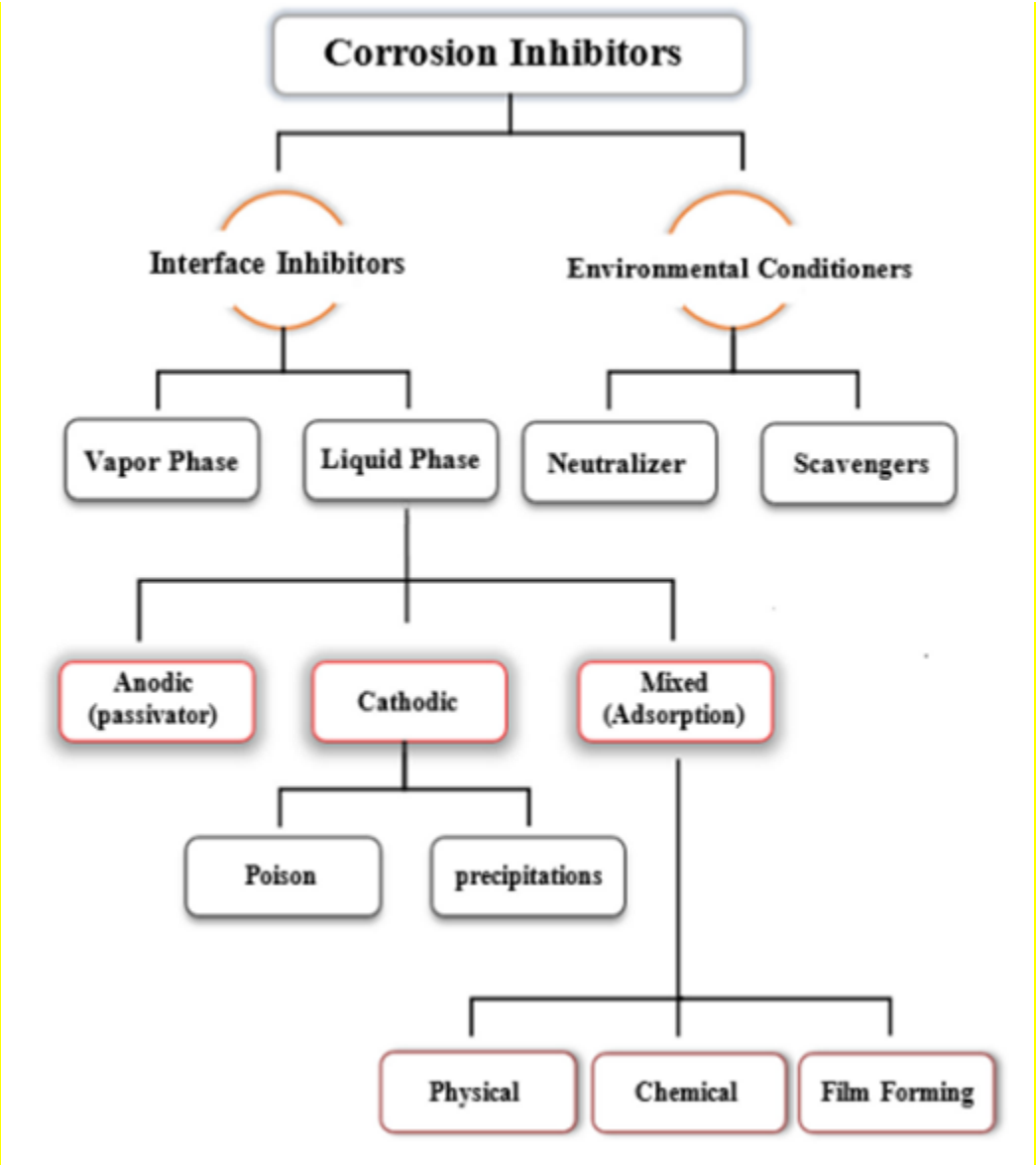


Figure. I.44. Classification of corrosion inhibitors.

I-8-7) Green based corrosion inhibitors :

Green-based inhibitors, such as plant extracts, are in high demand due to their non-toxic nature and environmentally friendly properties, outperforming commercial inhibitors【96–97】. Plant extracts are considered green and sustainable because of their natural and biological characteristics, which effectively inhibit the corrosion of metals and alloys【98】. Among plant parts, leaves are particularly preferred for their abundance of phytochemicals (active components) produced

through synthesis, which function similarly to commercial inhibitors. It is also important to note that extracts from other plant parts, such as roots, bark, flowers, fruits, wood, seeds, and peels, contribute to inhibition efficiency【99–100】. Additionally, the synthesis of phytochemicals utilizes carbon dioxide, a harmful greenhouse gas, in the process of photosynthesis, aligning with the principles of green chemistry.

Green corrosion inhibitors are effective at very low concentrations, protecting metal surfaces from corrosive environments. Plant extracts impact the corrosion rate by affecting the anodic or cathodic reaction kinetics during the adsorption process on the metal surface, thereby influencing the diffusion rate of aggressive ions and preventing their interaction with the metal surface. Consequently, a protective film layer is formed, increasing the electrical resistance of the metal surface【101】. Green corrosion inhibitors are also known for their adsorptive properties, allowing active molecules from the plant extract to adsorb onto exposed metal surfaces, acting as site-blocking elements【102】. Equation below illustrates the working mechanism of these inhibitor molecules, where neutral molecules from the plant extract adsorb onto the metal surface instead of hydrogen ions【103】:

$$\text{Inhibitor} + n\text{H}_{ads} \rightarrow \text{Inhibitor}_{ads} + \text{H}_2$$

where $n\text{H}_{ads}$ is adsorbed hydrogen ions sourced from water and Inhibitor_{ads} is adsorbed neutral molecules sourced from plant extract.

In conjunction with this, there are a few limitations that must be examined during the preparation of plant extracts. Typically, the solvents used for extraction diffuse into plant tissue, solubilize, and extract the available phytochemicals【104,105】. Therefore, selecting the appropriate solvent is crucial for optimal results. Water is a readily available, cheap, and safe solvent【106,107】, yet ethanol and methanol remain in demand for selective plant extracts【108,109】. Additionally, temperature significantly affects the extract preparation. Low temperatures hinder the solubility of phytochemicals, while high temperatures can cause their decomposition. The recommended temperature for ideal extraction is between 60–80°C【110,111】. For drying, oven drying is advisable as drying at room temperature can take months.

Green-based corrosion inhibitors can be divided into two classes: organic and inorganic【112–113】. The organic class consists of synthetic substances that are non-toxic to the environment, such as flavonoids, alkaloids, and plant byproducts【114】. In contrast, inorganic inhibitors are widely used in aqueous systems due to their high productivity【115】. However, the toxic nature of chromates limits their industrial use. To address this, lanthanide salts have been studied as eco-friendly inhibitor substitutes【116】.

Correspondingly, fruit wastes such as seeds and peels have gained significant attention for their natural antioxidant properties. For example, mango, orange, passionfruit, and cashew peels are known to contain substantial amounts of antioxidants like polyphenols, carotenoids, and vitamins C and E. The effectiveness of antioxidant activity, particularly from phenolic compounds like flavonoids, depends on their structural characteristics, including the arrangement and location of phenolic hydroxyl groups. Additionally, mango, orange, and passionfruit are noted for their high pectin content, a polysaccharide【117】.

Recently, studies have explored the use of banana peel extracts for protecting mild steel in acidic environments, and simultaneous research investigated the use of mango and orange peels to combat corrosion of mild steel, aluminum, zinc, and copper in acid solutions (HCl and H_2SO_4) [118】. These findings suggest that industrial waste and aqueous fruit peel extracts can serve as effective green-based corrosion inhibitors, meeting the criteria of green chemistry.

Chapter II : Corrosion in Upstream Production Operations

II) Corrosion in Upstream Production Operations

The upstream sector [119] encompasses activities such as exploration, drilling, completion, production, processing, and workover in oil and gas fields. Figure II-1 displays simplified process flow diagrams for oil and gas production, along with illustrations of typical midstream processing facilities [120].

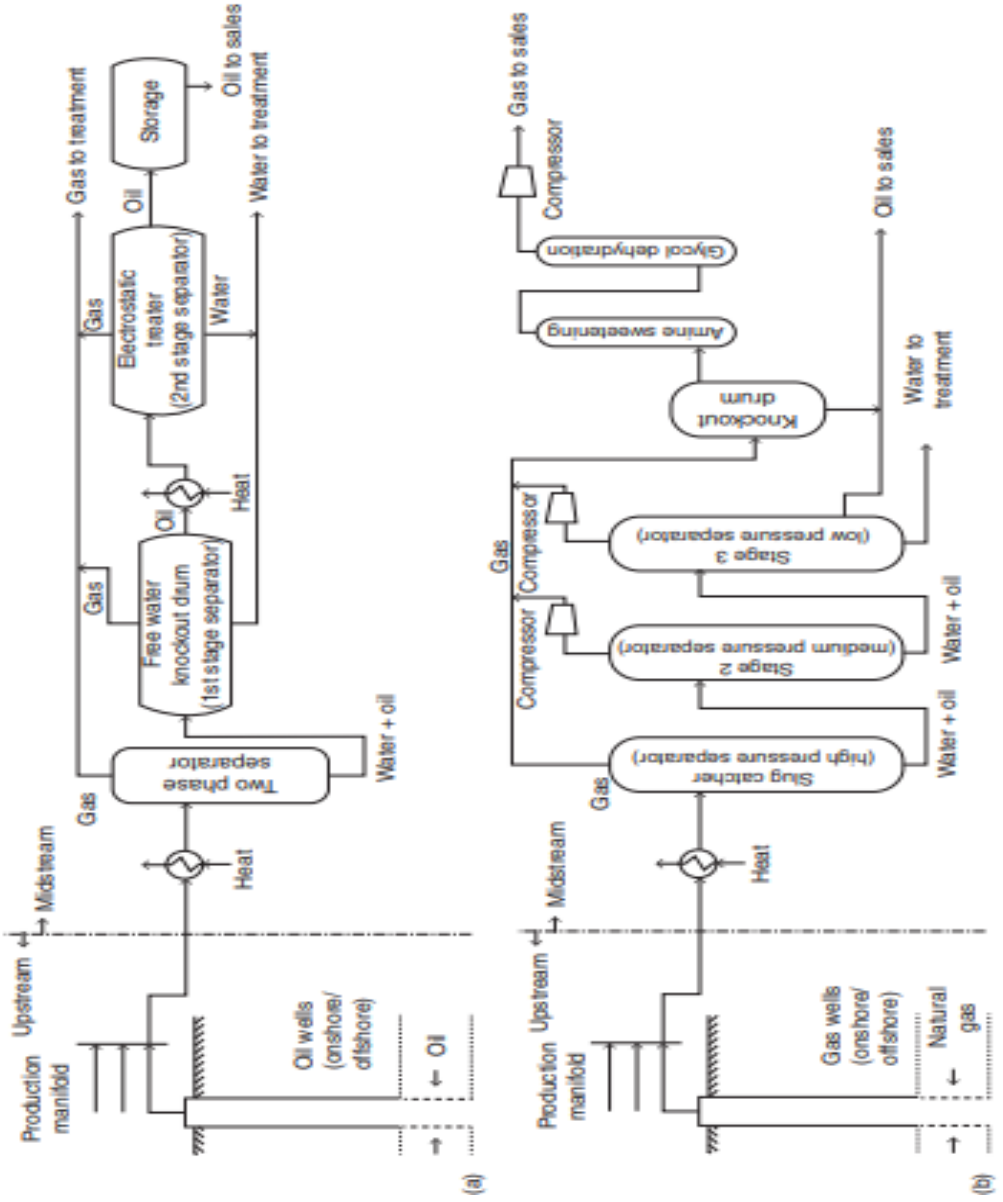


Figure II.1: Simplified upstream and midstream process flow diagrams for Oil wells and Gas wells [120]

Exploration entails the quest for both conventional and unconventional oil and gas reserves. Drilling operations for these reserves may involve vertical drilling exclusively or incorporate horizontal-lateral drilling techniques. The drilled wells are then finalized either using casings alone or with production tubing, along with various types of valves. Perforations are made in the production casing or tubing to facilitate flow from the reservoir.

Various valves are positioned within the well, at the wellhead, and at the assembly atop the wellhead, commonly referred to as the Christmas tree, to regulate flow. Fluids extracted from the wells are conveyed through flow-lines and trunk-lines to processing facilities for the separation of gas, oil, and water. Wells undergo workovers in the event of reduced production resulting from issues such as plugging or failure of a significant well component. Figure II.2 illustrates a schematic of a typical oil well.

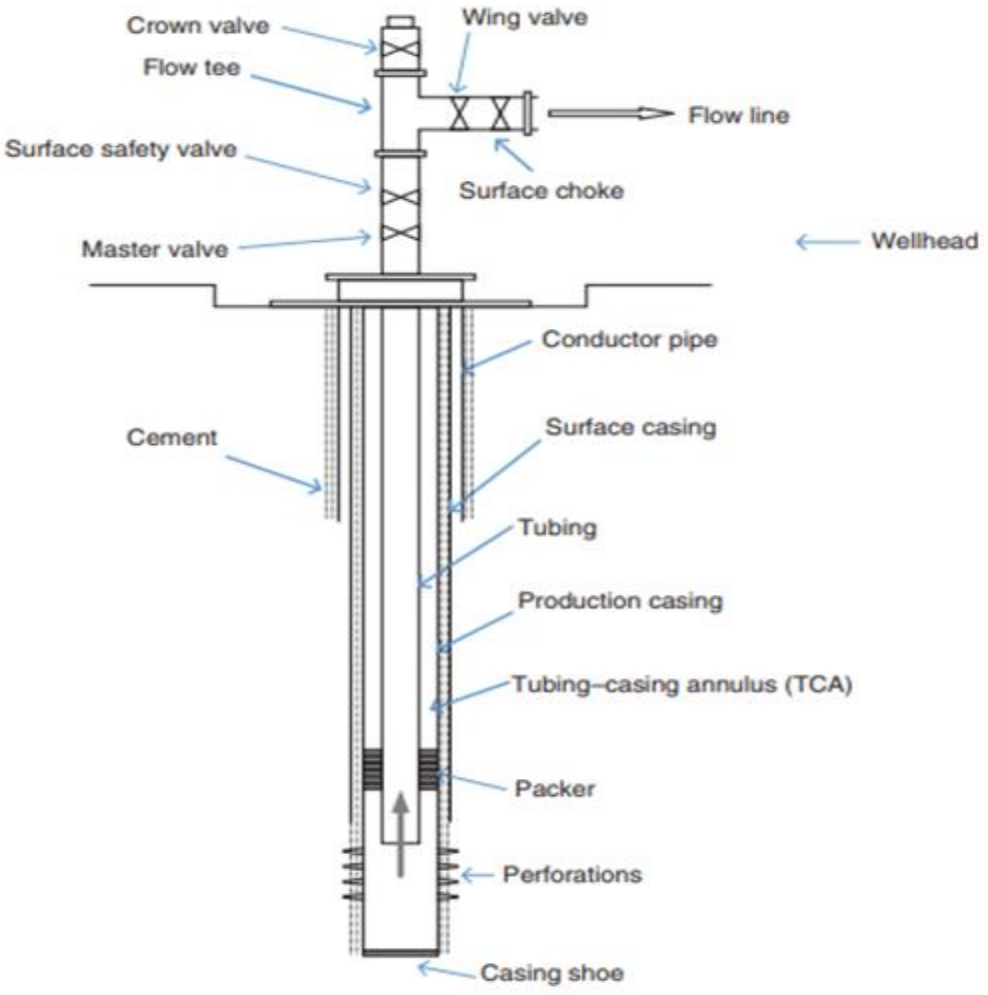


Figure II.2: Schematic of a typical Oil well

Hydrocarbon reservoirs may exist as gaseous, liquid, or a combination of both phases. Initially, a natural gas reservoir predominantly contains a single gaseous hydrocarbon phase. However, if this gaseous phase contains heavier components that condense into liquid form upon reaching the surface, the reservoir is termed a gas condensate reservoir. Conversely, an oil reservoir can exist as either a two-phase system (gas-liquid) or a single liquid phase. Gas wells extract from natural gas reservoirs, while oil wells extract from oil reservoirs.

Typically, natural gas reservoirs maintain higher temperatures compared to crude oil reservoirs. Consequently, gas wells experience higher downhole temperatures than oil wells. Two key characteristics of wells are the bottom-hole temperature (BHT) and the bottom-hole pressure (BHP). BHT represents the temperature at the center of the perforated interval, while BHP denotes the pressure at the same location under shut-in conditions. Pressure levels can exceed 90 MPa (approximately 13,000 psi), while temperatures can surpass 200°C (about 390°F) [119].

A reservoir or well is deemed "sweet" when it contains carbon dioxide (CO_2) with minimal or no presence of hydrogen sulfide (H_2S). Conversely, they are classified as "sour" if noticeable amounts of H_2S are present. CO_2 and H_2S are collectively referred to as acid gases. Because of the distinct corrosion mechanisms involved, sweet and sour wells typically necessitate different corrosion control strategies, spanning from drilling to transportation.

Gas can either be non-associated when produced independently or associated when extracted alongside oil. Condensate wells are gas wells that also yield condensed liquids. An important parameter is the gas-oil ratio (GOR), representing the ratio of produced gas to produced oil under standard conditions.

During the initial stages of their production life, oil and gas wells may either be devoid of formation water, referred to as "dry," or exhibit low water cuts. Typically, the water cut increases over time as the well matures, consequently leading to heightened damage from corrosion attacks. The propensity for scaling and the potential for emulsion formation are contingent upon the characteristics of the formation water. A thorough geochemical analysis of formation water is imperative for reservoir characterization.

Reservoirs are further delineated by their permeability and porosity, or the classification and distribution of pores. -

Permeability : denotes the ease of fluid flow through a body of porous material under standard pressure differentials, while **Porosity:** quantifies the reservoir's pore volume, distribution, and interconnectivity. These parameters collectively influence reservoir productivity.

Drilling operations may target conventional oil or natural gas, or even water reservoirs, and can occur either onshore or offshore. Wells can be drilled to varying depths, from the surface down to depths of up to 6000 meters. The drilling process utilizes circulating drilling fluids to aid in excavation as the drill bit penetrates through different formations, such as sandstone or limestone. To access various parts of the formation, the wellbore may be drilled vertically or directionally, intentionally deviating from the vertical axis, possibly leading to horizontal drilling.

During drilling, casings are installed to prevent well collapse and facilitate deeper drilling. The composition of drilling fluids includes corrosion inhibitors among other chemical additives. Corrosion inhibitors are incorporated into the drilling fluid formulation to safeguard against casing corrosion. Well completion techniques involve connecting the formation with the wellbore, which can be achieved through methods like perforated cemented casings or open-hole comple.

On the contrary, water wells are drilled either to provide water or to inject water into crude oil reservoirs, aiming to elevate their pressure and thus maintain oil production. The former is referred to as water supply wells, while the latter is termed water injection wells. Additionally, there are water disposal wells designated for reintroducing excess water back into the formation.

II-2) Factors Leading to Corrosion in Upstream Production facilities:

Upstream production facilities encompass various components such as producing wells, wellhead valve assemblies, flowlines, trunklines, and oil and gas processing facilities. The corrosive elements encountered in actual production formations include CO_2, H_2S, polysulfides, organic acids, and elemental sulfur. Oxygen (O_2), if present, is typically introduced into the formation from external sources.

Moreover, oil and gas production entail unique challenges such as extreme temperatures and pressures. In deep gas wells, temperatures can soar to as high as 230°C (450°F), while the partial pressures of CO_2 and H_2S may reach up to 20.7 MPa (3000 psi) and 48 MPa (7000 psi), respectively [119].

In oil and gas wells, increased water content along with elevated temperatures and pressures contribute to more corrosive conditions. The corrosiveness downhole is additionally influenced by the concentration of salts, such as chlorides, dissolved in the water phase.

Oxygen may infiltrate production formations through several means:

(a) During the drilling of wells, oxygen can be introduced through drilling muds.

(b) In certain cases, dense brines are utilized to fill the annulus between the production tubing and the casing, known as the casing-tubing-annulus (CTA), which can introduce oxygen.

(c) Injection of H_2O and CO_2 is employed to aid in oil lifting, potentially introducing oxygen.

(d) Hydrochloric acid (HCl) is injected to stimulate the well by improving formation permeability, thereby potentially introducing oxygen.

A prevalent practice observed in aging oil and gas production fields involves the widespread utilization of carbon and low-alloy steels, primarily due to their cost-effectiveness and widespread availability. The adoption of corrosion-resistant alloys (CRAs) has been a relatively recent development and has been implemented very selectively.

II-2-1 Corrosion due to Oxygen:

Corrosion attack by oxygen on internal surfaces in oil production is highly aggressive. Typically, oxygen is absent at depths exceeding approximately 100 meters (330 feet) below the surface. Contamination with oxygen is more probable in facilities involved in processing and handling produced oil operating at near-ambient pressure. Oxygen ingress may result from various sources such as leaking pump seals, casing and process vents, open hatches, and exposed handling during activities like mud pits and drilling.

Oxygen possesses distinctive properties, acting as a potent oxidant with relatively rapid reduction kinetics, as exemplified by the following reaction:

$$(1/2)\, O_2 + H_2O + 2e^- \rightarrow 2OH^-$$

Oxygen exhibits low solubility in both water and brines, which elucidates why the mass transport of oxygen constitutes the limiting factor in corrosion reactions involving carbon and low-alloy steels within non-acidic environments. This phenomenon also accounts for the localized attacks

observed in crevices and beneath deposits, attributed to the restricted mass transport within oxygenated systems.

Under ambient equilibrium conditions between air and water, the concentration of dissolved oxygen typically ranges between 7 and 8 parts per million (ppm). At this concentration and under stagnant conditions, the corresponding corrosion rate is approximately 0.25 millimeters per year (10 mils per year). However, under highly turbulent flow conditions with continuous oxygen replenishment, this rate could escalate to as high as 150 millimeters per year (600 mils per year).

By reducing the oxygen concentration to 7–8 parts per billion (ppb) through scavenging, the corrosion rate can be mitigated to less than 0.01 millimeters per year (0.4 mils per year). Additionally, the formation of a magnetite (Fe_3O_4 or $Fe_3H_2O_4$) corrosion product film further diminishes the corrosion rate by shifting the reaction to be controlled by the slower anodic step.

II-2-2) Corrosion due to Hydrogen Sulfide:

Although CO_2 and H_2S dissolve readily in water within natural gas, their concentrations fluctuate between different samples. When corrosion is primarily attributed to CO_2, it is referred to as sweet corrosion. Conversely, if H_2S is responsible for the corrosion, it is termed sour corrosion. According to NACE, the extent of corrosion is influenced by factors including partial pressure, natural gas acidity (pH), as well as environmental conditions, temperature, and velocity [121].

&-Mechanism of H_2S corrosion:

$$H_2S_{(aq)} \rightleftharpoons HS^-_{(aq)} + H_3O^+$$

$$HS^{-5}_{(aq)} \rightleftharpoons S^{2-} + H^+$$

$$Fe_s \rightarrow Fe^{2+}_{(aq)} + 2e^-$$

$$2H^+ + 2e^- \rightarrow H2_{(g)} \uparrow$$

$$Fe_s + H_2S_{(aq)} \rightarrow FeS_{(s)} + H_{2(g)}$$

The uptake of atomic hydrogen may contribute to hydrogen-induced cracking (HIC), stress-oriented HIC (SOHIC) in low-strength steels, and sulfide stress cracking (SSC) in high-strength steels, specifically those with a yield strength exceeding 690 MPa (100 ksi).

Corrosion products consisting of iron sulfide exhibit limited water solubility, leading to rapid precipitation on the surface of steel, thereby forming a barrier that mitigates the effects of velocity.

In the presence of these iron sulfide films, corrosion inhibitors can effectively operate even at velocities of up to 30 m/s (100 ft/s). These films of iron sulfide can exhibit either protective or non-protective characteristics.[121].

Table II.1: Differences between CO_2 and H_2S systems.

Parameter	H_2S	CO_2
Solubility in water	Relatively fast	Relatively slow
Velocity effects	Relatively unimportant	Relatively important
Corrosion rates	Low values	High values (~ 1000s mpy)
Presence of Cl^- ions	Important	Unimportant

III-2-3) Corrosion due to Carbon Dioxide (CO_2):

CO_2, similar to H_2S, exhibits weak acidic properties. However, unlike H_2S, CO_2 needs to undergo hydration to form carbonic acid (H_2CO_3) in order to become acidic. The hydration process of CO_2 into H_2CO_3 occurs relatively slowly compared to H_2S hydration. Table II.2 outlines several distinctions between CO_2 and H_2S systems.

The corrosion of steel induced by hydrated CO_2 results in the formation of a protective iron carbonate (siderite, $FeCO_3$) scale, which diminishes the corrosion rate.

$$\mathbf{Log\ R = A - (2320/\ T + 273) - (\ 5.55\ T/\ 1000\ ) + 0.67\ log\ P_{CO2}}$$

Where

R: is the corrosion rate (refer to the Table 1.2 for units)

T: is the temperature (°C)

A: is a constant (refer to Table III.2 for values)

P_{CO2} is the partial pressure of CO_2 (refer to Table III.2 for units)

Table II.2: Values of "A" appearing in Equation above.

R	P_{CO2}	A
mm/yr	atm	7.96
mm(mils/yr)	Psi (Pound per Square inch)	8.78

Higher temperatures facilitate the development of a protective $FeCO_3$ scale due to reduced scale solubility, decreased CO_2 solubility, and enhanced precipitation kinetics. Additionally, elevated pH levels and non-turbulent conditions further promote the formation of this protective $FeCO_3$ scale. In systems where both H2S and CO_2 are present, corrosion products of iron sulfide prevail when the H_2S/CO_2 ratio surpasses approximately 1/200 [121]. Pitting mechanisms are observed in systems containing O_2 and H_2S, whereas general corrosion manifests in systems containing CO_2.

II-2-4) Corrosion due to Strong Acids:

To dissolve scales and enhance formation permeability, potent acids are injected into wells. Typically, HCl (15 and 28 wt%) is employed for limestone formations, while hydrofluoric acid (HF, 3 wt%) is required for sandstone formations. In cases where corrosion inhibitors fail to sufficiently mitigate HCl attacks, formic acid (HCOOH, 12 wt%) is utilized, particularly in deep sour gas wells. Alongside chemical inhibitors, controlling corrosion from these potent acid solutions involves restricting exposure time to 2–12 hours.

II-2-5) Corrosion due to Concentrated Brines:

Dense halide solutions, known as concentrated brines or completion brines, are utilized to equalize formation pressures during production activities. These solutions may comprise calcium, zinc, or magnesium halides. Corrosion can occur in concentrated brines due to dissolved oxygen or entrapped air. Additionally, corrosion may result from the hydrolysis of metallic ions, as depicted in the following reaction:

$$Zn^{2+} + H_2O = ZnOH^{+} + H^{+}$$

To prevent exposure to zinc chloride ($ZnCl_2$) brines, higher-density calcium bromide ($CaBr_2$) brines exceeding 1.7 g/cm^3 (14 lb/gal) are alternatively employed, albeit at a greater cost.

II.3) Corrosion Types in Petroleum Production Operations

The primary forms of corrosion observed in petroleum production operations are as follows:

(a) Stray-current corrosion: Typically linked with cathodic protection (CP) systems.

(b) Under-deposit (Crevice) corrosion: A localized corrosion type often exacerbated by the presence of oxygen, particularly in the presence of chloride ions. This form of corrosion necessitates the existence of crevices or surface deposits such as sand, sludge, corrosion by-

products, or bacterial slime, which foster the development of differential concentration cells characterized by regions rich in oxygen and regions deficient in oxygen.

(c) Galvanic corrosion: This corrosion variant arises when two dissimilar metals are present, with the more active metal acting as the anode and the less active metal as the cathode. The situation worsens when there is a significant cathode-to-anode area ratio, hastening the dissolution of the metal occurring at the anode.

(d) Microbiologically-induced corrosion (MIC): A prevalent instance of MIC in oil and gas production is the production of H2S through sulfate-reducing bacteria (SRB) in systems initially free of H2S. Other bacterial varieties also play a role in MIC, including acid-producing bacteria (APB) and iron-oxidizing bacteria (IOB).

(e) Mechanical and mechanical/corrosive impact: The array of mechanical and mechanical/corrosive impacts encompasses cavitation, erosion, erosion-corrosion, and corrosion fatigue.

II-4) Corrosion Inhibitors for Oil and Gas Production

Approaches for managing the aforementioned types of corrosion may encompass materials selection, coatings, cathodic protection (CP), inhibitors, non-metallic materials, and environmental control. However, this section will focus solely on corrosion inhibition [122]. The prevalent choice for corrosion inhibition in oil and gas production is film-forming amine molecules and their salts. These inhibitors have enabled production from primary and secondary-recovery wells that would otherwise be highly susceptible to corrosion.

Before implementing a corrosion inhibitor in the field, several key characteristics must be considered, including its pour point, solubility, tendency to form emulsions, and performance. The pour point denotes the lowest temperature at which the inhibitor remains in liquid form. Film-forming amine corrosion inhibitors typically consist of an organic chain with a polar head, making them partially soluble in both hydrocarbons and aqueous phases. However, this composition can lead to varying degrees of oil-water emulsions, particularly with batch treatments of corrosion inhibitors. Tight emulsions can be challenging to disperse, potentially disrupting surface equipment operations. To address this issue, the inhibitor may be formulated to be non-emulsifying, or emulsion breakers may be added to the inhibitor package.

Before conducting field trials, it is crucial to evaluate the inhibitor's performance in the laboratory, often accomplished using methods such as the rotating cage test.

II-4-1) Oil and Gas Wells:

In oil and gas production, wells are typically classified into three main categories:
Oil wells, gas wells, and water wells. Oil wells are responsible for extracting hydrocarbons as well as water and can be further categorized into naturally flowing wells and artificially lifted wells. Artificial lifting methods include gas-lifting, electric submersible pumps (ESPs), rod pumps, and hydraulic pumps.
Gas wells, on the other hand, produce either dry gas or gas-condensate, which contains both liquid and gaseous hydrocarbons.
Water wells are utilized to extract aquifer water, which is then reinjected into water injection wells for processes such as waterflooding or tertiary recovery. Additionally, water injection wells serve the purpose of disposal. These different types of wells are depicted in the schematic illustrated in Figure below.

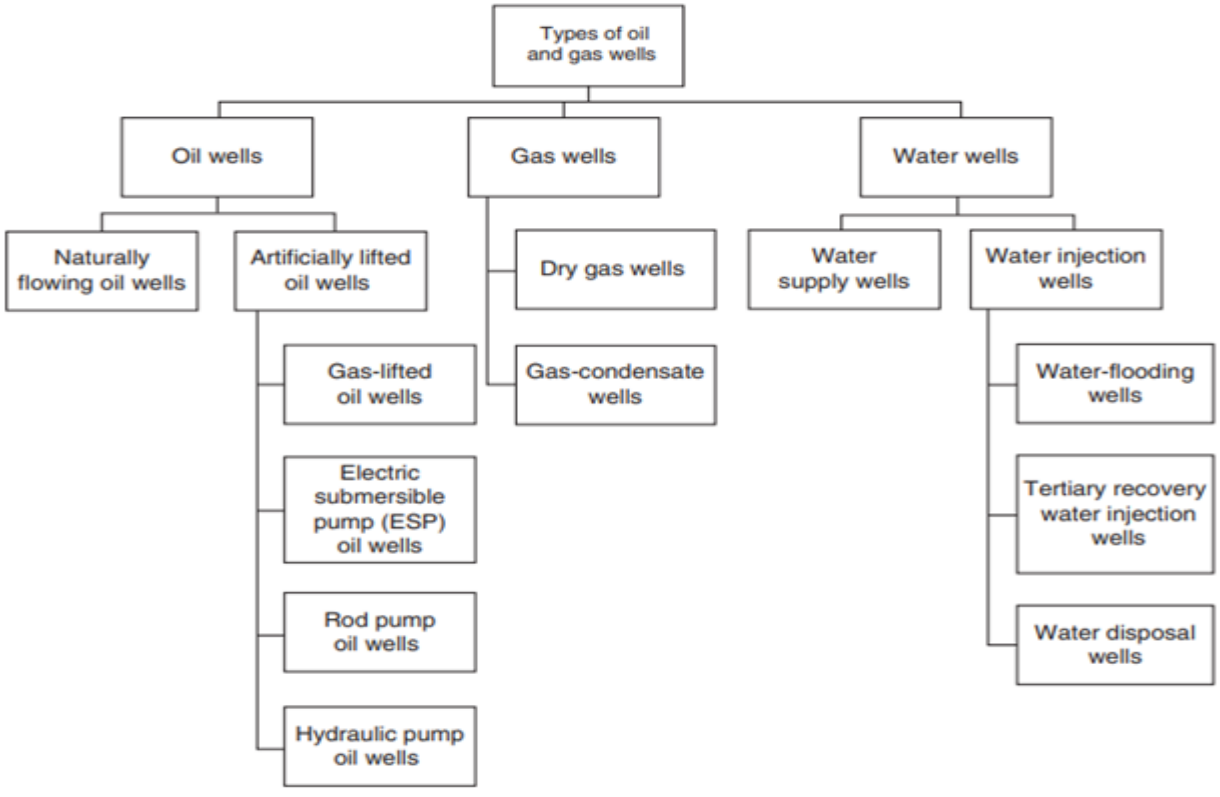


Figure II-3: Schematic of types of Oil ,Gas , and Water Wells.

Each type of well can be classified as either "sweet," characterized by dominance of CO_2, or "sour," when a measurable amount of H_2S is present. Sweet corrosion, besides being influenced by CO_2, can also be triggered by the presence of formic acid (HCOOH), acetic acid (H_3CCOOH), or other short-chain organic acids found in produced gas and/or liquids.

Newer oil and gas wells are being drilled at greater depths, where the Bottom Hole Temperature (BHT) can soar up to 205°C (400°F), and the Bottom Hole Pressure (BHP) can exceed 138 MPa (20,000 psi). Generally, the higher the encountered temperature within a well, the more challenging it becomes to manage corrosion. Similar to typical chemical reactions, corrosion rates tend to double for every 10°C (18°F) rise in temperature. Additionally, elevated pressures result in increased concentrations of dissolved acid gases, intensifying the corrosive nature of the water.

Drawing from field experiences with sweet wells, the following general guidelines have been established based on the partial pressures of CO_2 (PP_{CO2}) [122]:

- ✓ PP_{CO2} levels below 48 kPa (7 psi) are deemed non-corrosive.
- ✓ PP_{CO2} ranging from 48 to 207 kPa (7 to 30 psi) indicate a potential for corrosion.
- ✓ PP_{CO2} exceeding 207 kPa (30 psi) typically signify severe corrosion.

Various factors influence the corrosiveness of produced fluids, including water composition and quantity, velocity or flow pattern, and the presence of solid particles like sand. Higher chloride concentrations in water typically correlate with increased corrosiveness. At a certain water percentage, oil wells transition from an oil continuous phase to a water-wet phase. Depending on the velocity and the presence of other fluid phases, the flow pattern can take on different configurations such as bubble flow, slug flow, churn flow, and annular flow. The production of fine sand particles can result in the removal of corrosion inhibitor films and erosion, depending on the velocity. Therefore, sand control measures are necessary to prevent sand from being carried along with the produced fluid in such cases.

II-4-2) Inhibitor Selection

The selection of the appropriate inhibitor hinges on the specific system requiring protection, be it a pumping oil well, a gas-lift well, a gas well, a water flood system, or a flow line. For instance, if a conventional inhibitor is introduced upstream of a gas compressor, the heavier components might precipitate and cause fouling in the compressor valves. It's essential to consider both temperature

and pressure when choosing an inhibitor, as elevated levels of these variables could result in polymerization and the formation of sludge. Pressure levels are crucial in determining the corrosiveness of CO_2 and H_2S. The thermal stability of the inhibitor should be evaluated during the corrosion inhibitor assessment process.

Various factors influence the selection of inhibitors, including identifying the specific issue at hand, determining the corrosive agents present, and considering factors such as pressure, temperature, velocity, production composition, water-to-oil ratio, water salinity, and water and oil acidity. Parameters to assess when evaluating an inhibitor include whether the system is sweet or sour, the service pressure and temperature, water composition and water cut, and the method of corrosion inhibitor treatment (e.g., batch or continuous). The dosage and frequency of treatment are influenced by factors such as the severity of corrosion, the total volume of produced fluid, the percentage of water, the nature of the corrosive agent, and the type of chemical employed.

II-4-3) Practical Challenges with Inhibition

There are various practical challenges associated with inhibition, including foaming, emulsions, scale removal and plugging, as well as safety and handling concerns. Foaming may occur in areas where inhibitor-containing streams are agitated with gas, such as in a gas separator, counter-current stripper, or aerator. It's crucial to consider the compatibility of inhibitors with metals. For instance, amine-based inhibitors protect steel but can corrode copper and brass surfaces. Additionally, the reduction of nitrate inhibitors can lead to the formation of ammonia (NH_3), which can cause stress corrosion cracking (SCC) in copper and brass metals. Therefore, it's essential to identify the metallic components of a system and ensure the compatibility of the inhibitor with each exposed metal.

II-4-4) Inhibitor Application Methods

When deciding on a method for applying corrosion inhibitors, two key considerations must be kept in mind. Firstly, the initial concentration of the corrosion inhibitor should adequately coat the entire exposed surface of the steel structure. Secondly, if portions of the corrosion inhibitor are removed, a new film should spontaneously form. Common application methods for corrosion inhibitors include batch, continuous, and squeeze treatments.

(a) Batch treatment: This can be divided into standard batch, extended batch, annular slug, tubing displacement, and between-pigs batch methods.

(b) Continuous treatment: Employed in producing wells, injection wells, pipelines, and flow lines. Table 1.3 provides general criteria for selecting the treatment dosage in continuous corrosion inhibitor treatment.

(c) Squeeze treatment: Care must be taken when applying this method to avoid damaging or plugging the formation.

Corrosion severity	Recommended dosage rate (ppm)[a]
Mild corrosion	10–15
Moderate corrosion	15–25
Severe corrosion	>25

a) These concentrations are based on total produced fluid.

Corrosion Severity	Recommended dosage rate (ppm)[a]
Mild Corrosion	10-15
Moderate Corrosion	15-25
Severe Corrosion	>25

a) These concentrations are based on total produced fluid.

Various methods are available for the application of corrosion inhibitors to oil and gas production systems, each with its own set of advantages and drawbacks. Continuous treatment through a capillary treater string, often referred to as drip feed, stands out as an effective corrosion inhibition technique. Its viability is particularly enhanced if a capillary tube is already in place, as the installation of a new one can incur significant costs. Through a treater string, corrosion inhibitor is dispensed via a small-diameter stainless steel tube positioned within the annulus, extending from the wellhead to the depth of the packer. When the annulus is accessible from the tubing, the chemical can be continuously injected into the annulus, a variant of the method known as slip-stream flushing. It is recommended to maintain inhibitor concentrations ranging from 25 to 100 ppm in the produced fluid.

Due to the tendency of organic chemical inhibitors to condense on the tubing wall only at higher points along the tubing string, their application is generally not recommended for temperatures exceeding 150°C (302°F), although in some cases, this limit may be extended to 170°C (338°F).

This method typically requires one injection device per well, which can limit its feasibility in unmanned offshore platforms. Water-soluble inhibitors utilized in continuous injection systems involving water usually include quaternary amines, amine salts, or salted imidazolines. Chemical scavengers may be incorporated into these inhibitors if oxygen is present. Conversely, oil-soluble inhibitors often consist of long-chain primary amines, imidazolines, fatty acids, and phosphate esters.

Alternative treatment approaches should be explored for wells lacking a treater string or where the annulus isn't accessible from the tubing. In a squeeze treatment, corrosion inhibitor is injected into the formation and allowed to flow back. However, this method can lead to formation plugging and premature depletion of inhibitor concentration due to chemical losses. Batch treatment, another method, suffers from the disadvantage of requiring excessive amounts of corrosion inhibitor.

A refined approach to batch treatment is the tubing displacement method, which utilizes a lesser amount of chemical compared to traditional batch treatment. In this method, the chemical solution is displaced through the tubing to the depth of the packer using inert crude oil. In terms of effectiveness, the tubing displacement method ranks just below continuous treatment. Batch treatment inhibitors are typically oil-soluble to enhance their longevity against water exposure. Additionally, some corrosion inhibitor techniques, albeit with restricted applications, employ artificial lift systems and umbilicals. However, challenges such as gumming and valve blockages are commonly encountered with the use of artificial lift systems.

The typical dosage range for corrosion inhibition in surface facilities, flowlines, and trunklines under continuous treatment is typically between 10 and 50 parts per million (ppm). Sulfur inhibition is imperative to curtail excessive corrosion and to avert downstream facilities plugging.

When elemental sulfur deposition occurs, dosages as high as 2500 ppm are applied for continuous treatment, supplemented by batch treatment to prevent water and sulfur from contacting the internal surface of the pipe wall. Corrosion rates reaching as high as 30 mm/year (1200 mpy) have been observed. Batch treatments are employed to dissolve existing sulfur deposits, utilizing high sulfur solubility solvents such as carbon disulfide (CS_2), di-alkyl-disulfide (DADS), dimethyl-disulfide (DMDS), and aromatic solvents. These solvents are capable of dissolving sulfur efficiently, while some aromatic solvents, although less effective at sulfur dissolution, offer cost-effectiveness and operational simplicity.

Water-flooding systems comprise water intake units or supply wells, surface-gathering lines and tanks, water-treating equipment, surface water pumps and transport lines, and downhole tubing of water injection wells. The principal culprits of corrosion in these facilities are oxygen contamination and acid gases. As previously mentioned, oxygen can be eliminated through mechanical methods or the application of oxygen scavengers. If these approaches are impractical due to minimal water volume, alternative solutions such as oxygen corrosion inhibitors can be employed.

Produced water handling systems offer zinc amino methyl phosphonate and organic sulfophosphate corrosion inhibitors. Among acid gases, H_2S poses greater challenges than CO_2 in water handling systems. Corrosion products like iron sulfide can cause scaling problems in water supply wells and lead to deposition and under-deposit corrosion in surface lines. Additionally, iron sulfide solids may result in blockages in water injection wells and complications during the oil-water separation process.

III-4-5) Oxygen Removal

Oxygen stands out as a primary contributor to corrosion in oilfield water. The existence of dissolved oxygen notably diminishes the effectiveness of film-forming corrosion inhibitors. Dissolved oxygen can be eliminated through both mechanical and chemical methods. Mechanically, oxygen is physically extracted using methods such as counter-current gas stripping or vacuum de-aeration. Chemically, oxygen is neutralized through reactions with scavengers. Common oxygen scavengers include:

Sodium sulfite: $2Na_2SO_3 + O_2 \rightarrow 2Na_2SO_4$

Ammonium bisulfite: $2NH_4HSO_3 + O_2 \rightarrow (NH_4)_2SO_4 + H_2SO_4$

Sulfur dioxide: $SO_2 + H_2O + 1/2\ O_2 \rightarrow H_2SO_4$

Mechanical techniques are employed for eliminating significant amounts of dissolved oxygen, whereas chemical scavenging is feasible when dealing with smaller oxygen concentrations. Both approaches can be combined to guarantee thorough removal of dissolved oxygen. An essential characteristic of oxygen is its solubility in hydrocarbons, which is 5–25 times greater than its solubility in oilfield waters. Nevertheless, it is more cost-effective to prevent oxygen ingress rather than removing it. This can be accomplished by implementing gas blankets on water supply wells and storage tanks and ensuring the ongoing integrity of valve stems and pump packing.

II-5) Problems Encountered and Protective Measures

II-5-1) Drilling Fluid Corrosion

a) Causes of Corrosion:

The primary environmental factors contributing to corrosion in drilling fluids encompass O_2, CO_2, H_2S, dissolved salts (ionic strength), temperature, and low pH. Physical conditions include metal composition, metal properties, string design, and stress. Accelerators combining both physical and chemical factors include stress corrosion and erosion-corrosion. Additionally, microorganisms play a role in causing corrosion within drilling environments.

The major forms of attack are: • Under-deposit (crevice) corrosion • Corrosion fatigue • SCC • Erosion–corrosion (abrasion) • Uniform attack • Galvanic corrosion

b) Oxygen Corrosion Control:

For oxygen control in drilling muds, it is recommended to add 10 mg/l sulfite ion continuously for every 1 mg/l of oxygen. A constant residual sulfite concentration of 100 mg/l should be maintained in the drilling fluid. Any interfering side reactions hindering the oxygen-sulfite reaction should be prevented. Moreover, the effectiveness of filming inhibitors typically used during drilling diminishes in the presence of oxygen.

c) H_2S Corrosion Control:

H_2S initiates two types of corrosion by assaulting the surface: under-deposit (crevice) corrosion and SSC (Sulfide Stress Cracking). Strategies to mitigate these corrosive effects involve the selection of resistant materials, the use of chemical scavengers to eliminate H_2S, and stress reduction. H2S can originate from various sources, including naturally occurring sources within the formation, thermal degradation of mud products, or activities of sulfate-reducing bacteria (SRB). Additionally, H2S may be introduced through the use of make-up water.

Film-forming amine-type inhibitors are advised for the drill string to shield against hydrogen embrittlement. To mitigate corrosion fatigue and hydrogen embrittlement in the drill pipe, oil-soluble filming inhibitors can be directly applied. However, caution should be exercised in using cationic filming inhibitors as they may cause flocculation of anionic clays in drilling systems, potentially compromising mud properties. Control of the drill pipe's susceptibility to stress corrosion cracking (SSC) involves the selection of materials with appropriate hardness and yield

strength, as well as management of the drilling fluid. SSC risk diminishes when the temperature exceeds 80 ∘C (175 °F).

d) CO_2 Corrosion Control

CO_2 induces selective corrosion primarily through electrochemical cell action occurring beneath deposits. Corrosion management for CO_2 is akin to that for H_2S, involving the use of oil-soluble, film-forming corrosion inhibitors. These inhibitors are typically administered by spraying the exterior of the drill pipe and employing batch treatments for internal surfaces, enabling penetration of deposits and access to underlying pits.

e) Scale and Deposit Control

Factors contributing to under-deposit pitting corrosion on exposed metal surfaces primarily include mineral scale, corrosion by-products, and mud. Inhibiting scale formation proves effective in preventing and eliminating these deposits. Various examples of effective scale inhibitors include organic phosphonates, phosphate esters, acrylics, acrylamides, and maleic acid. To ensure corrosion protection, treatment levels are often elevated, sometimes reaching up to 1000 mg/l. However, it's important to note that the dispersing properties of these inhibitors may affect mud properties at such high levels. Hence, it's advisable to assess the proposed recipe before application.

II-5-2) Primary Production:

There exist two primary categories of oil-producing wells: flowing wells and artificial lift wells. Artificial lift wells can be further categorized into those employing downhole hydraulic pumps, gas-lift systems, and rod-pumped mechanisms.

III-5-2-1) Artificial Lift Wells:

a) Downhole Hydraulic Pumps:

In these well configurations, pumps function by moving unadulterated crude oil with a surface pump through a tubing string to power a downhole hydraulic pump. Corrosion management is achieved through the utilization of Corrosion Resistant Alloys (CRAs) and chemical treatments, encompassing corrosion and scale inhibitors along with demulsifiers.

b) Gas-Lift Wells:

In gas-lift wells, pressurized gas (such as nitrogen) is injected into the annulus and then through a gas-lift valve into the tubing. This decrease in density facilitates the flow of oil by reducing the pressure in the reservoir. Gas-lift valves typically employ Corrosion Resistant Alloys (CRAs), while tubing protection is ensured through the use of corrosion inhibitors. These inhibitors are introduced at the surface into the gas-lift stream, safeguarding the tubing surface located above the gas-lift valve. Should corrosion occur on the tubing surface below the valve, corrosion inhibitors can be administered via batch or squeeze treatments. The inhibitor chosen for such applications is typically oil-soluble and water-dispersible.

c) Rod-Pumped Wells:

Corrosion in rod-pumped wells can stem from various sources.

Galvanic corrosion: may arise due to dissimilar metal contact or variances in metallurgical composition resulting from cold working.

Pitting corrosion : might manifest due to stress concentration points induced during pumping activities, such as corrosion triggered by stray currents leaking from surface equipment or cathodic protection (CP) systems.

Oxygen-induced corrosion: may occur on rods stored outdoors or through oxygen infiltration into the wellbore via the annulus. This form of corrosion is often prevalent in the lower section of the well, encompassing the casing, pump, tubing, and lower portion of the rod string.

As corrosion reactions deplete oxygen, the upper portion of the well experiences reduced susceptibility to oxygen-induced corrosion. Under-deposit corrosion could emerge when rods are situated within the wellbore.

CO_2 corrosion is exacerbated by the concurrent presence of oxygen and organic acids. Organic acids exacerbate CO_2 corrosion by eroding the protective iron carbonate scale. H_2S corrosion can result in both metal loss and pitting. The introduction of oxygen can escalate the corrosion rate and potentially catalyze the formation of elemental sulfur through its reaction with iron sulfide. Additionally, the presence of organic acids can intensify corrosion by dissolving the iron sulfide scale and lowering the pH (below 6). The base of the corrosion pit may act as a stress concentrator, potentially leading to cracking. Stress corrosion cracking (SSC) occurs in the presence of H_2S and typically initiates and propagates along grain boundaries [123].

Mechanical damage may also occur due to abrasion between the rod and tubing, potentially resulting in galling, characterized by the removal of significant amounts of metal. Typically, flow velocities in pumped wells are not sufficiently high to significantly impact corrosion. However, elevated velocities are encountered at constricted flow areas, which could elevate corrosion rates. Besides coating, effective control of rod corrosion can be attained by ensuring smooth mechanical operation and implementing a robust corrosion inhibition regimen. Various methods for treating corrosion with inhibitors in a well include batch treatment, continuous treatment, squeeze treatment, tubing displacement, weighted inhibitors, as well as the utilization of sticks or encapsulated inhibitors.

II-5-2-2) Flowing Wells:

In flowing wells, velocities and pressures tend to be higher compared to artificial lift wells. Gas condensate wells, for instance, are a common example, capable of producing gas, hydrocarbons, formation water, acid gases such as CO_2 and H_2S, as well as organic acids. In such scenarios, corrosion is influenced by factors such as the volume of produced formation or condensed water, concentrations of CO_2 and H_2S in water, and the presence of dissolved oxygen, which typically wouldn't be naturally occurring in the production stream unless introduced artificially. The corrosion mechanisms in these wells are predominantly associated with CO_2, H_2S, and O_2.

CO_2-induced corrosion can result in significant pitting, and the presence of organic acids can exacerbate the corrosion process. H_2S-related corrosion, on the other hand, may lead to metal loss, pitting, hydrogen embrittlement, and Stress Corrosion Cracking (SSC). Oxygen, if introduced, can induce pitting in ferritic stainless steels. Typically, gas wells are constructed using low-alloy steels supplemented with coatings and corrosion inhibitors. During wireline operations, the protective film may be compromised, necessitating the application of corrosion inhibition thereafter.

Crucial factors to consider when choosing an inhibitor include minimizing inhibited corrosion and pitting rates. Additionally, significant traits include robust film persistence, non-detrimental impact on the producing formation during squeezing, and minimizing system disturbances that may arise from emulsion stabilization caused by the introduction of corrosion inhibitors. Treatment methods for corrosion inhibition in flowing wells encompass tubing displacement, a variant of batch treatment, continuous injection, and squeezing techniques.

II-5-2-3) Monitoring:

Monitoring is crucial for assessing the corrosiveness of streams both before and after treatments. Common methods for corrosion monitoring include iron count analysis, corrosion coupons, electrical resistance probes, linear polarization instruments, side-stream test loops, and caliper surveys. A recommended industry practice, outlined in NACE SP0775 [123], has been developed for preparing, installing, and interpreting coupons. Other corrosion monitoring methods encompass hydrogen probes, galvanic probes, electromagnetic logging devices, and chemical analysis of produced water for alloying metals like manganese and chromium. Additionally, gathering field data, including failure records, is a valuable source of information.

II-5-3) Corrosion in Secondary Recovery Operations

Secondary recovery, commonly known as waterflooding, often aggravates corrosion issues due to the presence of water. The infrastructure involved in secondary recovery operations encompasses producing wells, production flowlines, separation facilities, tanks, injection pumps, injection lines, and injection/disposal wells.

II-5-3-1) Types of Corrosion Problems in Oil and Gas Industries:

a)-Producing Wells:

In producing wells, dissolved acid gases (H_2S and CO_2) stand out as the primary contributors to corrosion. The presence of organic acids can further intensify H_2S and CO_2 corrosion. Moreover, the increased water content resulting from water-flooding operations can escalate corrosion levels. Water cut may rise to 90% or even higher. During water-flooding, previously "sweet" fields containing only CO_2 may turn "sour" due to the generation of H_2S by sulfate-reducing bacteria (SRB) within the formation. This transformation can lead to corrosion issues associated with H2S, such as pitting beneath SRB deposits and sulfide stress cracking (SSC) in high-strength materials. Additionally, the use of different water sources may lead to the deposition of mineral scales such as $CaCO_3$, $CaSO_4$, or $BaSO_4$, which can exacerbate wear and under-deposit corrosion.

b)-Producing Flow-lines:

Corrosion typically manifests at the bottom of flow-lines when flow rates decrease to a point where water droplets settle, leading to continuous moisture accumulation. Under these circumstances, severe pitting is frequently observed beneath deposits of sludge or scale that accumulate within the flow-lines.

c)-Oil/Water Separation Facilities:

Separation facilities typically employ heat to facilitate the process of separating oil and water. Scale buildup in these facilities can diminish heat transfer, potentially resulting in pronounced under-deposit corrosion due to elevated localized temperatures. In direct-fired heaters, this scenario could lead to creep rupture-type failures if areas beneath deposited scale reach high temperatures. Moreover, if the separation equipment is exposed to the atmosphere, the ingress of oxygen can exacerbate corrosion in the water phase.

d)-Tanks/Water Storage:

The presence of acid gases (CO_2 and H_2S) entrained in produced water contributes to corrosion in water storage tanks. Under-deposit corrosion becomes a significant concern beneath accumulated sludge at the tank bottoms, where conditions are conducive to the growth of sulfate-reducing bacteria (SRB). Without proper protection, tank roofs may fail due to condensation. As water condenses on the roof surface, it absorbs corrosive gases, resulting in pitting corrosion of the tank roof. Additionally, the entry of oxygen accelerates the rate of corrosion significantly in conjunction with acid gases.

e)-Injection Pumps:

Apart from conventional corrosion processes, pumps are susceptible to failure due to cavitation and erosion. When utilizing 304 and 316 stainless steels, there is a risk of failure from chloride stress corrosion cracking (SCC) in produced brines if temperatures exceed 52–65°C (125–150°F). Pumps experience cyclic stresses, which may result in fatigue failures at locations with elevated stress concentrations, such as grooves and areas prone to pitting [123].

f)- Injection Flow-lines and Wells:

The corrosion mechanisms mirror those observed in producing well tubulars and flowlines, primarily involving corrosion induced by H_2S, CO_2, and organic acids. Under-deposit corrosion at the bottom of the lines, as well as corrosion beneath scale and under colonies of sulfate-reducing bacteria (SRB), are common occurrences. Oxygen contamination notably intensifies corrosion, although SRB thrive in anaerobic environments. Nonetheless, corrosion may persist in regions with limited oxygen ingress, such as beneath scales and sludge. The transition of aerobic bacteria slime to anaerobic conditions can facilitate SRB proliferation.

II-5-3-1) Corrosion Mitigation Methods:

a) Producing Wells

Corrosion control strategies for both primary and secondary recovery operations share similarities. Various production methods, such as beam lift, Electric Submersible Pump (ESP), or gas lift, may be employed. The choice of corrosion control approach depends on factors like the production method, well design, and economic considerations. In all types of production wells, corrosion inhibitors are utilized to safeguard tubulars and other downhole equipment. Methods for injecting corrosion inhibitors downhole include squeeze treatments, batch treatments, and continuous treatments. It is essential to select an effective corrosion inhibitor tailored to the specific environmental conditions, whether dominated by CO_2, H_2S, or both.

A corrosion inhibitor package can be designed to possess various properties such as oil-solubility, oil-insolubility, water-dispersibility, or water-solubility. It is essential to conduct tests to ensure that the corrosion inhibitor does not generate stable emulsions. These tests should ideally utilize real well fluids for accurate evaluation. Typically, the dosage of the inhibitor and the treatment frequency are escalated during secondary treatment processes.

The treatment regimen should be tailored according to corrosion monitoring data. A prevalent method of monitoring involves the installation of corrosion coupons in the flowlines near the wellhead. However, downhole corrosion monitoring has posed challenges. To address this, short sucker rods and abbreviated joints of production tubing can be utilized for downhole corrosion monitoring purposes. Guidance on the preparation, installation, and assessment of corrosion coupon data can be found in NACE SP0775 [123].

Inspecting downhole equipment for corrosion is imperative as it yields valuable insights. Corrosion inhibitors may lose effectiveness in areas prone to wear, such as in rod pumps. NACE MR0176 [124] offers guidelines for selecting pump materials.

ESP wells and rod-pumped wells typically undergo similar treatment procedures. However, due to the configuration of ESP systems, inhibitors placed in the annulus may not effectively reach pump components in the production zone above the fluid intake, such as the motor housing.

Corrosion inhibitor solutions are typically atomized into the gas stream to treat gas-lift wells. However, this method only offers protection above the injection valve used for the lift gas. Additional measures are necessary to safeguard regions below the injection valve.

b) Producing Flowlines:

The corrosion inhibitor brought up from downhole typically offers ample protection for the flowlines near the wellhead. Extra safeguarding can be achieved through batch or continuous treatments.

c) Oil/Water Separation Facilities:

To safeguard these facilities, supplementary injection of corrosion inhibitors is employed. In addition to corrosion inhibitors, coatings and cathodic protection (CP) are utilized. Regular removal of scale and debris, particularly from areas with heat transfer surfaces, is essential. High-grade alloys are employed in locations where under-deposit corrosion poses a concern.

d) Tanks/Water Storage:

Tanks can be shielded through internal coatings, cathodic protection (CP), and/or non-metallic liners. Regular tank cleaning is necessary to eliminate accumulated sludge and debris, which can serve as precursors for under-deposit corrosion and sulfate-reducing bacteria (SRB) issues. Tanks are often identified as the primary source of oxygen contamination in injection systems. Typically, inert gas blanketing is employed to prevent oxygen infiltration.

e) Injection Pumps:

To prevent corrosion of injection pumps and related equipment, Corrosion Resistant Alloys (CRAs) are utilized. To deter pitting of such equipment, it is advised to periodically flush them with deaerated and inhibited fresh water.

f) Flowlines and Injection Wells:

Corrosion management for flowlines and injection wells typically involves continuous injection of corrosion inhibitors. Various corrosion damage mechanisms observed in these facilities include CO_2 and H_2S attacks, Microbiologically Influenced Corrosion (MIC), oxygen ingress, and deposition of scale and sludge. The corrosion inhibitors chosen for these applications can either be oil-soluble/water-dispersible or water-soluble chemicals. Additionally, internal coatings and nonmetallic linings are employed.

Injection well tubulars may either be bare steel or internally coated, with corrosion inhibition applied accordingly. In certain instances, nonmetallic liners or tubulars, such as fiber-reinforced plastic (FRP), have been utilized. However, the high cost associated with Corrosion Resistant Alloys (CRAs) hinders their widespread adoption.

To restore injectivity in water injection wells following a decline, inhibited solutions of strong acids are employed. This includes the use of 15 wt% HCl for limestone formations and 12 wt% HCl with 3 wt% HF for sandstone formations. Laboratory assessment of the acid formula is conducted to confirm that the corrosion rate of steel test specimens remains below 245 g/m^2 (0.05 lb/ft^2) [123] .

II-5-4) CO_2 Injection:

After primary and secondary methods of crude oil recovery, such as assisted-lifting and water-flooding, tertiary recovery can be achieved by injecting CO_2. Compared to other gases, injecting CO_2 gas requires lower pressure and readily dissolves in oil, resulting in a potential 10-fold reduction in the viscosity of heavy crudes. Prior to utilization, collected CO_2 undergoes purification and compression, and in certain cases, it is transported via pipelines to the injection site. However, handling CO_2 can lead to the corrosion of carbon steel materials and the dissolution and transportation of scales. These dissolved scales may then redeposit in surface equipment. A comprehensive CO_2 production facility typically includes a CO_2 source well, a wellstream heater and contactor for water removal, a scrubber, compressor, and transportation pipeline.

To safeguard the tubing and wellhead of a CO_2 source well against corrosion, continuous downhole injection of water-soluble filming amine inhibitors is implemented. Alternatively, these wells could be constructed using 316L and 304L stainless steels, or Fiber-Reinforced Plastic (FRP). Dehydration of the steam is carried out to prevent corrosion and hydrate formation at low temperatures. Water and CO_2 may be injected using the same system. In the case of CO_2 injection, it's essential to maintain the water content below 50 ppm to minimize corrosion. For water lines, corrosion mitigation involves cement lining and corrosion inhibition. Corrosion control for tubing materials in oil-producing wells can be achieved through internal coatings and/or inhibition, or by utilizing 9Cr–1Mo and 13%Cr steels. Linear polarization technique, along with weight-loss coupons, iron counts, and caliper surveys, can be employed for corrosion monitoring in producing wells.

II-5-5) Corrosion of Oil and Gas Offshore Production Platforms:

Offshore drilling and production platforms may extend to water depths exceeding 305 meters (1000 feet). Platform corrosion can be categorized into four zones: soil, seawater, splash zone, and marine atmosphere. The splash zone typically experiences severe corrosion, which is managed through coating or sheathing with Monel alloy. Factors influencing seawater corrosiveness include salinity, temperature, oxygen content, velocity, conductivity, and biofouling.

To reduce atmospheric corrosion, coatings are applied. Both coatings and Cathodic Protection (CP) are utilized to manage corrosion of steel structures submerged in seawater. CP typically extends to safeguard the piles submerged in the mud. Additionally, CP proves effective in mitigating corrosion fatigue arising from cyclic stresses induced by environmental factors. Regular inspection of the platform is imperative to uphold structural integrity and ensure personnel safety.

II-5-6) Corrosion of Gathering Systems and Tanks:

The gathering systems encompass all production facilities stretching from the wellhead choke valve to the point of oil and/or gas sales. These facilities include flowlines, trunklines, separation, dehydration, and gas processing, focusing primarily on internal corrosion of gas and oil systems. This corrosion is influenced by various factors such as the composition of produced fluids, temperature, pressure, and flow conditions. A gas stream is classified as sour if the partial pressure of H_2S exceeds 0.34 kPa (0.05 psi_a); otherwise, it is categorized as sweet. In a sweet system, CO_2 corrosion mechanisms are typically assumed to be predominant, which tend to be more severe than H_2S corrosion at lower temperatures.

II-5-6-1) Sweet Gas Corrosion:

Various methods can be employed to mitigate corrosion in sweet gas systems. For flowlines, options include using low-alloy steel with a corrosion allowance, applying internal coatings, or utilizing Corrosion Resistant Alloys (CRAs) such as 316 or duplex stainless steels. However, it's important to monitor these materials for chloride Stress Corrosion Cracking (SCC) at elevated temperatures. Additionally, the use of CRA liners is a common practice. If downhole tubulars in gas wells are protected using corrosion inhibitors, the inhibitive effect will extend to the flowlines. Effective inhibition is ensured by turbulent flow, mixing, and lower temperatures in the flowlines. The corrosion inhibitor can be injected at the surface as well. Batch treatments are necessary when flow velocity is low, while continuous injection may be required for higher velocities.

II-5-6-2) Sour Gas Corrosion:

In sour gas environments, materials must possess resistance to Stress Corrosion Cracking (SSC). Typically, at temperatures commonly found in flowlines, corrosion rates in sour conditions are usually lower than those in sweet conditions. Additionally, sour corrosion is not contingent on flow velocity when protective iron sulfide films are established. An acceptable corrosion rate is expected under the following conditions: (a)
The hydrocarbon liquid volume exceeds 100 barrels per 28,300 m^3 (1 MSCF) of gas. (b) The water content in the liquid phase is below 10% by volume. (c)
Turbulent flow is maintained, facilitating water entrainment in the hydrocarbon phase.

Corrosion inhibition may be required in streams that do not meet the specified criteria. The rationale applied to safeguarding flowlines and facilities handling sweet gas is equally relevant for sour gas streams.

II-5-6-3) Oil Wells Corrosion:

In most crude oil wells, the presence of H_2S, along with oil, facilitates corrosion control more effectively compared to gas systems containing only CO_2. Corrosion becomes problematic when water cuts exceed 30 vol%. While downhole equipment inhibition should sufficiently manage corrosion in flowlines, if oil velocity is low and water droplets settle in the flowlines, alternative corrosion control measures are necessary. These measures may involve pigging to remove accumulated water and deposits, as well as to evenly distribute corrosion inhibitors across the internal surface of the flowline. Typically, low-carbon steel is utilized in constructing gas-oil separation plants (GOSP) and free water knockout systems. Corrosion control for saltwater handling facilities primarily relies on cathodic protection (CP), supplemented by internal organic coatings if temperature conditions allow. Galvanizing is commonly employed for large tank

Chapter III : Corrosion in Midstream Production Operations

III) Corrosion in Midstream Production Operations

The midstream sector encompasses gas plants, liquefied natural gas (LNG) production and regasification facilities, as well as oil and gas pipeline transportation systems. Gas plants play a crucial role in separating hydrocarbons and fluids from raw natural gas to yield high-quality dry natural gas suitable for pipeline transmission. When natural gas is associated with crude oil, it comprises a blend of hydrocarbons like ethane, propane, butane, and pentanes, collectively referred to as "natural gas liquids" (NGL). These NGLs serve as essential feedstock for oil refineries and petrochemical plants, as well as energy sources. Conversely, non-associated natural gas contains varying amounts of water vapor, hydrogen sulfide (H_2S), carbon dioxide (CO_2), helium, nitrogen, and other compounds.

If the gas maintains adequate pressure, it is introduced directly into the pipeline network, or if pressure decreases during the separation process, it undergoes recompression. Gas turbines drive compressors responsible for pressurizing and propelling the natural gas along the pipeline. Compression operations entail additional auxiliary equipment like scrubbers to eliminate liquid droplets and heat exchangers.

LNG liquefaction and regasification plants manage light hydrocarbons, primarily methane, which cannot be condensed into a liquid state at normal temperatures. To transport natural gas across extensive distances, it is liquefied at temperatures as low as -162°C (-260°F) through multiple cooling stages. Specialized insulated tank vessels transport LNG, and upon arrival at the destination, a regasification facility heats the LNG to return it to its gaseous state for distribution through pipelines.

To handle inhibited sweet streams in separation and dehydration facilities, typically, low-alloy steel with corrosion allowance proves adequate. In cases where this level of protection falls short, resorting to 316 stainless steel materials or cladding may become necessary. Sour gas processing facilities, separators, and sweetening systems commonly employ low-alloy steel with corrosion allowance in their construction.

Pipelines constitute the primary element of the midstream sector [125–126], offering an exceptionally efficient method for transporting gases and liquids across extensive distances. Globally, pipeline networks span vast distances, surpassing 3.5×10^6 kilometers.

Pipeline systems facilitate the transportation of a variety of substances including crude oil, multiphase fluids, condensate, liquid petroleum products, NGL, oilfield water, oilfield steam, liquid or dense phase CO_2, and gas. Multiphase fluids encompass a mixture of oil, gas, and water, occurring in either liquid or vapor forms, in various combinations derived from one or more oil wells or recombined from fluids extracted from oil wells.

A pipeline system comprises pipelines, pump stations, and ancillary facilities essential for measuring, processing, storing, gathering, transporting, and distributing fluids within the oil and gas industry. Its components encompass the pipeline structure along with fittings, flanges, valves, bolts, and gaskets. Pipelines sizes range from 6 to 48 in. (15–120 cm) in diameter.

Following installation and prior to operation, newly installed pipelines undergo pressure testing using either gas or liquid. When liquid is utilized, measures are taken to safeguard the medium or the entire piping system against corrosion and other forms of damage. If water serves as the testing medium, corrosion inhibitors, biocides, and oxygen scavengers may be incorporated as additives.

Pipelines exist in offshore or onshore settings, with onshore pipelines being either exposed to the atmosphere or buried underground. They face the risk of external, internal corrosion, or both. Buried transmission and distribution pipelines are primarily shielded from external corrosion through the application of appropriate dielectric coatings along with Cathodic Protection (CP) or Corrosion-Resistant Alloys (CRAs). Similar protective measures, including coatings and CP systems, are employed for submerged piping. These protective systems undergo inspection during and after installation and receive regular maintenance thereafter.

Internal corrosion poses a risk to a pipeline when it houses a corrosive gas phase with a water dew point exceeding the pipeline's operating temperature, or when it contains a liquid phase with free water, combined with other corrosive elements such as O_2, H_2S, CO_2, suspended or dissolved solids, and bacteria. Strategies to mitigate internal pipeline corrosion include [126] :

- ✓ Removing water through scraping or pigging.
- ✓ Treating residual water or dehydrating the pipeline.
- ✓ Introducing environmentally friendly corrosion inhibitors and biocides.
- ✓ Eliminating dissolved gases via chemical or mechanical methods.
- ✓ Employing gas blanketing.

- ✓ Applying internal coating or lining.
- ✓ Incorporating design considerations.

During the design phase of a pipeline, corrosion/erosion allowance is factored into the calculated wall thickness, taking into account the intended service conditions for pressure containment. To validate the efficiency of corrosion control measures, various monitoring techniques are employed, including:

- ✓ Monitoring physical and chemical operating conditions.
- ✓ Utilizing corrosion monitoring devices like weight-loss coupons, corrosion probes, and hydrogen probes.
- ✓ Conducting non-destructive inspections such as ultrasonic thickness measurements.
- ✓ Performing visual inspections of internal surfaces of cut sections from failed pipes.
- ✓ Employing internal electronic inspection equipment.

Comprehensive records of both internal and external corrosion control programs are diligently kept, documenting any incidents of failure and subsequent corrective measures taken. Various factors that could compromise the integrity of existing pipeline systems include mechanical damage, manufacturing defects, corrosion and stress corrosion cracking (SCC), as well as coating damage or deterioration.

One of the primary concerns with pipeline systems containing hydrocarbons is the occurrence of leaks and the subsequent need for leak detection. Hydrocarbon fluid leaks can lead to significant safety hazards, environmental damage, and financial losses. Regular leak-detection surveys and analyses are conducted to mitigate these risks. Additionally, if there are any modifications to the service or a re-rating of piping pressure, it is essential to repeat pressure testing before returning the line to service. These considerations apply specifically to low-temperature pipelines operating within the temperature range of -70°C (-94°F) to 230°C (446°F) [126] .

High-temperature pipelines function at metal temperatures surpassing 230°C (446°F), encompassing systems like steam distribution pipelines. These pipelines are vulnerable to external corrosion beneath insulation and internal corrosion/erosion processes such as caustic embrittlement and oxygen-induced pitting.

III-1) Managing Internal Corrosion within Carbon Steel Oil Pipeline Networks

Globally, carbon steel remains the predominant material choice for pipeline construction. This section focuses on carbon steel pipelines employed in conveying oil, natural gas, and water for both sweet and sour services [127]. Pitting corrosion along the pipeline bottom is identified as the primary corrosion mechanism leading to failures in these systems. Contributing factors to such failures typically include water retention, CO_2, H_2S, bacterial presence, flow velocity, solids accumulation, and oxygen exposure. To address corrosion resulting from these factors, both batch and continuous chemical inhibitor treatments are extensively utilized.

To guarantee the efficacy of these treatments, various corrosion monitoring and inspection methods are utilized. Typical direct and indirect corrosion monitoring techniques comprise:

- ✓ Gas analysis (H_2S and CO_2) and oil analysis.
- ✓ Comprehensive water analysis, including geochemical analysis.
- ✓ Production monitoring, encompassing pressure, temperature, flow rates, and water cut.
- ✓ Corrosion coupons.
- ✓ Bio-spools.
- ✓ Electrochemical monitoring methods, such as electrochemical noise, linear polarization, and electrical resistance.

In terms of inspection, magnetic flux leakage (MFL) stands as the prevailing inline inspection method. Additional techniques encompass:

- ✓ Non-destructive examination (NDE) employing ultrasonic inspection and radiography.
- ✓ Visual inspection utilizing video cameras and borescopes.
- ✓ Destructive examination involving sections cut out from the pipeline.

As for repair and rehabilitation methods, these comprise:

- ✓ Replacing pipe sections.
- ✓ Installing repair sleeves.
- ✓ Installing thermoplastic liners.
- ✓ Replacement with composite or plastic pipeline.
- ✓ In-kind replacement of the entire pipeline.

III-2) Managing Internal Corrosion within Carbon Steel Gas Pipeline Networks

This section focuses on carbon steel pipelines dedicated to gas transportation, where internal corrosion emerges as the primary cause leading to failures and leaks [126]. Pitting corrosion along the pipeline bottom or at the water-gas interface stands as the predominant corrosion mechanism behind such failures. Additionally, less common corrosion mechanisms include top-of-the-line corrosion (also known as vapor-phase corrosion), stress-oriented hydrogen-induced cracking (SSC), and hydrogen-induced cracking (HIC). Standardized test methods and material requirements have been established for SSC and HIC [128–129]. The most prevalent contributing factors to internal corrosion in gas pipelines encompass H_2S, CO_2, oxygen infiltration, bacterial presence, water retention, chlorides, solids accumulation, methanol, polysulfides, elemental sulfur, and critical gas velocity.

Both intermittent and continuous application of corrosion inhibitor chemicals are utilized, requiring a clean pipeline surface for effective adsorption. To ensure the treatment's efficacy, the same corrosion monitoring techniques mentioned earlier are applicable. Analyzing chloride levels in water samples provides insights into the propensity for localized corrosion. Monitoring for hydrogen-related damage in gas lines is crucial, necessitating the use of hydrogen probes. Inspection, repair, and rehabilitation can utilize the techniques detailed previously.

III-2) Managing Internal Corrosion within Carbon Steel Water Pipeline Networks

In this section, we examine carbon steel pipelines handling water, where, akin to oil and gas pipelines, internal corrosion stands as the primary cause of failures and leaks [130]. These carbon steel water pipelines transport either fresh or produced water, encompassing various types such as fresh source water (aquifer water), produced water for waterflooding, disposal water, or steam condensate. Like their counterparts in the oil and gas sectors, uncoated carbon steel pipelines primarily experience failures due to pitting corrosion. Typically, pitting occurs along the pipeline's bottom and, to a lesser extent, at other circumferential positions. Common characteristics observed in these water services include:

- ✓ Presence of water containing corrosive elements such as O_2, $CO_2(aq)$, $H_2S(aq)$, bacteria, chlorides, scale, or solids.
- ✓ Low or intermittent flow conditions where water and deposits can accumulate.

Other forms of failures may stem from inadequate coating systems, linings, or joining methods. In such scenarios, corrosion attacks can intensify due to partially exposed steel surfaces, resulting in a larger cathodic-to-anodic area ratio that accelerates anodic dissolution. The primary contributors to internal corrosion in water pipelines typically include oxygen infiltration and contamination, CO_2(aq), H_2S(aq), microorganisms, scale formation, and solid accumulation. Both intermittent and continuous corrosion inhibitor chemical treatments can be utilized, with batch treatment often proving more effective for enhanced adsorption onto the pipeline steel surface. Similar techniques outlined in the preceding Section , can be applied for corrosion monitoring, inspection, and repair and rehabilitation purposes.

III-3) Chemical Inhibition of Internal Corrosion in Carbon Steel Pipeline Systems

Carbon steel pipelines typically offer the most economical life-cycle option for hydrocarbon services, encompassing various phases such as oil, gas, condensate, and water. Chemical inhibition is incorporated into the corrosion control regimen for carbon steel pipelines, aligning with the calculated corrosion allowance. The initial phase involves assessing the uninhibited corrosion rate under real-world conditions, either through existing data from comparable fields or through laboratory testing and corrosion modeling. Maintaining a repository of both field and laboratory data is standard practice, proving advantageous during the design phase of new pipeline systems.

Before conducting corrosion rate calculations, it's crucial to assess the application limits of corrosion models. These limits may encompass various parameters, such as the acceptable ranges of acid gas partial pressures, temperature, pressure, types of production fluids, CO_2/H_2S ratio assumptions, and corrosion mechanisms.

To streamline the management of extensive pipeline networks, pipelines are categorized into similar corrosion circuits based on their predominant service type. Each corrosion circuit is assigned failure modes, along with necessary corrosion control measures and recommended corrosion monitoring and inspection techniques.

The subsequent step involves selecting a target inhibited corrosion rate, which also relies on the availability of inhibitor systems and the required corrosion allowance. The recommended inhibited corrosion rate values for different temperature ranges in new designs and inhibitor testing programs are as follows [131]:

- ✓ For temperature ranges up to 70°C (104°F), the inhibited corrosion rate should be ≤ 0.05 mm/yr (2 mpy).
- ✓ For temperature ranges >70°C (104°F) and ≤120°C (248°F), the inhibited corrosion rate should be ≤ 0.1 mm/yr (4 mpy).
- ✓ For temperature ranges >120°C (248°F) and ≤150°C (302°F), the inhibited corrosion rate should be ≤ 0.2 mm/yr (8 mpy).
- ✓ For temperature ranges above 150°C (302°F), the inhibited corrosion rate would be determined based on the outcomes of the laboratory testing program.

The subsequent phase involves conducting laboratory evaluations of the proposed corrosion inhibitors, which may be necessitated for any of the following reasons:

- ✓ To ascertain the corrosion inhibition effectiveness of potential chemicals and rank them based on their performance.
- ✓ To examine the influence of service water on inhibitor efficacy.
- ✓ To evaluate the impact of velocity on inhibitor performance, considering that inhibitors are typically applicable to velocities up to 20 m/s (approximately 66 ft/s).
- ✓ To determine whether the oil in the field exhibits natural inhibition effects.
- ✓ To investigate the effect of corrosion product film formation on inhibition.

The inhibitor selection process should encompass the following tasks:

- ❖ Establishing the limits of the service operating window to determine representative inhibitor test conditions.
- ❖ Identifying the required corrosion inhibitor application method(s), such as batch, continuous, squeeze, or a combination thereof.
- ❖ Defining acceptance criteria for the tested inhibitors, which may include:
  - o Absence of localized corrosion attacks, especially at pipeline welds, potentially necessitating the acquisition of test samples from the actual pipeline.
  - o An inhibited general corrosion rate below a predefined target value.
  - o Setting a maximum concentration for the corrosion inhibitor (e.g., 100 or 200 ppm) to achieve the targeted inhibited general corrosion rate.
  - o Ensuring compatibility with other chemicals in the system.
    - ❖ Assessing the impact of corrosion inhibitors on downstream facilities.

- ❖ Establishing test protocols for residual chemical analysis of the selected chemical (typically provided by the chemical manufacturer).
- ❖ Recommending appropriate corrosion monitoring techniques

III-4) Methods to Prevent or Mitigate Corrosion on Buried Pipelines

III-4-1) Internal Corrosion of Pipeline:

Internal corrosion typically doesn't initiate within a pipeline unless there's an electrolyte present to facilitate the corrosion process. Water or aqueous substances (such as glycols from dehydration procedures) are essential to create the necessary electrolyte. Additionally, the presence of other chemicals is usually required; for instance, carbon dioxide (CO_2) for the production of mild organic and inorganic acids, or sulfur for the generation of acidic environments or bacterial growth. Once these corrosive substances are introduced, they can persistently deteriorate the pipeline until they are eliminated or consumed in corrosion reactions.

a) Gas Pipelines

In general ,interior surfaces of gas pipelines are not prone to corrosion when conveying sales-quality dry gas. Nevertheless, natural gas, as extracted from wells, may carry trace amounts of impurities like water, carbon dioxide, and hydrogen sulfide. In instances where water condenses, it can interact with carbon dioxide or hydrogen sulfide to produce an acidic compound, which may accumulate in low points within the pipeline and trigger internal corrosion.

b) Liquid Pipelines:

Likewise, internal corrosion poses a risk in hazardous liquid pipelines conveying corrosive liquids or those containing corrosive impurities. Throughout the length of liquid pipelines, internal corrosion can manifest wherever electrolytes or solid particles settle and moisten the surface, creating an environment conducive to electrolyte accumulation. Figure V-4 illustrates an example of internal corrosion occurring within a liquid pipeline.

Figure III-1: Internal corrosion of a crude oil pipeline (Source http://www.corrosioncost.com/pdf/gasliquid.pdf)

III-4-2) External Corrosion on Buried Pipelines

The predominant approach to prevent or minimize external corrosion on buried pipelines combines cathodic protection with coatings. Cathodic protection entails applying an external current to the pipeline through the soil, effectively superseding local anodes and rendering the entire exposed pipeline surface cathodic. Coatings serve to insulate the steel from the electrolyte, thereby thwarting corrosion.

Relying solely on cathodic protection to combat corrosion wouldn't be feasible due to the considerable amount of current required, which is directly proportional to the exposed surface area. It would be financially impractical to provide cathodic protection for an extensive, uncoated pipeline. Hence, coatings are indispensable to minimize the exposed surface area as much as possible, making them the primary method for corrosion control and prevention. However, coatings alone cannot ensure complete effectiveness, as achieving a flawless coating over an entire pipeline is unattainable. Additionally, some damage during construction and gradual degradation over time are inevitable. Consequently, cathodic protection becomes necessary to thwart corrosion at any breaks (known as holidays) in the coating.

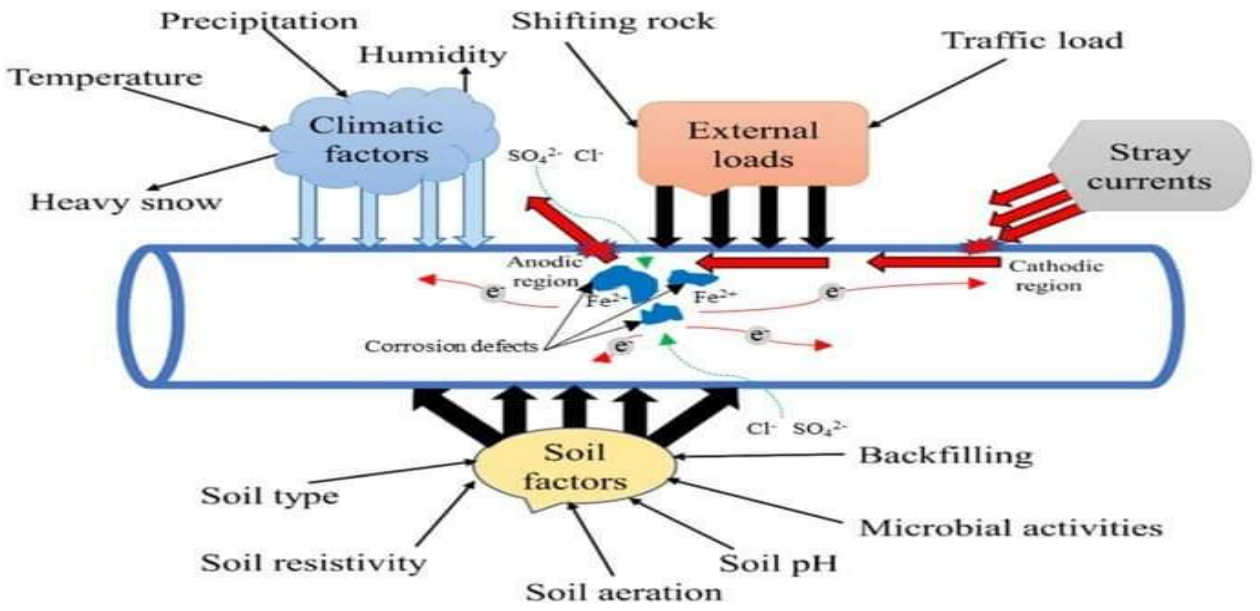


Figure III-2: Buried Pipelines corrosion

a) Coatings: Pipeline coatings have experienced significant technological advancements in the last twenty years. Nowadays, coatings are required to withstand elevated in-service operating temperatures, remain undamaged during construction handling or by soil stress during operation, and offer outstanding corrosion protection. Additionally, coatings need to be user-friendly and applicable either at a mill or in the field.

The adoption of thermal sprayed metallic coatings, such as Aluminum and Zinc, has been increasingly favored in submerged offshore applications, including certain pipelines. This type of coating presents advantages such as affordability combined with superior corrosion protection across various temperatures and conditions. Although thermal sprayed coatings offer some degree of cathodic protection, additional anodes are still necessary, albeit in reduced quantities. While these coatings are still undergoing refinement for widespread pipeline applications, ongoing advancements are anticipated.

b) Cathodic Protection :

As mentioned previously, anodic areas, where corrosion takes place, release current to cathodic areas, where corrosion is inhibited. By directing current to the pipe through the surrounding environment, as depicted in Figure below, it's possible to counteract the anodic currents, effectively

converting the entire pipe into a cathode. Simultaneously, this process generates a favorable alkaline environment at the pipe surface. In seawater and numerous soil types, this alkaline environment prompts the formation of a calcareous deposit, which offers additional protection to the steel.

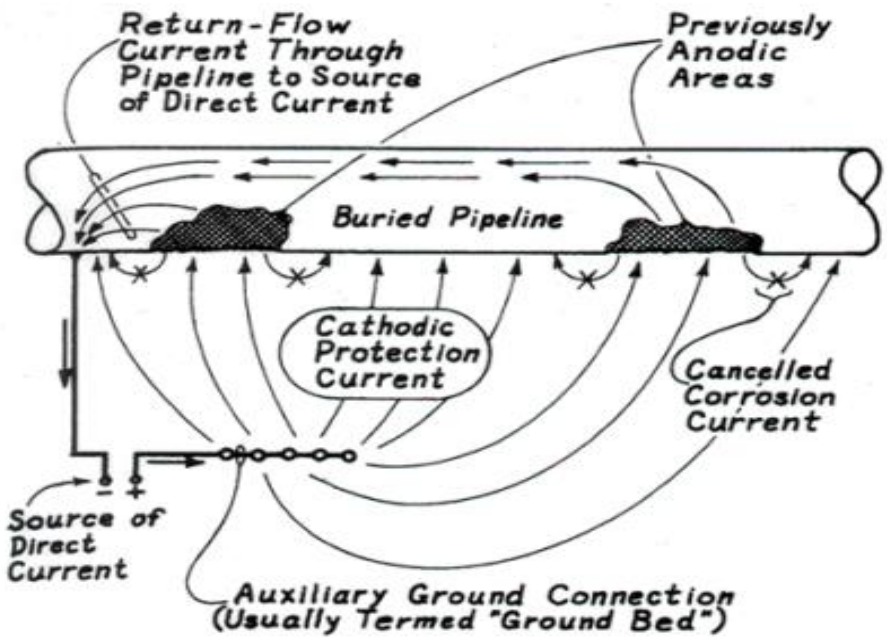


Figure III-3: Basic concept of cathodic protection (Source: Steel Structures Painting Council)

There are two main types of cathodic protection systems: sacrificial anode and impressed current anode. Sacrificial anode systems involve the use of an externally connected sacrificial metal with a higher relative activity value than steel (iron), thus shielding the steel from corrosion. Zinc and magnesium alloys are commonly used as sacrificial metals. The sacrificial anode is connected to the pipeline via a wire and positioned at a distance from the pipeline. Current flows from the anode into the surrounding soil (electrolyte) and is then intercepted by the pipeline at coating holidays. The circuit is completed by a wire connecting the anode to the pipe. The selection and placement of anodes depend on the specific requirements of the pipeline being protected at the site. A pipeline with effective coating and only a few minor coating imperfections requires fewer anodes.

Impressed-current anode systems, as depicted in Figure below, utilize direct-current voltage applied between an anode and the pipeline. These anodes can be crafted from various materials such as graphite, high-silicon cast iron, lead-silver alloys, precious metals, mixed-metal oxides, or

steel. Similar to sacrificial anodes, the selection of shapes, locations, and quantities depends on the geological characteristics of the area and the specific attributes of the pipeline system.

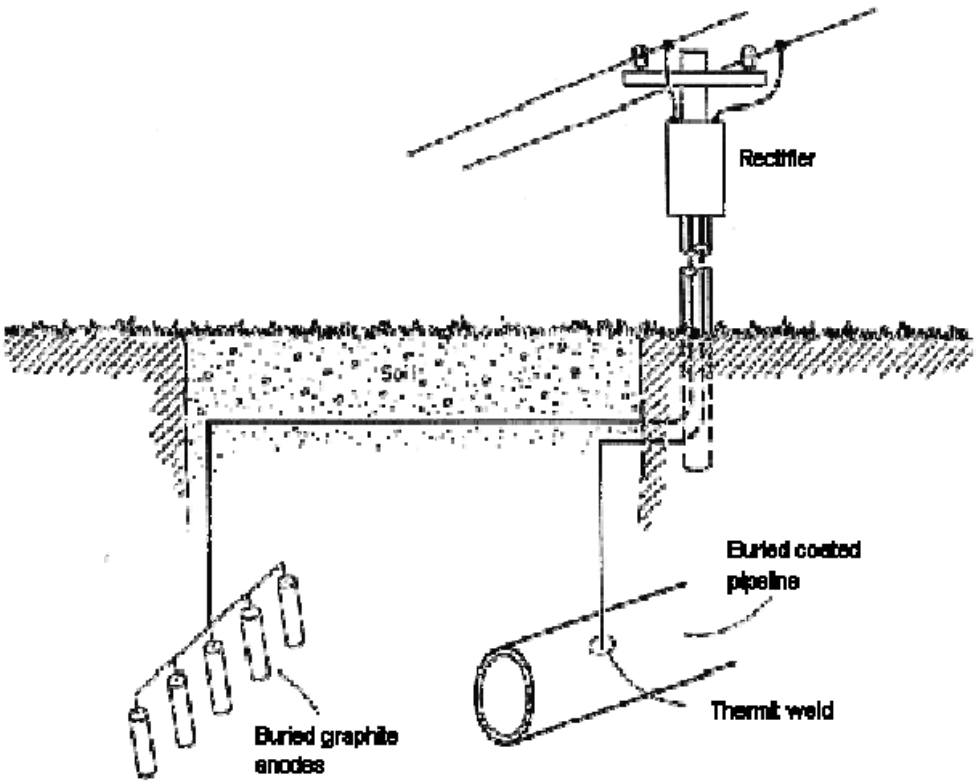


Figure III-4: Impressed-current cathodic protection of a buried pipeline (Source: http://www2.mtec.or.th/th/research/famd/corro/cathodic.htm)

Chapter VI : Corrosion in Downstream Production Operations

IV) Corrosion in Downstream Production Operations

The downstream sector encompasses petroleum refining and petrochemical operations [132]. Refining involves the use of atmospheric and vacuum distillation columns to fractionate crude oil into various cuts or fractions. Refineries are tailored and built according to the characteristics of the crude oil feedstock, whether it be light, medium, or heavy; for instance, an efficient refinery can process any available type of crude. Alongside distillation, refining processes encompass catalytic cracking, hydrocracking, hydrotreating, and reforming. Refinery operations also encompass product distribution terminals that supply bulk customers such as airports and gasoline stations.

Petrochemical plants are responsible for producing a wide array of chemical compounds and are typically categorized into three primary product groups:

- **Olefins,** encompassing ethylene, propylene, and butadiene, serve as the primary feedstocks for plastics (such as polyethylene, polyester, and polyvinylchloride), synthetic rubber, and various industrial chemicals.
- **Aromatics**, including benzene, toluene, and xylenes, are also utilized as feedstocks for plastics (including polyurethane, polystyrene, and acrylates) and find application in the production of synthetic detergents and dyes.
- **Synthesis gas (syngas)** is generated through the steam reforming reaction between methane and steam, yielding a blend of carbon monoxide (CO) and hydrogen. Syngas serves as a precursor for methanol, utilized as a solvent and chemical intermediate, as well as for ammonia (NH_3), used in fertilizer production. Additionally, syngas plays a role in the Fischer–Tropsch process for synthetic diesel production.

Corrosion issues can significantly escalate the operational and maintenance expenses of refineries and petrochemical plants. These expenses primarily stem from scheduled shutdowns for turnaround and inspection (T&I), as well as higher costs incurred during unscheduled shutdowns for repairing corroded piping and equipment. During these periods, the equipment is exposed to the atmosphere, which can introduce air and moisture to the internal components. If not meticulously planned, this exposure may trigger pitting corrosion and stress corrosion cracking (SCC). Rectifying these damages could further prolong the shutdown period. Conversely, facilities equipped with robust

maintenance and corrosion management programs can optimize the shutdown period, resulting in substantial cost savings.

The fluids and streams encountered in refining and petrochemical operations encompass flammable hydrocarbons, toxic or explosive gases, as well as potent acids and caustics. These elements, combined with high temperatures and pressures, pose limitations on the selection of appropriate construction materials.

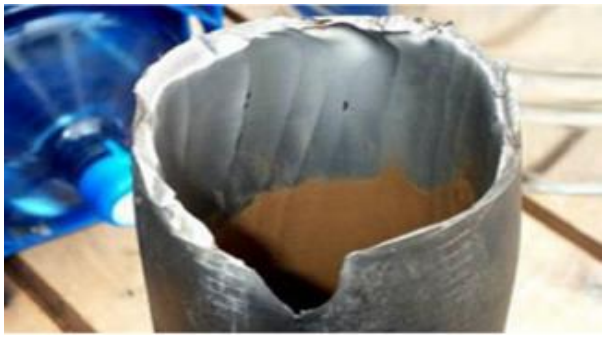


Figure IV.1: Oil and Gas pipeline after being attacked by Stress Corrosion Cracking

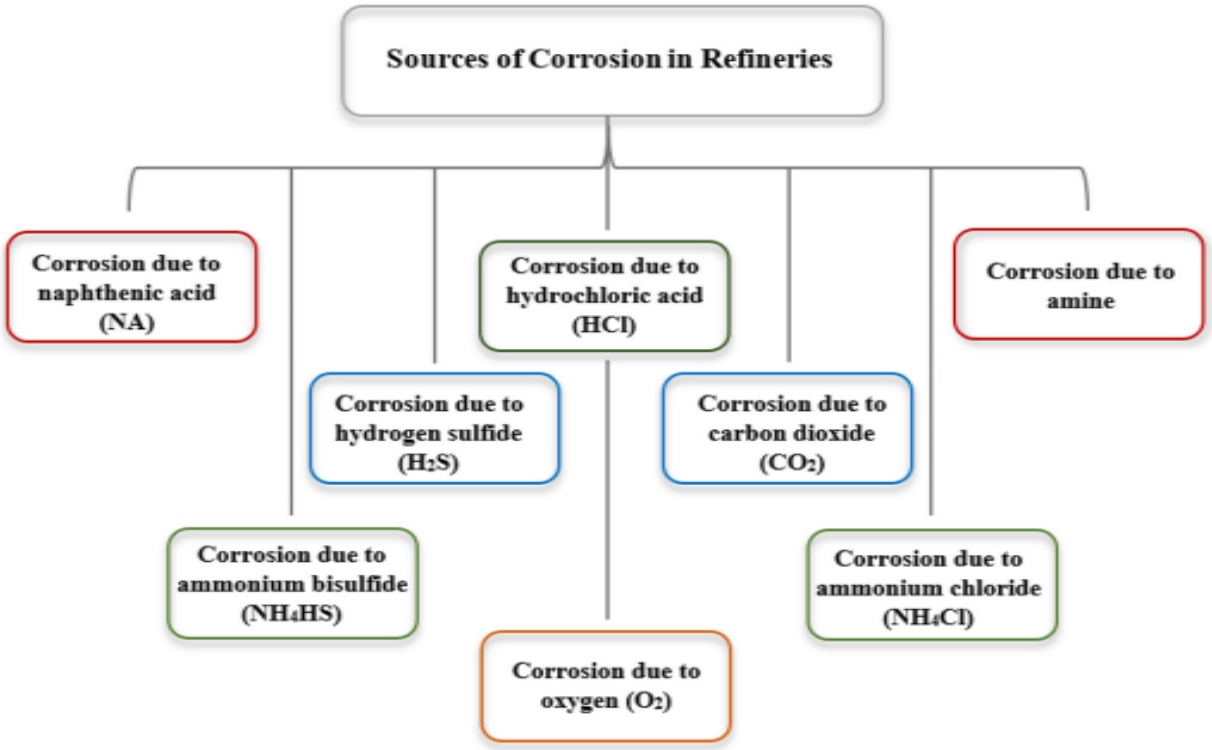


Figure IV-2: Main sources of corrosion in refineries.

IV-1) Materials of Construction

The predominant materials employed in refineries and petrochemical plants are carbon steel components [132]. Within refineries, these components include fractionation towers, separator drums, heat-exchanger shells, storage tanks, and the majority of piping. Low-alloy steels are utilized for applications requiring higher temperatures, such as furnace tubes. In petrochemical plants, stainless steels find extensive use in fabricating linings, tray components for fractionation columns, piping, heat-exchanger tubes, reactor cladding, as well as tubes and tube hangers in furnaces. Cast irons are employed in pumps and valve components due to their high hardness, which mitigates the corrosive effects of high velocities resulting from impingement, erosion, and cavitation.

Copper and aluminum alloys find widespread application in water-cooled condensers and coolers across most refineries. Additionally, aluminum is prominently utilized in vacuum towers due to its resistance to naphthenic acid corrosion. Nickel alloys, renowned for their resistance to potent acids and bases such as sulfuric acid (H_2SO_4), HCl, HF, and caustic solutions, are commonly employed. High-nickel alloys are specifically chosen in scenarios where polythionic acid corrosion is a concern, such as in flare stack tips. Titanium is favored for the tubes of overhead coolers and condensers due to its resilience against attacks by aqueous chlorides, sulfides, and sulfur dioxide (SO_2). Moreover, titanium finds application in systems handling seawater or brackish water, such as in multistage flash distillation processes.

In the event of localized hard zones developing during the welding process of carbon steel, with hardness values surpassing 200 HB (Brinell Hardness Number), there's a risk of stress corrosion cracking (SSC) if the steel comes into contact with aqueous sulfide solutions. To mitigate this risk, heat treatment becomes necessary in such instances.

Compressors and pumps are susceptible to fatigue failures. The majority of equipment fabricated from carbon steel typically operates within a temperature range spanning from ambient to 425°C (800°F). Examples of refinery and petrochemical plant equipment operating at lower temperatures include liquefied-propane storage, ammonia storage, solvent dewaxing units, and facilities handling liquefied petroleum gas (LPG).

Corrosion allowance serves as a provision for general corrosion, characterized by uniform metal loss, and can be easily identified through non-destructive testing (NDT) techniques. To mitigate pitting corrosion, the most effective strategy involves preventing the process conditions that facilitate its occurrence. Stress corrosion cracking (SCC) poses a significant challenge as it is challenging to detect. In industry, materials standards are employed to select appropriate SCC-resistant materials tailored to each specific application [133].

IV-2) Sources of corrosion in refineries and petrochemical plants

In refining operations, corrosion stems from various sources, which can be categorized into three main groups: corrosion caused by crude oil components, corrosion resulting from chemicals used in refining processes, and environmental corrosion [134]. Understanding the corrosion mechanisms at refineries necessitates a grasp of the physicochemical properties of crude oil and natural gas. Crude oil constitutes a fluid blend of hydrocarbons, spanning from volatile to non-volatile compounds. While crude oil isn't inherently corrosive, impurities and constituents containing nitrogen, sulfur, and oxygen, present in crude oil, can induce corrosion [135].

These impurities exist in crude oil in various forms: as liquids, solids, gases, and microorganisms. While the same compounds are present in all crude oils, their proportions differ [121]. Within crude oil, natural gas primarily comprises nitrogen, carbon dioxide (CO_2), hydrogen sulfide (H_2S), and water, all of which can render metals corrosive at any stage of the manufacturing process. The corrosiveness of crude oil is influenced by factors such as total acid number (TAN), total sulfur content, water and salt content, as well as the presence of microorganisms [136].

The combination of these elements leads to corrosion of metallic equipment at various points within the refinery, resulting in different forms of corrosion such as localized pitting corrosion, erosion corrosion, stress corrosion cracking, hydrogen embrittlement, and intergranular corrosion [136]. Nasirpouri et al. [137] examined the localized corrosion damage in steel tube material grade CK45 (AISI 1045) following a brief period of use in an output desalination unit of an oil refinery. The investigation revealed that the primary cause of corrosion on the internal surface of the steel tube material was the presence of a mixture of corrosive gases including H_2S, CO_2, and NA, in proximity to boiled water within the desalination unit.

Comprehending the mechanisms of corrosion degradation, selecting appropriate materials, deploying corrosion control and mitigation techniques, and promptly identifying corrosion sites through inspection programs are all imperative for ensuring the safety of refinery operations.

IV-3) Corrosion in Refineries and Petrochemical Plants

Corrosion in refineries and petrochemical plants can be categorized into two types: low-temperature and high-temperature corrosion. Low-temperature corrosion occurs below approximately 260°C (500°F) in the presence of water, while high-temperature corrosion occurs above this temperature and does not necessitate the presence of water. This discussion will focus solely on low-temperature corrosion, as it pertains to corrosion inhibition [132].

The majority of corrosion issues in refineries and petrochemical plants stem from water, H_2S, HCl, HF, H_2SO_4, and caustic substances. Organic acids like H_3CCOOH also pose challenges in petrochemical plants. During shutdowns or turnarounds, air ingress can lead to corrosion and fouling, particularly in equipment operating under vacuum conditions. Additionally, trace amounts of oxygen may enter with the boiler feedwater, exacerbating corrosion concerns.

Corrosion within refining and/or petrochemical process units may arise from various process chemicals, including H_3CCOOH, aluminum chloride catalysts, organic chloride solvents, HCl, H_2SO_4, caustic, amines, and phenol. Acetic acid, for instance, plays a role in synthesizing organic intermediates like terephthalic acid. Aluminum chloride serves as a catalyst in processes such as butane isomerization, ethylbenzene production, and polybutene production. Organic chlorides function as solvents for removing wax deposits and metal degreasing, often being reintroduced into the crude feed. Both aluminum chloride and organic chlorides can lead to the generation of HCl. HF is occasionally employed in alkylation processes as a substitute for H_2SO_4. Acids, when in contact with water, exhibit corrosive behavior.

Carbon steel finds application in the construction of H_2SO_4 alkylation units, where corrosion resistance is facilitated by a protective iron sulfate ($FeSO_4$) film. To maintain the integrity of the $FeSO_4$ film, flow velocities are limited to below 1.2 m/s (4 ft/s). During alkylation reactions, esters generated as by-products may decompose in reboilers, leading to the production of SO_2. The resulting SO_2 can react with water to form corrosive sulfurous acid (H_2SO_3) in the upper section and overhead system of the fractionation towers.

In refineries and petrochemical plants, caustic is employed to neutralize acids. Caustic corrosion may occur in crude distillation units if a 40 wt% caustic solution is introduced into a hot, desalted crude oil transfer line. Corrosion by amines is prevalent in gas-treating and sulfur recovery units, where corrosion stems from dissolved H_2S or CO_2, as well as from amine degradation products. Carbon steel is commonly used as the primary construction material for amine units. Due to the inefficacy of filming-amine corrosion inhibitors in these scenarios, proprietary oxidizing corrosion inhibitors are utilized.

Phenol (carbolic acid) is utilized in converting heavy distillates into lubricating oils. The corrosiveness of phenol arises from its acidity in the presence of water. To mitigate HF corrosion, filming-amine corrosion inhibitors are injected into the overhead systems of various towers.

Stress corrosion cracking (SCC) may manifest in refining and petrochemical process units in the presence of chlorides, caustic, ammonia, amines, and polythionic acid. Other forms of corrosion observed in refineries and petrochemical plants include corrosion fatigue and erosion-corrosion, which are managed using corrosion inhibitors. Cavitation and impingement represent examples of erosion-corrosion damage mechanisms observed in refinery and petrochemical equipment and units.

V-4) Corrosion Inhibitors in Refinery and Petrochemical Plants

Corrosion management techniques in refinery and petrochemical operations encompass a range of strategies including materials selection, design modifications, process adjustments, corrosion inhibitors [138], protective coatings, and refractory linings. To mitigate corrosion in various process units, minute quantities of filming-amine corrosion inhibitors are introduced. These inhibitors typically exhibit an upper temperature limit of around 175°C (350°F). This threshold is determined by the desorption of the inhibitor film from the metal surface rather than by the thermal degradation of the inhibitor itself. Elevated temperatures accelerate the rate of desorption, surpassing the rate of adsorption of the inhibitor film, rendering it ineffective. These inhibitors primarily safeguard overhead condensing equipment, such as the overhead system of crude unit distillation columns. Surfactants are incorporated into the corrosion inhibitor formulation to enhance water dispersibility.

To establish corrosion-resistant films, higher dosages of inhibitors are initially injected for several days at the onset of treatment. Subsequently, the dosage is tapered down to the lower recommended rate to optimize costs and prevent the formation of emulsions in downstream units resulting from excessive surfactant concentrations. Initially, an increase in foulant materials may be observed in downstream equipment. This is attributed to the dissolution of deposits and corrosion products by the corrosion inhibitor, which had accumulated prior to treatment. Additionally, these inhibitors may induce foaming in amine units.

Traces of oxygen present in the boiler feedwater are eliminated using oxygen scavengers such as hydrazine and sodium sulfite, as mechanical methods would be economically unfeasible.

IV-5) Corrosion Control of Water-Recirculating Systems

Water recirculation systems [139] are employed to extract surplus heat from heat transfer surfaces. These systems come in three variants: once-through, open recirculating, and closed recirculating systems. In once-through systems, cooling water traverses the plant heat exchangers only once. Open recirculating systems involve the reuse of cooling water, with makeup water being introduced to offset evaporative losses. Such systems typically result in water saturated with oxygen. Conversely, closed recirculating systems may accumulate corrosion by-products, leading to fouling of heat transfer equipment.

&- Typical Corrosion Reactions in Water-Recirculating Systems

Corrosion processes within water cooling systems are electrochemical and involve two half-reactions. The anodic oxidation half-reactions for common heat transfer materials, such as Fe, Cu, and Al-based metals, are as follows:

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

$$Cu \rightarrow Cu^{+} + e^{-}$$

$$Al \rightarrow Al^{3+} + 3e^{-}$$

The cathodic reduction half-reactions are:

$$O_2 + 4H^{+} + 4e^{-} \rightarrow 2H_2O$$

(Reduction of oxygen under acidic environment)

$$2H^+ + 2e^- \rightarrow H_2 \uparrow \text{ (Hydrogen evolution)}$$

$$Cu^{2+} + 2e^- \rightarrow Cu \text{ (Metal deposition)}$$

Interactions of the two half-reactions lead to the formation of several corrosion products:

$$Fe^{2+} + 2OH^- \rightarrow Fe(OH)_2$$

$$4Fe(OH)_2 + O_2 + 2H_2O \rightarrow 4Fe(OH)_3$$

$$2Fe(OH)_3 \rightarrow Fe_2O_3 + 3H_2O$$

Hydrated ferric oxide (Fe_2O_3), commonly known as red rust, is frequently encountered. Additionally, protective metal oxides are also generated.

$$2Cu^+ + 2OH^- \rightarrow Cu_2O + H_2O \text{ (Cuprous oxide)}$$

$$Al^{3+} + OH^- \rightarrow Al(OH)_3$$

$$2Al(OH)_3 \rightarrow Al_2O_3 \cdot 3H_2O \text{ (aluminum oxide)}$$

Corrosion forms common in heat transfer equipment are:

- General corrosion or uniform attack
- Galvanic corrosion
- Erosion–corrosion
- Crevice corrosion
- Pitting corrosion

IV-6) Water Corrosivity:

Various factors affect the corrosiveness of water, including dissolved gases, temperature, suspended solids, pH levels, dissolved salts, scaling propensity, fouling deposits, and bacterial presence. Common dissolved gases found in water-recirculating systems include O_2, CO_2, Cl_2, and NH_3. The corrosiveness induced by dissolved oxygen has been addressed earlier. In its absence, however, a uniform protective layer of magnetite (Fe_3O_4) is typically established.

$$3Fe + 4H_2O \rightarrow Fe_3O_4 + 4H_2$$

Increasing the temperature will tend to increase rates of corrosion reactions. This will also increase the formation of protective corrosion products films that will suppress the corrosion rates. Deposition of suspended solids in low-flow areas will lead to crevice corrosion. Normally, the pH in an open recirculating cooling system is 6.5–9; in closed systems the pH is 8.5–9; while in boilers the pH is 11. Carbon steel is sensitive to pH, while copper alloys are not as sensitive due to the formation of a protective cuprous oxide film. Increasing the pH can lead to precipitation of $CaCO_3$ in waters of moderate calcium levels. As dissolved salts increase, the water conductivity increases extending the effects of galvanic corrosion over longer distances. Soft waters are more corrosive than hard waters. Hard waters are high in calcium, which precipitates forming a protective $CaCO_3$ film. Chlorides tend to interfere with the formation of surface passive films leading to pitting attack. Both stainless steels and copper alloys are susceptible to chloride attacks.

The predominant scale encountered in water cooling systems is calcium carbonate ($CaCO_3$), with its deposition being most pronounced in the hottest regions along the heat transfer surfaces. Various indices have been devised to assess the propensity of $CaCO_3$ deposition, which can be managed through the addition of acids or specific chemicals like polymeric inorganic phosphates and poly-carboxylates. Calcium sulfate, typically present as gypsum ($CaSO_4 \cdot 2H_2O$), is another common compound in cooling water systems. Poly-acrylates are effective in controlling this type of scale.

Another scale prevalent in recirculating cooling water systems is calcium phosphate ($Ca_3(PO_4)_2$), which poses challenges in control due to its formation from phosphate additives in chemical treatment. Special copolymers have been employed to tackle this scale. Additionally, silicate scales such as calcium silicate ($CaSiO_3$) and magnesium silicate ($MgSiO_3$) are difficult to remove from heat transfer surfaces. Maintaining the concentration of SiO_2 below 150 mg/l in the recirculating cooling water is the most effective strategy to mitigate these scales.

Fouling deposits encompass a variety of materials suspended in water, which can be managed by maintaining high flow rates (1.5–2.5 m/s, or 5–8 ft/s), utilizing mechanical methods such as coarse filters or side-stream filters, employing chemical treatment, and implementing periodic cleaning procedures.

Biological growth or biofouling has the potential to disrupt water flow and heat transfer within heat exchangers, thereby exacerbating corrosion issues. By impeding heat transfer and flow, biofilms can cause an elevation in the energy required for pumping. Microorganisms commonly encountered in water-recirculating systems include algae, fungi, and bacteria, which can contribute to under-deposit, crevice, and pitting corrosion. Sulfate-reducing bacteria (SRB) can particularly accelerate corrosion rates in carbon steel, reaching levels as high as 2.5 mm/year (100 mpy), with the following general reactions occurring:

$$10H^{+} + SO_4{}^{2-} + 4Fe \rightarrow 4Fe^{2+} + H_2S + 4H_2O \text{ (facilitated by SRB)}$$

$$H_2S + Fe^{2+} \rightarrow FeS + 2H^{+}$$

Additional bacteria commonly found in cooling systems include nitrifying bacteria, iron-depositing bacteria, and slime-forming bacteria. Biocides, encompassing both oxidizing and non-oxidizing agents, are employed to manage bacterial proliferation.

IV-7) Corrosion Control

To manage corrosion in water systems, one can utilize corrosion-resistant alloys (CRAs), protective coatings, or sacrificial anode cathodic protection (CP). An efficient chemical treatment or corrosion inhibitor program should exhibit the following essential characteristics:

- Offer corrosion resistance to all exposed metal surfaces.
- Effectiveness at low concentrations.
- Avoidance of undesirable deposits on metal surfaces.
- Applicability across a broad spectrum of pH, temperature, water quality, and heat flux.
- Prevention of scale formation and dispersal of deposits.
- Minimal to no toxicological effects upon discharge.

In once-through systems, opting for corrosion-resistant alloys (CRAs) may present a more cost-effective solution compared to alternative corrosion control methods. However, for the other two types of water cooling systems—open recirculating and closed recirculating systems—the economic justification for adding corrosion inhibitors could be made. These inhibitors are categorized based on their interaction with the two electrochemical half-reactions of the corrosion process: anodic or cathodic. In addition to anodic and cathodic inhibitors, mixed inhibitors are compounds that inhibit both anodic and cathodic reactions. Anodic inhibitors include chromates,

nitrites, molybdates, and phosphates, while cathodic inhibitors consist of polyphosphates, phosphonates, and multi-component systems like zinc chromate and zinc phosphonates. For copper-based alloys, three cathodic inhibitors belonging to the azole group—mercaptopropylthiazole (MBT), benzotriazole, and tolyltriazole, have been employed.

General Conclusion

General Conclusion

Since the leading role of the oil and gas industry in future energy development, addressing corrosion challenges is crucial. The frequency of maintenance and the cost of repairs, which can reduce operational efficiency, must be carefully considered. Most corrosion-related issues arise in petrochemical refining, where numerous processes and complex equipment are involved. As part of future development strategies, the use of corrosion inhibitors to mitigate or eliminate corrosion remains essential, particularly since galvanic corrosion is prevalent in the industry.

One potential solution involves applying a magnetic field around materials, which influences the electrochemical corrosion process. In this scenario, electrons released from the anode encounter the magnetic field, causing them to spin and remain trapped within the field, thereby reducing the corrosion rate. By preventing the electrons from reaching the environment, the oxidation-reduction reaction is slowed.

Additionally, improving the durability of coatings in harsh environments presents another challenge. The use of smart, self-healing coatings offers a promising approach, as they release functional species to repair coating damage without the need for frequent maintenance and repairs. This is particularly beneficial for the oil and gas sector. Selecting materials and coatings tailored for future processes, environments, and working conditions is critical for ensuring the structural stability of the industry.

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