



REVIEW

# Corrosion challenges in petroleum refinery operations: Sources, mechanisms, mitigation, and future outlook



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## KEYWORDS

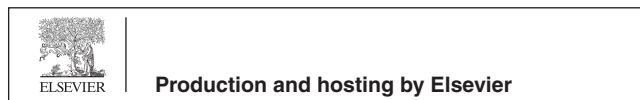
Corrosion;  
Refinery units;  
Naphthenic acid corrosion;  
Cathodic protection;  
Coating;  
Corrosion inhibitors

**Abstract** Corrosion is one of the most important challenges facing petroleum refineries. It has received wide attention in recent decades due to the continued dependence of the global economy on industries based on oil and natural gas. With annual corrosion cost estimated at billions of dollars, suitable corrosion mitigation approaches are required to prevent assets failure due to the menace of corrosion. A vast amount of information on corrosion mitigation in the petroleum refinery is available. However, it is spread in various scientific publications, and gathering such information is critical in building a body of knowledge on the corrosion issues arising from refinery operations. A perusal of the literature reveals that a review focused on corrosion mitigation in the refinery is scarce. So, a comprehensive and up-to-date review of corrosion mitigation in the refinery is timely. In the present review, the corrosion issues at the different units of the refinery are presented. Physicochemical basics in corrosion at refinery units have been considered. In addition, the sources of the corrosion problem and the current mitigations approaches such as engineering design, cathodic protection, the use of corrosion inhibitors and metal coating were discussed. Finally, the existing knowledge gaps were identified, and future research directions were proposed. The review concludes that corrosion in the refinery has not received wide attention in the literature like other corrosion issues in the petroleum industry. The advancement of research in the area of real time and accurate prediction models, collection of sufficient data regarding ammonium bisulfide ( $\text{NH}_4\text{HS}$ ) corrosion in

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the refinery plant, development of novel smart nanomaterials coating, and environmentally friendly high temperature corrosion inhibitors are needed for effective mitigation of refinery corrosion.

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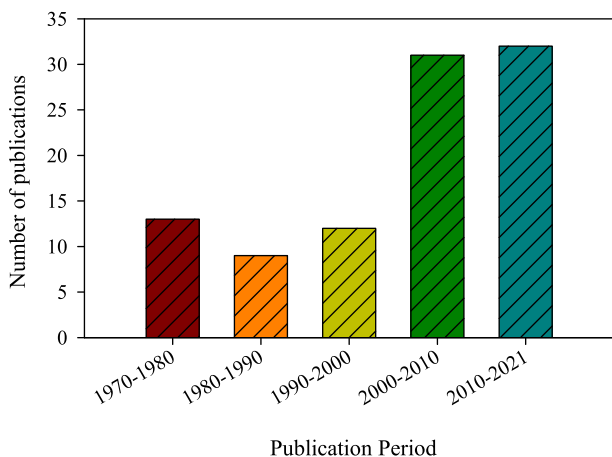
## 1. Introduction

In the global economy, the petroleum refining industry continues to be the focus of interest. Refined petroleum products are crucial to the thriving transportation industries, in addition to being an essential source of energy for households and businesses. Plastics, industrial fabrics, paints, dyes, medications, fertilizers, and a variety of other consumer goods are all made

from refined oil products and by-products like ammonia and sulfur. The presence of this sector in any country is important not only for the country but also for neighboring regions. Despite these benefits, the refining industry is regarded as high-risk because refineries are large and complex sites that carry out numerous operations while operating at high levels of pressure and temperature. This combination of factors makes refineries vulnerable to a variety of corrosion



**Fig. 1** Examples of some refinery's accidents caused by corrosion failure. (a) Golden Eagle Refinery, (b) Richmond Refinery, (c) and (d) Chevron Refinery.



**Fig. 2** Distribution of scientific publications for corrosion in refineries between 1970 and 2021 based on number of publications.

phenomena, which can result in serious accidents that lead to the loss of process fluid containment and have an impact on workers, the environment, and the economy [1].

Corrosion is a major problem that affects most industries worldwide, causing devastating issues to the global economy. Corrosion is the deterioration of a material as a result of its interaction with its surroundings, and it can occur at any point or at any time during petroleum and natural gas processing. Although this definition applies to any material, it is mostly commonly associated with metallic alloys. Furthermore, corrosion processes affect not only the chemical properties of metal or metal alloys, but also cause changes in their physical properties and mechanical behaviors [2]. The global cost of corrosion was estimated in 2013 to be 2.5 trillion US dollars, accounting for 3–4% of global GDP [3]. The United States has the world's largest refining capacity, producing more than 18 million barrels of refined petroleum products per day [4]. According to National Association of Corrosion Engineers (NACE), the annual cost of corrosion in US refineries is more than 3.7 billion dollars [5]. Corrosion is the most serious threat

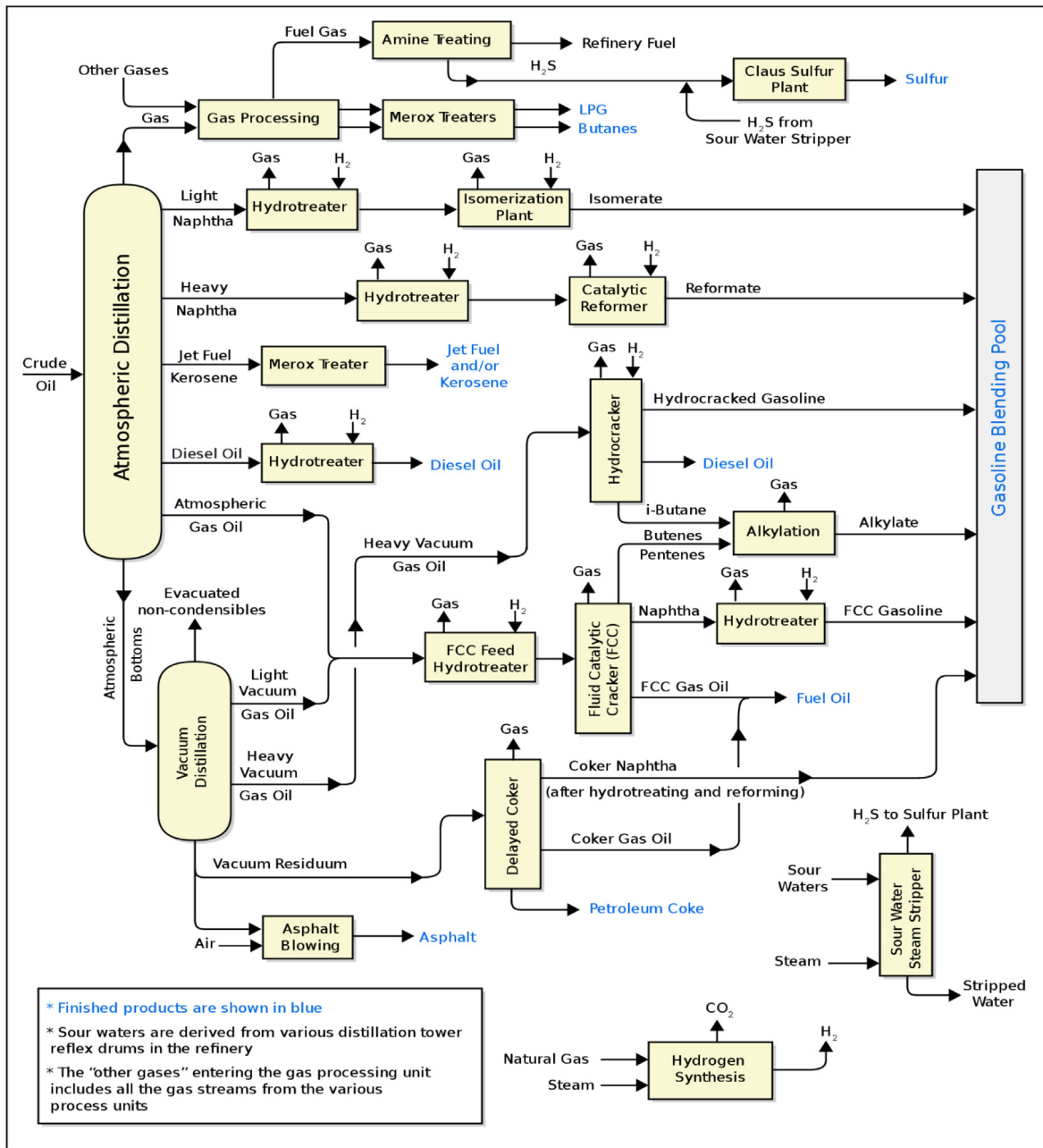


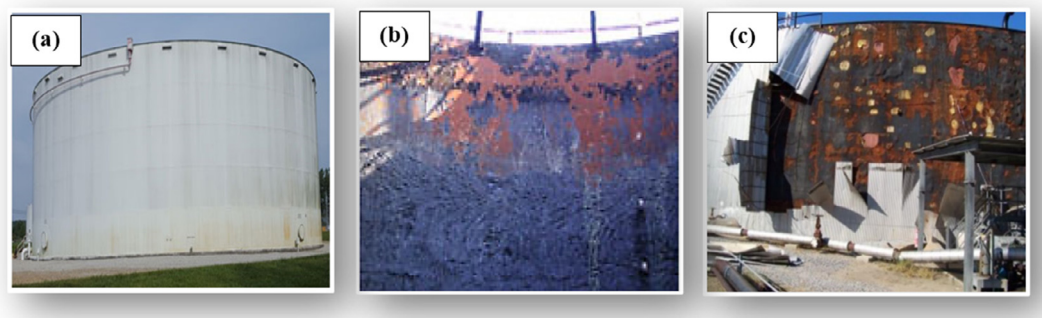
Fig. 3 Process flow diagram of a typical refinery.

to refineries, owing to the presence of aggressive substances on metallic equipment. Different types of corrosion occur in various segments of petroleum refineries depending on the interaction between the material and the environment. In sour water stripping, for example, the presence of hydrogen sulfide ( $H_2S$ ) and ammonia ( $NH_3$ ) creates a hostile environment for the stripping unit, making it vulnerable to multiple types of corrosion [6]. Despite the appearance of corrosion and failure in various places throughout the oil industry, cases of failure in petroleum refineries receive the most attention due to their size and severity [7]. Corrosion can cause disruptions in refinery operations such as unplanned shutdowns, leaks, and product loss [8]. If the proper mitigation methods were not used, it is common to find general corrosion, localized pitting corrosion, hydrogen induced cracking, erosion-corrosion, microbiologi-

cally influenced corrosion (MIC), sulfide stress cracking, stress corrosion cracking (intergranular or transgranular), chloride stress corrosion cracking, corrosion fatigue, high temperature corrosion, hydrogen flaking, corrosion under insulation, metal dusting, carburization, and graphitization throughout the refinery equipment. The extent of the damage caused by catastrophic failures in oil refineries, such as those that occurred in the Golden Eagle Refinery in 2009, the Regina Refinery in 2011, the Richmond Refinery, and the Chevron Refinery in 2012, was all due to corrosion [7]. Fig. 1 depicts some of the refinery accidents caused by corrosion failure and the massive damage that resulted from them.

The refinery is a production facility comprised of multiple processing units that convert raw materials into valuable products. To protect the integrity of these processing units





**Fig. 4** (a) General view of the aboveground storage tank, (b) Inner surface of the tank, (c) Outer surface of the tank (corrosion under insulation) [26].

and avoid product loss, corrosion must be controlled. More corrosion problems in refineries are expected as the demand for highly acidic crude oil rises to maximize profit. Because of its operating environment, the overhead distillation unit is one of the most affected by acidic corrosion. Hydrotreaters are used in a variety of locations throughout the refinery to remove impurities such as sulfur and nitrogen, hence the reason they are subjected to a corrosive environment. Hydrotreaters are susceptible to naphthenic acid (NA) corrosion, which can compromise the integrity of the unit. The process of corrosion mitigation begins with selecting the appropriate material while designing the plant to handle the aggressive substances used in refineries. To reduce the corrosion rate of the exposed metal surface, the appropriate coating, injection of corrosion inhibitors, removal of corrosive components from crude oil, and other methods must be used throughout the plant's life [9].

Researchers have been racing to develop green corrosion inhibitors that are effective at high temperatures, environmentally friendly, non-toxic, and biodegradable. Furthermore, there is a demand for new coating materials that can withstand the harsh environment found in refineries [8]. The development of smart coating will provide several benefits to refineries because it can respond to changes in pH, temperature, and other important factors that are essential for corrosion mitigation [10]. The superhydrophobic coating is another type of coating that has recently gained popularity. This type of coating will provide a high level of resistance to the corrosive environment found in refineries [11].

Fig. 2 presents the number of scientific publications on corrosion in refineries published between 1970 and May 2021. The data was obtained from the Web of Science (WoS) by searching for “corrosion-refinery” in titles and topics. The analysis of this figure clearly reflects the scarcity of research in this area. This presents a challenge for researchers to conduct additional research in this field to gain a better understanding of the causes and types of corrosion that occur in refineries and then identify the best mitigation solutions. This review paper is aimed to provide an up-to-date information on the corrosion problems in the petroleum refinery operations. The sources of corrosion in the refineries, current techniques used to mitigate corrosion, existing knowledge gaps and future research directions are also discussed. Implementing various corrosion mitigation methods could result in a 15–35% reduction in corrosion costs, or up to 875 billion US dollars annually [12].

## 2. Corrosion at the refinery

As shown in Fig. 3, a petroleum refinery is a large industrial complex where crude oil is transformed into usable products such as gasoline, diesel fuel, kerosene, and asphalt using continuous processing units. Refineries typically process 100,000 to 2,000,000 barrels of crude oil per day into petroleum products. Simple refineries use desalter, overhead distillation, fluid catalytic cracking, and hydrotreating units to process crude oil to usable products. Additional units, such as catalytic reforming, alkylation, polymerization, hydrocracking, and coking units, may be used in more complex refineries [9]. Because of its contact with aggressive substances, flow rate, and operating temperature, the majority of the processing units in an oil refinery are vulnerable to common corrosion problems [13].

### 2.1. Storage tanks

Before being transferred to the refinery, crude oil, which is the refinery feedstock, is stored in steel storage tanks. Depending on the working capacity of the plant, storage tanks can be as high as 50 feet and as wide as 100 feet. The majority of storage tanks are built to withstand varying degrees of temperature and pressure. However, corrosion can occur regardless of geometry, size, or function [13]. Their exterior is typically coated with a thermally insulating material. However, if that protective condition fails, the inner walls of storage may corrode (Fig. 4). When  $H_2S$  gas inside the tank reacts with other corrosion products, iron sulfide compound, which can act as an ignition source is formed [9]. Furthermore, allowing water to accumulate at the bottom of storage tanks will cause corrosion.

Microorganisms are unavoidable in crude oil stored in storage tanks. Contamination of crude oil is unavoidable, and it occurs immediately after it is pumped from the reservoir. Aerobic and anaerobic microorganisms both colonize crude oil storage facilities. The generation of their metabolism product causes serious issues such as fuel biodeterioration and corrosion [14,15]. Licina and Nekoksa [16] found that the presence of water and microbes in the storage tank can cause biocorrosion, which can increase the corrosion rate of a material by up to 1000 times. When there is a material leakage, the cost of repair will be high, and the treatment will be extremely difficult. The accumulation of water at the bottom of the storage tank is the primary requirement for microbe development and growth in the tank. Furthermore, according to Jack [17],

microorganisms need water as a source of energy to drive their metabolism, and nutrients provide essential building materials (carbon, nitrogen, phosphorus, and trace metals, etc.) for cell renewal and growth, which is readily available at the bottom of the tank.

Microbiologically influenced corrosion refers to corrosion caused by bacteria (MIC). According to Licina and Nekoksa [16], one of the factors enhancing MIC on pipelines and storage tanks is a complex action of various bacteria inside the bio-film structure formed on the metals' surface. Lane [18] noticed that biofilms are resistant to many chemicals due to their protective membrane and have the ability to break down a wide range of compounds. It is also significantly more resistant to biocides (chemicals used to kill microorganisms) than planktonic organisms. Some bacteria can even metabolize corrosion inhibitors like aliphatic amines and nitrites, reducing the inhibitor's ability to control corrosion. Metal corrosion-related metabolic reactions of microorganisms involving the products of sulfide, acid, ammonia, metal deposition, and metal oxidation and reduction.

To control corrosion in storage tanks, a liner on the internal floor and walls are included to prevent contact between metal shells and any accumulated water or other corrosive sediments.

## 2.2. Desalting unit

Small amounts of inorganic salts dissolved in water, such as magnesium, chloride, and calcium chloride ( $\text{CaCl}_2$ ), are present in crude oil sent to the refinery. Desalters remove inorganics from crude oil to reduce fouling and corrosion in other processing units [19]. Desalting can be accomplished through two methods: chemical desalting and electrical desalting. In chemical desalting, water and demulsifiers are added to the crude, heated to attach salts and other impurities to the water, and then held in the tank to settle out. In electrical desalting, high voltage is applied to concentrate the suspended water particles at the bottom of the tank [13]. In both methods, chemicals such as ammonia are often used to reduce the impact of corrosion. The majority of desalting chemicals are either demulsifiers or used to adjust the pH of the wastewater [19].

The constituents of crude oil containing NA have emulsification properties. As the pH of the water inside the desalter rises, the sodium naphthenates will form stable emulsions [20]. To combat the role sodium naphthenates play in desalter upsets, it is critical to maintain an acidic effluent desalter water. Many factors can impair desalter performance, including high crude density and viscosity, which makes separation more difficult, and high salt content [19]. When a high NA concentration combines with asphaltene precipitation, the likelihood of forming a rag layer (stable water in an oil emulsion), which can lead to fouling increases [13].

## 2.3. Crude oil distillation

The crude oil distillation unit separates raw crude oil into fractions of useful products, which are then processed further at other units in the refinery. The crude oil distillation system is the beating heart of any oil refinery. A heat exchanger network, pre-flash drum, atmospheric distillation, and vacuum distillation are all common components of a distillation system

[21,22]. A distillation column has several perforated trays that allow vapors to rise to the top of the column. High temperatures are required to separate light hydrocarbons from heavier ones. Heavy hydrocarbons with higher boiling points will be collected as liquids at the column's bottom. Lower boiling point hydrocarbon products such as kerosene and gasoline are collected at successively higher points on the tower [21].

Reduced pressure is required to prevent thermal cracking when further distilling the crude from the atmospheric tower at high temperature, hence the use for vacuum distillation towers. The principle of vacuum distillation is similar to that of atmospheric distillation, with the exception that a larger diameter column is used to maintain vapor velocities at low pressure. However, some vacuum towers differ from atmospheric towers in that random packing and demister pads are used instead of trays [9]. The vacuum heater tubes, vacuum tower transfer lines, lining, trays, packing, oil pumps, vacuum tower bottoms line, and heat exchangers are all vulnerable to NA corrosion in the vacuum distillation unit [13].

Despite an efficient desalting operation, corrosion agents can still be passed over from the desalter, causing serious corrosion problems to the units [21]. The desalter brine and aqueous condensate from the main fractioning column's overhead reflux drums, as well as, the water from the vacuum distillation unit, contain some hydrogen sulfide [13]. Steam is injected into the distillation unit and condenses in the upper part of the unit to improve fractionation. Stress corrosion cracking will appear in the top section of the tower and the condenser if hydrogen sulfide is dissolved in the condensate [21].

In both atmospheric and vacuum distillation columns, sulfur and NA corrosion occur at similar temperatures. NA corrosion occurs primarily in the high-velocity area of a crude distillation unit at temperatures ranging from 220 to 400 °C. However, as the temperature rises above 400 °C, the corrosivity of the NA decreases [23]. Many areas of the crude distillation unit can be vulnerable to NA corrosion. These areas are those that are exposed to corrosive levels of NA in hydrocarbon fluids, operate at temperatures ranging from 220 to 400 °C, and are built with metallurgy that is not generally thought to be resistant to NA corrosion attack [13]. To protect the distillation unit from elevated temperatures, HCl,  $\text{H}_2\text{S}$ , and NA, various types of stainless steel, such as 316SS and 317SS, are used in its construction [20].

The presence of hydrogen chloride (HCl) is another common cause of corrosion in the crude distillation unit. At temperatures above 120 °C, hydrogen chloride can be formed by the decomposition of sodium chloride (NaCl), calcium chloride ( $\text{CaCl}_2$ ), and magnesium chloride ( $\text{MgCl}_2$ ). At this temperature, the water vapor in the overhead system condenses to water, which absorbs the hydrogen chloride to produce hydrochloric acid. Water can absorb ammonia, which can then combine with hydrogen chloride to form ammonium chloride ( $\text{NH}_4\text{Cl}$ ) [13]. These salts are extremely acidic and can form a layer on the surface. Pitting corrosion can occur when water allows these acid salts to form. Fig. 5 depicts various types of crude distillation unit corrosion.

## 2.4. Hydrotreating units

Impurities such as sulfur and nitrogen must be removed from petroleum refineries to maintain the stability and reduce the

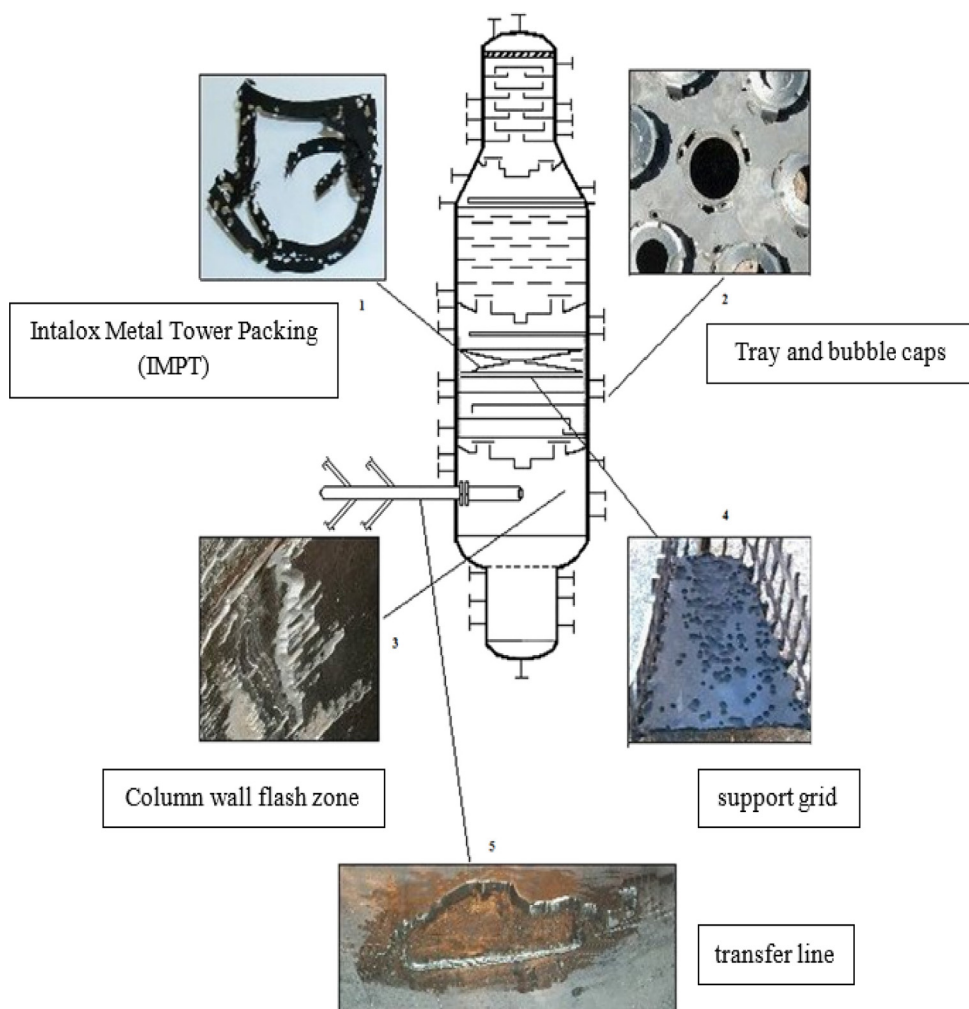


Fig. 5 Different type of crude distillation unit corrosion [34].

corrosivity of fractions. If these impurities are not removed, they will have a negative impact on the refinery's equipment, catalysts, and the quality of the finished product [20]. Hydrotreating units are found throughout the refinery. The hydrotreating unit can be classified as distillate hydrotreating, jet fuel hydrotreating, or catalytic feed hydrotreating, depending on the stream being treated [20,22]. All hydrotreating units, however, have the same basic objective: to remove chemically bonded sulfur from hydrocarbon. In hydrotreating for sulfur removal operations, hydrogen reacts with sulfur and nitrogen at high temperature (315–420 °C) and pressures (up to 1000 psi), producing  $H_2S$  and  $NH_3$ . After cooling, the product exits the reactor and enters a liquid/gas separator. Finally, using a gas treating unit,  $H_2S$  is removed from the rich hydrogen sulfide gas stream [13].

In the hydrotreating unit, gaseous streams containing  $H_2S$ ,  $NH_3$ , and  $HCl$  can precipitate acid salts such as  $NH_4Cl$  and ammonium bisulfide ( $NH_4HS$ ). The main issue with hydrotreating units and their ability to handle high acid crude is directly related to metallurgy. Carbon steel, low alloy steels, 300 series SS, Alloys 400, duplex SS, Alloys 625 and C276 and titanium are the materials most susceptible to acid corrosion when used to construct hydrotreating units [24].

The presence of  $H_2S/NH_4HS$  in low temperature operating sites causes hydrogen embrittlement in alloyed steel, which

occurs concurrently with  $FeS$  formation [25]. Furthermore, due to the presence of a high concentration of  $H_2S$ , sulfuric acid, and hydrogen gas, the components of the hydrotreatment unit may experience stress corrosion cracking [13]. Carbon steel is highly corrosive to concentrated  $NH_4HS$  [25]. Because  $NH_4HS$  is highly soluble in water, wash water will be added to the system to reduce the  $NH_4HS$  corrosion rate. However, if the flow velocity of the  $NH_4HS$  is increased, the corrosion may accelerate.

### 2.5. Fluid catalytic cracking unit

In contrast to crude unit distillation, which uses physical separation processes, fluid catalytic cracking is a chemical separation process that uses a catalyst to break heavy gas oil into smaller hydrocarbons under high temperature and pressure. The vacuum distillation unit provides the majority of the heavy gas oil feedstock for the catalytic cracking unit. A typical catalytic cracking unit is divided into four sections: the reaction section, the catalyst, the regenerators, and the fractionation column [9,22].

In a typical fluid catalytic cracking unit process, a hydrocarbon stream is mixed with hot catalyst as it enters the riser leading to the reactor. The charge is then combined with the

**Table 1** An Overview of Refinery Units with their Corrosion Susceptibility [9].

Unit	Temperature (°C)	Corrosion Type	Primarily effect
Desalter	50	Localized pitting corrosion.	Salt
Atmospheric Distillation	371	Localized pitting corrosion, and flow-induced localized corrosion	Sulfur, Naphthenic acid, HCl
Vacuum Distillation	400	Localized pitting corrosion	Sulfur, Naphthenic acid, HCl
Catalytic cracking	600	Intergranular corrosion, SCC, erosion-corrosion	
Hydrotreater	670	SCC, Hydrogen embrittlement, Pitting	H <sub>2</sub> S, Ammonium salts, polythionic acid
Sour water stripper	245	Localized pitting corrosion, erosion-corrosion	H <sub>2</sub> S, flow velocity, chloride

SCC: Stress Corrosion Cracking.

recycle stream within the riser and raised to 485–540 °C temperature range by the hot catalyst. The charge is cracked at 10–30 psi as it travels up the riser. The cracking process is repeated until the oil vapor has been separated from the catalyst. The product is then charged to a fractioning column, where it is fractionated [9].

The majority of cracking units are made of alloys that are resistant to sulfidic acidic corrosion. However, if the total acid number (TAN) in the feed is significantly increased, the metal becomes vulnerable to NA corrosion. The heater temperature, fortunately, causes the NA to decompose, concentrating the risk of corrosion in the feed area. As it is a sulfurizing environment, the temperature at the reactor's entry side ranges between 495 and 525 °C, making it vulnerable to acidic corrosion [13]. Furthermore, carbon steel is widely used in the components and piping connecting the units, which is prone to erosion-corrosion and pitting as a result of the fluid catalyst's motion. Once the feedstock is mixed with the catalyst, an acidic attack on the NA is a concern. As a result, a thorough examination of the unit metallurgy and configuration is required to ensure that NA corrosion is kept under control. Table 1 provides an overview of refinery units and their corrosion susceptibility [9].

### 3. Physicochemical basics of corrosion at refinery units

Corrosion of metallic equipment and structures in refinery units occurs in a variety of environments and phases under different conditions. Corrosion in refineries and petrochemical units can be classified into the following groups [26]:

- Low temperature ( $T < 100$  °C) corrosion in the presence of electrolytes, usually aqueous solutions of electrolytes and water, such as dissolved corrosive gases (H<sub>2</sub>S, HCl, and NH<sub>3</sub>), or dissolved salts (NaCl and Na<sub>2</sub>SO<sub>4</sub>);

- High temperature ( $T > 200$  °C) corrosion by non-electrolytes (usually gaseous H<sub>2</sub> and H<sub>2</sub>S, NA corrosion, oxidation by oxygen in furnaces, hot ash corrosion);
- Intermediate temperature ( $100$  °C  $< T < 200$  °C) corrosion which can occur either in the presence of electrolytes or non-electrolytes depending on substances and conditions;
- Corrosion in natural environments: soil, atmosphere, and natural waters as a result of constructions and equipment at oil refineries and petrochemical plants coming into contact with them;
- Specific corrosion phenomena: corrosion under thermal insulation, acid dew point corrosion, steam condensate corrosion, and boiler feed water corrosion.

#### 3.1. Low-temperature corrosion

Low-temperature ( $T < 100$  °C) corrosion occurs through an electrochemical mechanism, with corrosion occurring in acid, neutral, and alkali aqueous solutions. This category includes corrosion in aqueous amine solutions (in amine treating units). The majority of low-temperature corrosion problems in oil refineries and petrochemical plants are caused by inorganic compounds rather than processed hydrocarbons, such as H<sub>2</sub>O, HCl, H<sub>2</sub>S, NH<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub>, NaOH, Na<sub>2</sub>CO<sub>3</sub>, and dissolved

**Table 2** Crude oil constituents [26].

Constituent	Chemical type
Hydrocarbons:	
Paraffinic (Alkanes)	Straight chain; branched chain
Naphthenic Aromatic	Alkyl cyclopentanes; alkyl cyclohexanes Alkyl benzenes; aromatic naphthenic fluorenes; polynuclear aromatics
Dissolved gases	Nitrogen (N <sub>2</sub> ); carbon dioxide (CO <sub>2</sub> )
Sulfur compounds	Elemental sulfur (S <sub>8</sub> ), hydrogen sulfide (H <sub>2</sub> S) <sup>a</sup> , mercaptans; organic sulfides, disulfides and polysulfides; thiophenes and benzothiophenes; sulfones
Organic nitrogen compounds	Pyridine, quinoline
Organic oxygen compounds	Carboxylic acids (including naphthenic acids) <sup>b</sup> , alcohols, phenols <sup>b</sup> , aldehydes, ketones, esters, ethers, oxyacids
Organic metallic compounds	Porphyryns
Colloidal particles	Asphaltenes; resins; paraffin waxes
Surfactants	Sulfonic acids, sulfonates, sodium naphthenates
Metals	Vanadium, nickel <sup>c</sup> , iron <sup>c</sup> , aluminum, sodium, potassium, calcium, copper
Water (S & W <sup>d</sup> or BS & W <sup>d,c</sup> )	Fresh or saline
Solids	Sand, dirt, silt, soil dust, mud, corrosion products (metals' oxides, sulfides, salts)

<sup>a</sup> Hydrogen sulfide is present as dissolved gas.

<sup>b</sup> They are surfactants.

<sup>c</sup> They are present in porphyryns.

<sup>d</sup> S&W—sediment and water; as previously called BS&W—bottoms sediment and water.

<sup>e</sup> Microorganisms can be present in crude oils.



oxygen. Organic acids that are contained or sometimes formed in hydrocarbons, corrosion in the overhead of distillation systems, and amines used as neutralizers may all promote low-temperature corrosion [26,27].

There are two principal sources of compounds causing corrosion: contaminants contained in crude oil (such as air, water, HCl, H<sub>2</sub>S, and NH<sub>3</sub>) and process chemicals including solvents, neutralizers, and catalysts. Long-term sulfolane use can cause the formation of destructive corrosive products (acids) at petrochemical plants. Additionally, the use of aqueous solutions of amines for the absorption of acid gases CO<sub>2</sub> and H<sub>2</sub>S at amine treating units can result in the formation of corrosive heat stable amine salts. Temperature, pressure, flow regime, and media are the primary factors influencing low-temperature corrosion rate and intensity. Changes in conditions and process parameters can also have an impact on all of these factors [26,27].

### 3.2. High-temperature corrosion

High-temperature ( $T > 200\text{ }^{\circ}\text{C}$ ) corrosion relates to the second major group of corrosion phenomena that occur when exposed

to non-electrolytes: sulfidic corrosion (oxidation by S<sub>8</sub>, H<sub>2</sub>S, and some other sulfur compounds), hydrogen attack, NA corrosion, carburization, hot ash (fuel ash or salt deposit) corrosion, oxidation (by oxygen gas), and “metal dusting”. A non-electrochemical mechanism is realized in corrosion phenomena of this type. Non-electrolytes are high-temperature gases (H<sub>2</sub>S, H<sub>2</sub>, O<sub>2</sub>, and hydrocarbons) or liquids (NA or S<sub>8</sub>). These corrosive components are occasionally found together. In these cases, sulfidic corrosion should be investigated in the presence of H<sub>2</sub>, and NA corrosion should be investigated in the presence of H<sub>2</sub>S. Such circumstances complicate the corrosion mechanism and, depending on the circumstances, can either accelerate or slow corrosion [26].

The importance of high-temperature corrosion problems in refineries cannot be overstated. Failures in equipment can have serious consequences because high-temperature processes typically involve high pressures as well. When there is a rupture in a hydrocarbon stream, there is always the risk of fire and noxious substance emissions. They can result in unpredicted destruction of equipment and structures, but more importantly, injury and even death to personnel as well as severe environmental damage. On a more positive note, high-

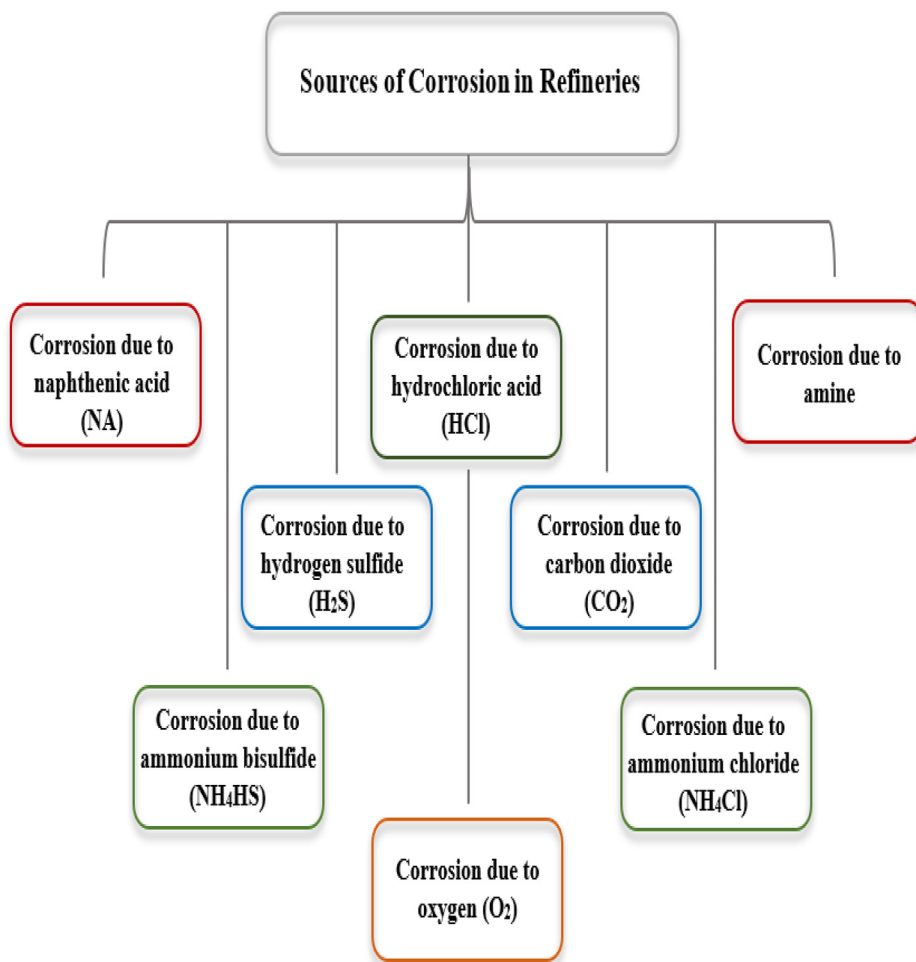


Fig. 6 The main sources of corrosion in refineries.

**Table 3** Examples of aromatic and nonaromatic naphthenic acid structures [31].

Key	Structure
Acyclic $Z = 0$	$\text{CH}_3(\text{CH}_2)_m\text{CO}_2\text{H}$
Monocyclic $Z = -2$	
Bicyclic $Z = -4$	
Tricyclic $Z = -6$	

R: is a small aliphatic group such as methyl; Z is loss of hydrogen atoms due to ring formation; m is the number of  $\text{CH}_2$  units.

temperature refinery corrosion is primarily caused by various sulfur compounds originating from crude oil. Extensive research has been conducted over the years to determine the mechanism of various forms of high-temperature sulfide corrosion. Corrosion rate correlations are available; therefore, equipment life can be predicted with some degree of reliability [27].

#### 4. Sources of corrosion in refineries

There are numerous sources of corrosion in refining operations, but they can be divided in three groups: corrosion from crude oil components, corrosion from chemicals used in refining processes, and environmental corrosion [23]. To comprehend the corrosion phenomena at refineries, it is necessary to first comprehend the physicochemical properties of crude oil and natural gas. Crude oil is a liquid mixture of hydrocarbons ranging from a volatile hydrocarbon compound to a non-volatile hydrocarbon compound. Although crude oil is not corrosive in and of itself, impurities and components containing nitrogen, sulfur, and oxygen can be found in crude oil and can be corrosive [28]. These impurities can be found in crude oil as liquids, solids, gases, and microorganisms. The same compounds are present in all crude oils, but in different proportions [5]. Natural gas in crude oil is primarily a mixture of nitrogen, carbon dioxide ( $\text{CO}_2$ ), hydrogen sulfide ( $\text{H}_2\text{S}$ ), and water. These gases can make the metal corrosive at any point in the manufacturing process. The total acid number (TAN), total sulfur content, water, salt content, and microorganisms are all factors that influence the corrosiveness of crude oil [29]. Table 2 shows the crude oil constituents and their chemical type [26]. The combination of these components will corrode metallic equipment at various locations throughout the refinery, resulting in various types of corrosion such as localized pitting corrosion, erosion corrosion, stress corrosion cracking, hydrogen embrittlement, and intergranular corrosion [29]. Nasirpouri et al., [30] investigated the localized corrosion damage in the steel tube material grade CK45 (AISI 1045) after a short period of service in an output desalination unit of an oil refinery industry. The study found that the presence of mixed corrosive gases of  $\text{H}_2\text{S}$ ,  $\text{CO}_2$ , and NA adjacent to boiled water in the desalination unit was the primary cause of corrosion in the internal surface of the steel tube material.

Understanding the corrosion degrading mechanism, making proper material selection, implementing corrosion control and mitigation methods, and early detection of corrosion sites using inspection programs are all necessary for safe refinery operations. The main sources of corrosion common in refineries are depicted in Fig. 6, and the following section will discuss some of the corrosion mechanisms that are commonly encountered in refinery operations.

##### 4.1. Corrosion due to naphthenic acid (NA)

Among the most typical corrosive agents in crude oil, NA proved to be one of the most aggressive, with numerous effects

**Table 4** Forms of corrosion in refinery units due to naphthenic acid [26].

Corrosion Form	Refinery Unit	Remarks
Shallow, deep, large, and round pits	Inside the vacuum and atmospheric distillation columns (wall shell, trays, and bubble caps)	This form occurs as a result of boiling and condensation of NA on metal surface and occurs primarily in liquid and mixed liquid/vapor streams
Thinning of metal and uniform etching	Stainless steel cladding on the shell of the vacuum distillation column	
Grooves, striations, and deep localized attack	In transmission lines and heating tubes (furnace)	Severe NA corrosion appears in bends, elbows, tees, and pumps when the flow is turbulent
General corrosion	Carbon steel trays and bubble caps	This form occurs if using continuous change of acid (low sulfur) and non-acidic (high sulfur) crudes in the refinery

NA: naphthenic acid.



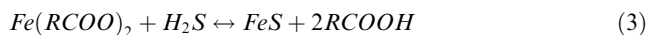
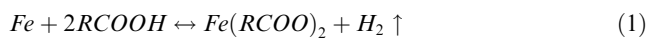
Fig. 7 Some failure parts caused by naphthenic acid corrosion (NA) [33,39].

on refinery equipment. To address the problem of NA corrosion, it is necessary to first understand the structure and behavior of such chemicals. NA are aliphatic acids with zero to three cycloalkene rings, an alkyne chain, and a terminal carboxylic acid group, according to the literature. The general formula of NA is  $C_nH_{2n+z}O_2$ , where  $n$  is the number of carbon and  $z$  is the hydrogen deficiency [7,31–33]. The varying NA structure is related to the oil's biodegradation, which occurs as the oil field matures [9]. Table 3 contains examples of aromatic and non-aromatic NA structures [31].

At room temperature, naphthalene acids are not corrosive. However, it becomes more aggressive at temperatures where refining takes place. NA becomes corrosive to carbon steel at temperatures ranging from 200 to 220 °C, respectively and

reaches its peak activity at 350 °C. The corrosivity of NA is minimal above 400 °C due to its decomposition at high temperatures. The corrosivity of NA is related to its TAN, which is a measure of acidity and is expressed in milligrams KOH required to neutralize the acids in one gram of crude oil [34]. Crude oil with a TAN value greater than 0.5 is thought to be corrosive when processed in a fractional distillation column [35], whereas crude oil with a TAN value greater than 1.5 is thought to be corrosive to vacuum distillation towers [34,35]. It was discovered that NA corrosion only occurred in the liquid phase. Furthermore, it was proposed that the corrosion rate was affected by the sulfur and NA concentrations in crude oil. The chemical equations summarize the combined corrosive effects of sulfur and NA compounds [35,36].





As a result of the direct reaction between NA and iron, iron naphthenates are formed in reaction (1). Simultaneously,  $H_2S$  reacts with the metal (reaction (2)), resulting in the formation of solid  $FeS$ , which is then deposited on the metal surface.  $H_2S$  reacts with iron naphthenates in reaction (3) to form  $FeS$  and regenerate NA. The scenario of the NA corrosion mechanism is represented by these three reactions. However, NA corrosion is more complicated and is influenced by a variety of factors, including crude oil type, temperature, flow velocity, alloy type and surface condition (presence of passive layers), and sulfur content [13]. Some

studies [7,33–39] comprehensively discussed the NA corrosion in oil refineries. Table 4 summarizes the various types of corrosion caused by NA in refinery units [26]. Fig. 7 also shows examples of some failure parts caused by NA corrosion in refinery units.

#### 4.2. Corrosion due to $H_2S$

While  $CO_2$  and  $H_2S$  are well dissolved in water in natural gas, their concentrations vary from one sample to the other. When  $CO_2$  is the cause of corrosion, the phenomenon is known as sweet corrosion. If  $H_2S$  was the cause of the corrosion, the phenomenon is known as sour corrosion. According to NACE, the level of corrosion is affected by partial pressure and natural gas acidity (pH), as well as other factors such as environment, temperature, and velocity [8].



Fig. 8 Examples of corrosion caused by hydrogen sulfide.



H<sub>2</sub>S corrosion can manifest as general (uniform corrosion), localized pitting corrosion, and hydrogen embrittlement. The latter will result in the appearance of a crack at the metal, releasing H<sub>2</sub>S gas into the environment, causing environmental damage and serious health issues for workers. Temperature is an important factor in H<sub>2</sub>S corrosion, with severe corrosion occurring in the distillation unit if the temperature exceeds 400°F [9]. Popoola et al. [40] found that when H<sub>2</sub>S and moisture come into contact with metals, they deteriorate, and this is most noticeable in drill pipes used in the oil industry.

#### 4.2.1. Mechanism of H<sub>2</sub>S corrosion

The mechanism of H<sub>2</sub>S corrosion is still not fully understood. In general, a mechanism that includes two main reactions can be developed: (i) oxidation of Fe metal (anodic reaction) and (ii) reduction of aqueous H<sub>2</sub>S (cathodic reaction). The overall

reaction includes the formation of FeS scales. All reactions can be illustrated by the following equations [8].

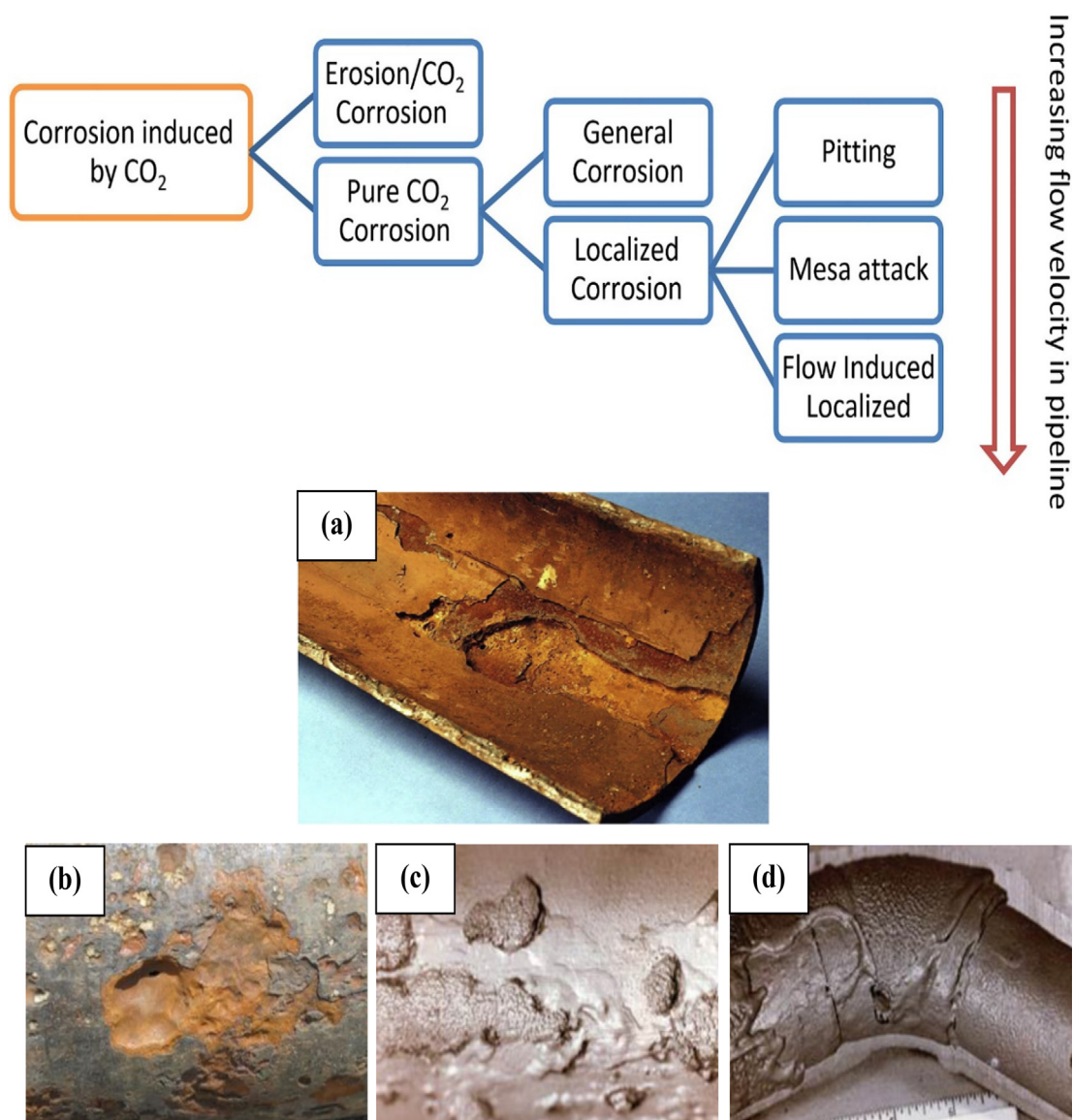
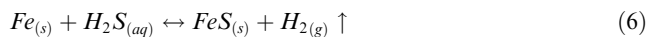
The main anodic reaction:



The main cathodic reactions:



The overall reaction



**Fig. 9** Corrosion induced by CO<sub>2</sub>. (a) general corrosion, (b) pitting, (c) mesa attack, and (d) flow induced localized [52].

One of the most important factors influencing corrosion rate is the formation of FeS scales in the presence of H<sub>2</sub>S. The formation of FeS scales is primarily determined by the kinetics of scale formation. In a H<sub>2</sub>S environment, different types of FeS may form depending on the temperature, pH, and concentration of H<sub>2</sub>S such as amorphous ferrous sulfide, mackinawite (Fe<sub>1+x</sub>S), smythite (Fe<sub>3+x</sub>S<sub>4</sub>), cubic ferrous sulfide, pyrrhotite (Fe<sub>1-x</sub>S), greigite (Fe<sub>3</sub>S<sub>4</sub>), troilite (FeS), and pyrite (FeS<sub>2</sub>). At temperatures lower than 90 °C, mackinawite is considered to be the main form on the steel surface in the oil and gas environment. At higher temperatures, troilite and/or pyrrhotite are the most common corrosion products [41,42]. However, because the mechanism of H<sub>2</sub>S corrosion is still unknown, determining the kinetics of FeS scale formation is difficult.

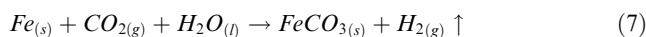
#### 4.2.2. Factors influence H<sub>2</sub>S corrosion

Several factors have been reported to influence the rate and behavior of H<sub>2</sub>S corrosion in the oil and gas environment [8,43]. Flow velocity, temperature, H<sub>2</sub>S partial pressure, exposure time, concentration of dissolved salts and organic acid (such as NaCl and CH<sub>3</sub>COOH), concentration and dissociation of H<sub>2</sub>S, chemistry of steel, nature of the deposits in the metal surface (such as corrosion products, scales, and wax), presence of oxygen, and chemistry of fluid (such as pH, water cut, phase ratios, organic acids, oil wettability) are among these factors. Because all of these factors are interconnected and influence H<sub>2</sub>S corrosion, understanding the influence of a single factor on H<sub>2</sub>S corrosion is difficult. However, H<sub>2</sub>S corrosion has been extensively studied in the oil and gas industry [8,44–48]. Fig. 8 depicts examples of corrosion caused by H<sub>2</sub>S.

#### 4.3. Corrosion due to CO<sub>2</sub>

CO<sub>2</sub> corrosion, also known as sweet corrosion, is by far the most common type of corrosion in the oil and gas industry. The majority of failures in the oil and gas industry, approximately 60%, are the result of corrosion caused by CO<sub>2</sub> [49,50]. According to research, corrosion caused by CO<sub>2</sub> accounts for approximately 10–30% of the maintenance budget for oil refineries and natural gas industries [51].

CO<sub>2</sub> is only corrosive when dissolved in water to form carbonic acid. When dissolved CO<sub>2</sub> reacts with iron, the overall equation is as follows:



In the preceding equation, FeCO<sub>3</sub> is a passive film that forms on carbon steel and low alloy metals under specific conditions. This film will prevent corrosion on the metal surface. The passive film, on the other hand, will degrade under stress or in high-velocity streams, making it susceptible to pits and cracks [8].

Different forms of metal corrosion induced by CO<sub>2</sub> can be classified [49,52] as presented in the flowchart in Fig. 9. Additionally, the figure includes examples of each type of CO<sub>2</sub> corrosion. The dissolution of the metal is the primary cause of uniform or general corrosion. As shown in Fig. 9a, the corrosion mechanism consists solely of metal loss and the formation of carbonate scales on the metal surface as a corrosion product. Pitting corrosion (Fig. 9b) occurs at low fluid flow velocities.

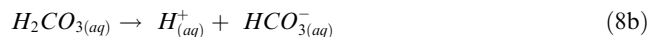
The high temperatures and partial pressures of CO<sub>2</sub> help to accelerate this type of corrosion. Mesa attack (Fig. 9c) is associated with a low to medium flow pattern with the formation of a protective but unstable carbonate film. Flow induced attack (Fig. 9d) is characterized by high flow velocities and a turbulent pattern.

#### 4.3.1. Mechanism of CO<sub>2</sub> corrosion

The phenomenon of sweet corrosion of steel has been extensively studied over the years to effectively understand the mechanism, as many mechanisms have been proposed [50,53–57]. The following steps were included in the mechanism that was most widely accepted by researchers:

(i) Hydration of CO<sub>2</sub> gas.

CO<sub>2</sub> gas is dissolved in the aqueous phase of crude oil where carbonic acid is produced. The resulting carbonic acid undergoes further dissociation, producing hydrogen ions.



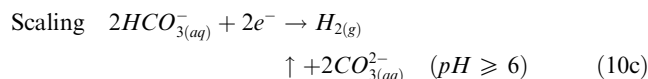
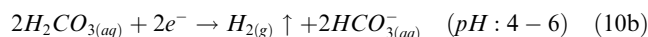
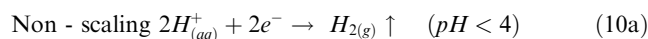
(ii) Anodic reaction

This step involves dissolution of the metal surface and releases of iron (II) ions.



(iii) Cathodic reactions

Cathodic reactions involve the production of hydrogen gas by reducing hydrogen ions. This step includes non-scaling and scaling.



The combination of all previous equations results in the formation of FeCO<sub>3</sub> scale (Eq. (7)). FeCO<sub>3</sub> scale may be protective or non-protective, depending on the environmental conditions in which they were formed.

#### 4.3.2. Factors influence CO<sub>2</sub> corrosion

The severity of CO<sub>2</sub> corrosion depends on a number of factors that affect the formation and properties of the carbonate film. These factors include [49]:

- Temperature;
- Partial pressure of CO<sub>2</sub>;
- pH;
- water content and chemistry of water;
- flow type and its velocity;
- The presence of oxygen, organic acids and H<sub>2</sub>S.

The intensity of corrosion was discovered to increase with flow velocity, high partial pressure of CO<sub>2</sub>, water content, and low pH. Several studies [58–63] have looked into the fac-

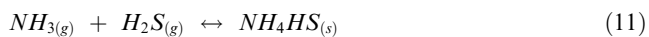


**Fig. 10** Some failure parts caused by ammonium bisulfide ( $\text{NH}_4\text{HS}$ ) [65,70].

tors that influence the rate of  $\text{CO}_2$  (sweet) corrosion in oil and gas facilities.

#### 4.4. Corrosion due to ammonium bisulfide ( $\text{NH}_4\text{HS}$ )

Usually,  $\text{NH}_3$  is added as a neutralizer or formed in the reactors when nitrogen is present in the feed. Wherever  $\text{NH}_3$  reacts with  $\text{H}_2\text{S}$  the result is  $\text{NH}_4\text{HS}$ , as shown in Eq. (11)



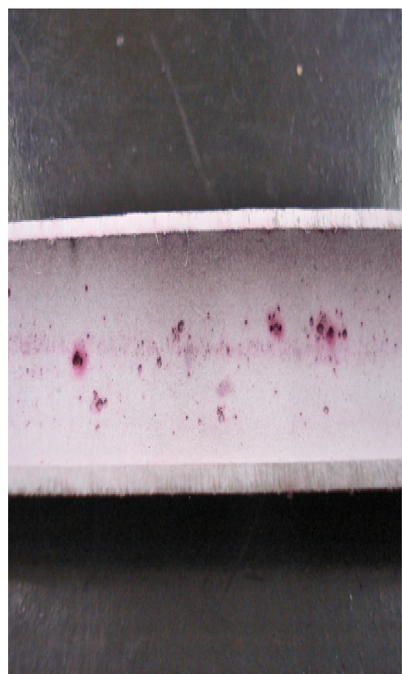
$\text{NH}_4\text{HS}$  will cause aggressive corrosion in various locations throughout the refinery, but it will primarily affect strippers and hydrotreaters [64,65]. Because carbon steel is the most commonly used metal in refineries, it is highly susceptible to  $\text{NH}_4\text{HS}$  corrosion. Horvath et al. [66] conducted a study to further investigate the effect of these factors on carbon steel. The results showed that with the increasing concentration of  $\text{NH}_4\text{HS}$  and its velocity, the corrosiveness also increases. According to one source, severe corrosion should be expected once the concentration of  $\text{NH}_4\text{HS}$  exceeds 1 wt% [64]. Scherrer et al., [67] reported laboratory corrosion tests results for  $\text{NH}_4\text{HS}$  concentrations ranging from 4.5 to 10 wt%. In their tests, increasing the velocity from 3.4 m/s to 6.4 m/s, the high-

est velocity tested, increased the corrosion rates of carbon steel by 40–64%. The  $\text{NH}_4\text{HS}$  solution, in particular, has caused erosion corrosion failure in petrochemical plants and their associated piping, causing a slew of issues for Health and Safety Executive. Toba et al., [68] used a simulation technique to discuss the high concentration of  $\text{NH}_4\text{HS}$  in gas phase, which was the most important influence factor causing localized tube thinning. Zhu et al., [69] concluded that when the  $\text{NH}_4\text{HS}$  concentration reached 10 wt%, the corrosion rates increased dramatically in a corrosion experiment. A current study [70] discovered a window-type failure of carbon steel pipes in an oil refinery's hydro-processing plant. The hydro-processing plant had been in operation for nearly 43 years when the process plant failed during normal operation, resulting in an emergency shutdown. The investigation determined that the root cause of the pipe failure was severe corrosion caused by  $\text{NH}_4\text{HS}$  and turbulence. Fig. 10 depicts some examples of this type of corrosion.

#### 4.5. Corrosion due to ammonium chloride ( $\text{NH}_4\text{Cl}$ )

In today's refining industry, ammonium chloride ( $\text{NH}_4\text{Cl}$ ) corrosion is one of the leading causes of equipment and piping





**Fig. 11** Pitting corrosion in tube made of AISI 304L steel in the E-04A heat exchanger that presents deposits of  $\text{NH}_4\text{Cl}$  [25].

failures. Because of the associated material, maintenance, and repair costs,  $\text{NH}_4\text{Cl}$  corrosion has a devastating impact on refineries. It can also wreak havoc on the structural integrity of the refinery and jeopardize the safety of the equipment. Corrosion caused by  $\text{NH}_4\text{Cl}$  has affected equipment and piping in areas such as hydroprocessing effluent systems, overhead systems of crude distillation, and fractionation columns of thermal and catalytic conversion units.  $\text{NH}_4\text{Cl}$  causes general or localized corrosion, which frequently results in pitting [71].

Carbon steel is the most common construction material used in the above-mentioned processes. The corrosion rate of carbon steel is generally considered unacceptably high when  $\text{NH}_4\text{Cl}$  is present. Unfortunately, many common alloys (such as common austenitic stainless steels) are not suitable replacements in these environments due to their susceptibility to chloride stress corrosion cracking (Cl-SCC). The use of duplex stainless steels has had mixed results, with some reports of pitting corrosion and stress corrosion cracking under the combined effect of chlorides and sulfides. Only nickel alloys have demonstrated satisfactory performance in these services thus far [72].

Ammonium chloride is considered an acid salt because it is formed from a strong acid (HCl) and a weak base ( $\text{NH}_3$ ).



Dilute solutions of  $\text{NH}_4\text{Cl}$  (<0.1 wt%) are generally not considered to be very corrosive. Corrosion is most severe at or near the aqueous dew point, where  $\text{NH}_4\text{Cl}$  concentrations can be extremely high [72]. Fig. 11 depicts an example of pitting corrosion caused by  $\text{NH}_4\text{Cl}$  deposits in an AISI 304L steel tube.

The following critical factors for  $\text{NH}_4\text{Cl}$  corrosion must be considered [73]:

- Concentration of ( $\text{NH}_3$ , HCl,  $\text{H}_2\text{O}$  or amine salts), temperature, and water availability are critical factors;
- Depending on the concentration of  $\text{NH}_3$  and HCl, ammonium chloride salts may precipitate from high temperature streams as they cool, and may corrode piping and equipment at temperatures well above the water dew point (> 149 °C);
- Ammonium chloride salts are hygroscopic, and readily absorb water. A small amount of water can lead to very aggressive corrosion (> 2.5 mm/y);
- Ammonium chloride and amine hydrochloride salts are highly water soluble, highly corrosive, and form an acidic solution when mixed with water.

#### 4.6. Corrosion due to oxygen ( $\text{O}_2$ )

Oxygen serves two functions: on the one hand, it is an oxidizing agent, and on the other, it is a depolarizing agent, allowing it to continuously consume electrons from iron oxidation (corrosion) [74]. The amount of oxygen dissolved in the oil or associated water, as well as the temperature, have a strong influence on the corrosion of carbon steel and low alloy steels [75].

Oxygen can penetrate equipment and processing streams in a variety of ways, including pumps and vacuum systems if seals or connections are not tight, during transportation, storage in tanks, various operations (filling-emptying of tanks and other vessels), and during shutdowns. When oxygen enters atmospheric or vacuum distillation system,  $\text{H}_2\text{S}$  can be oxidized to sulfate ions ( $\text{SO}_4^{2-}$ ), which decrease pH values and increase corrosion of carbon steel. During shutdown, hundreds of ppm  $\text{SO}_4^{2-}$  are occasionally detected in atmospheric and vacuum water condensate [26].

Corrosion by dissolved oxygen causes pits to form in various pieces of equipment. In addition to corrosion, oxygen at concentrations > 50 ppm can oxidize glycols and amines at appropriate units, resulting in the formation of corrosive substances, react with hydrocarbons during regeneration at high-temperature adsorption beds, resulting in the formation of water, influence inhibitor efficiency, and influence resistance of stainless steels to Cl-SCC (Stress Corrosion Cracking), and galvanic corrosion [5].

Corrosion products (mostly rust) can be washed away during start-up in different locations of equipment, contaminate hydrocarbon streams and plugged heat exchangers, strainers, and piping. As a result, oxygen can be harmful not only in terms of corrosion but also in fouling [26].

#### 4.7. Corrosion due to amine

Amine corrosion is the general and/or localized corrosion that occurs in amine treating processes, primarily on carbon steel. Corrosion is caused by dissolved acid gases ( $\text{CO}_2$  and  $\text{H}_2\text{S}$ ), amine degradation products, Heat Stable Amine Salts (HSAS), and other contaminants, not by the amine itself [72].

The following critical factors for amine corrosion must be considered [73].



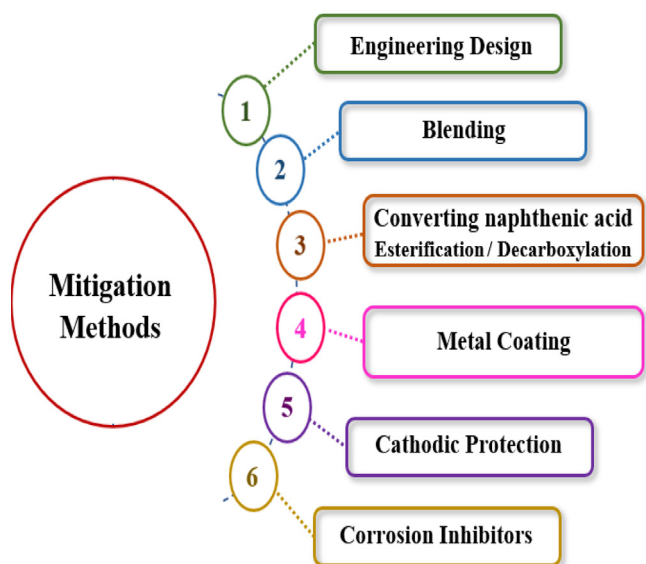


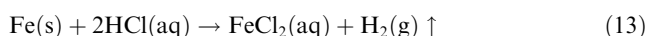
Fig. 12 Mitigation methods currently implemented in the refineries.

- Corrosion depends on design and operating practices, the type of amine (for example, monoethanolamine (MEA), diglycolamine (DGA), diisopropylamine (DIPA), diethanolamine (DEA), and methyldiamine (MDEA), amine concentration, contaminants, temperature, and velocity;
- Amine solutions are generally not corrosive because they have either low conductivity or high pH;
- Corrosion rates increase with increasing temperature, particularly in rich amine service. If the pressure drop is large enough, temperatures above about 104 °C can cause acid gas flashing and severe localized corrosion due to 2-phase flow;
- Process stream velocity will influence the amine corrosion rate and nature of attack. Corrosion is generally uniform; however, high velocities and turbulence will cause localized thickness losses.

#### 4.8. Corrosion due to HCl

The most destructive chemicals encountered at the refineries are H<sub>2</sub>S and HCl. HCl is not corrosive in its dry form but is highly corrosive when mixed with water. HCl causes both general and localized corrosion and is very aggressive to most common materials of construction across a wide range of concentrations. Damage in refineries is most often associated with dew point corrosion in which vapors containing water and HCl condense from the overhead stream of a distillation, fractionation or stripping tower. The first water droplets that condense can be highly acidic (low pH) and can promote high corrosion rates [72].

The process of separating crude oil from brine results in the formation of HCl. When NaCl and MgCl<sub>2</sub> dissolve in water, hydrolysis at 300–400°F produces HCl. When HCl reacts with iron, corrosion occurs as shown in equation [24].



When the temperature is less than the dew point (100 °C) at the top of the distillation column, HCl can come into contact with water and cause corrosion. When H<sub>2</sub>S is present, the above equation will be repeated several times, resulting in more corrosion [34].



The following critical factors for HCl corrosion must be considered [73]:

- HCl acid concentration, temperature, and alloy composition. The severity of corrosion increases with increasing aqueous HCl concentration and increasing temperature;
- Aqueous HCl can form in exchangers and piping beneath deposits of ammonium chloride or amine hydrochloride salts. The deposits readily absorb water from the process stream or injected wash water;
- Carbon steel and low alloy steels are subject to excessive corrosion when exposed to any concentration of HCl acid solution at pH below about 4.5.

## 5. Mitigation methods

In an aggressive environment, it is critical to protect metallic equipment from corrosion by using mitigation methods such as the application of a coating or the injection of corrosion inhibitors. Indeed, mitigation methods should be incorporated into the refinery's engineering design. Fig. 12 depicts the most recent state-of-the-art corrosion protection methods used in refineries.

### 5.1. Engineering design

When designing a refinery, one must consider the factors that could lead to corrosion. For example, by considering the geometry of the equipment, one can control the fluid velocity and avoid areas where sour water can accumulate, thereby reducing erosion-corrosion problems [20]. It is also critical to choose a construction material that is suitable for the harsh environment of the refinery processes. It is critical to understand that there is no single ideal material that is resistant to all types of media and under all conditions. Corrosion in refineries can be classified into low and high-temperature corrosion as previously discussed in section 3 [13].

Except where aqueous corrosion by inorganic containment is present, carbon steel can be used where low-temperature corrosion occurs [13]. For example, corrosion by HCl or H<sub>2</sub>S necessitates the use of a more resistant alloy. The proper removal of corrosive contaminants using processing units such as desalters and hydrotreaters is associated with the mitigation of low-temperature corrosion problems. More durable metals, such as stainless steel, nickel alloy, and copper alloy, are required for a corrosive area in the plant that is exposed to high-temperature corrosion [9].

Titanium has a wide range of applications in a variety of industries and life fields. Titanium alloys were first used in the chemical and biochemical industries due to their high corrosion resistance in various media. When the price of titanium fell in the 1960 s, it became commercially viable due to its high

resistance in various aggressive media such as brackish, saline, and cooling water, as well as other media (hydrocarbons containing  $H_2S$ ,  $HCl$ ,  $NH_3$ , and organic acids) used in oil refineries. Since 1967, titanium-based equipment such as heat exchangers, vessels, pipes, tanks, valves, and others have been used in petroleum refining. The increased use of titanium in petroleum refining and petrochemical plants from 1970 to the present is due to a combination of high corrosion resistance, low density, and high strength with few failure cases [76].

In the refinery sector, polymeric materials and composites hold a prominent position. These materials are distinguished by their high chemical resistance in the presence of various gases and solvents. However, when compared to metals, polymers are thought to have low temperature resistance as well as low mechanical properties. Polymeric materials are used as gaskets, seals, sumps, rings, pipes, and tanks in petroleum refinery systems that come into contact with water, cooling water, sea water, fire-fighting water, acid and alkali solutions, soil, and atmosphere. Thermal, electrical, mechanical, and chemical resistance are characteristics of polymeric materials. Temperature has a significant impact on the properties of polymers. Excessive heating causes the polymer material to chemically degrade, while cooling causes it to become brittle. As a result, the selection of polymeric materials and composites is determined by the purpose of their use in refinery operations [77–79].

In addition to material selection, corrosion monitoring equipment, such as electrical resistance probes, should be installed in several locations throughout the refinery to continuously display the corrosion situation [9].

### 5.2. Blending

With the growing popularity of opportunity crude oil, high acid content remains one of the most difficult corrosion control challenges for refineries. Blending is one option for dealing with high TAN crude oil. The blending of heavy and light crude oil is an effective method for lowering the acid concentration in the feed and, as a result, the corrosion rate [80]. However, every crude oil varies in composition and properties, resulting in varying levels of compatibility in crude oil blends. Some oils are inherently incompatible, owing to the insolubility of asphaltene in more paraffinic light crude [13]. It should be noted that blending does not de-acidify the high acid crude, but rather reduces the acid concentration. The NA is still present in the blended product and has the potential to react with the catalyst, resulting in catalyst deactivation. However, Dettman et al., [81] reported that blending may cause additional problems during refining if the crude being blended contains high levels of sulfur compounds or other corrosive agents.

### 5.3. Conversion of naphthenic acid

Crude oil with a high TAN contains cyclopentane, cyclohexane, and NA, which are saturated linear hydrocarbons with either a terminal carboxylic group or unsaturated aromatic rings. The refineries use a variety of methods to transform NAs, including neutralization, esterification, and catalytic decarboxylation. Each method, however, has its own set of

drawbacks and disadvantages. For example, using caustic treatment to neutralize acidic components can result in non-soluble emulsions, product loss, and pollution [82]. The esterification and decarboxylation of NA by catalysts has been studied to develop efficient catalysts with lower treatment costs and fewer environmental issues.

#### 5.3.1. Esterification

The conversion of carboxylic acids to esters in the presence of heat and alcohol is known as catalytic esterification [83]. A catalytic esterification using  $SnO/Al_2O_3$  as the catalyst system was used in a study [84] to remove naphthenic acids from diesel fuel. The reaction temperature, methanol/oil ratio, and space velocity were all mentioned in the study. The esterification is favored by a high reaction temperature, a high methanol/oil ratio, and a low space velocity, according to the data. Quiroga-Becerra et al., [85] investigated the effect of esterification of NAs on steel ASTM A106 Gr.B corrosion. The corrosion rate was reduced by 91% after esterification, according to the results. Wang et al., [86] used catalytic esterification to remove NA from oil using alcohol and a  $SnO/Al_2O_3$  catalyst in their research. They were able to remove more than 85% of the TAN in this experiment, reducing it from 2.8 mg KOH/mg to 0.5 mg KOH/mg. However, there has been little research on catalytic esterification to reduce the TAN of heavy crude [82]. In a previous study Wang et al., [87] found that NAs with a lower molecular weight and boiling point are more reactive during esterification. Without the use of a catalyst, Exxon Research and Engineering Company used batch reactor systems to reduce the acidity of crude oil. However, because of the long reaction times, this process was not adopted in refineries [82].

#### 5.3.2. Decarboxylation

Decarboxylation is a chemical reaction that removes the carboxyl group from NA, which is used in the refinery to remove the carboxyl group from high acidity crudes [13]. Thermal decarboxylation can occur in the refinery's distillation column, where temperatures can reach 400 °C [9]. Researchers have recently concentrated their efforts on developing a catalyst that can maximize reaction rate while operating at a lower temperature. The effectiveness of calcium oxide (CaO) and magnesium oxide (MgO) catalysts in converting carboxylic compounds based on the formation of  $CO_2$  has been determined. MgO application to crude oil resulted in lower TAN as a result of significant NA removal. The majority of the reaction would take place in the range of 150 to 300 °C, respectively. The effectiveness of  $ZnO$ ,  $Ag_2O$ ,  $ZrO_2$ , Cu-based catalysts, and zeolite catalysts in catalytic decarboxylation for the removal of NA has been investigated and has produced effective results. The majority of these studies, however, are limited to delicate catalyst systems with low temperature stability [88–91]. Furthermore, using Cu-based catalysts to upgrade crude oil is impractical because they can easily poison the sulfur compound in the oil [88,89].

### 5.4. Metal coating

Metal coating is a method of reducing the rate of corrosion by coating the metal surface with a thin layer of a substance. The coating prevents corrosion by controlling electrochemistry or forming a barrier between the metal surface and the hostile

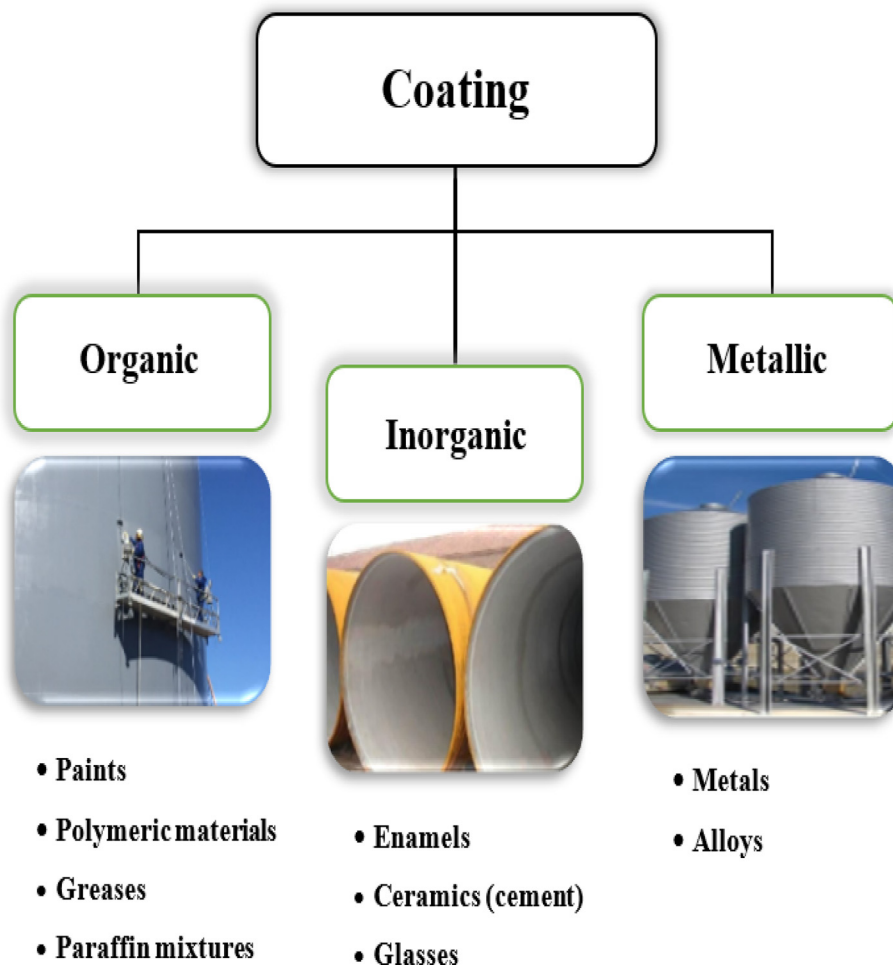


Fig. 13 Different types of coating used in refineries.

environment [92]. It can be used to provide resistance to heat, erosion, pitting, and general wear [93].

The ability of coating to improve a metal's corrosion resistance is characterized by a number of properties. The coating's ability to resist water, chemicals, abrasion, weather, bacteria and fungus, and extreme temperatures are among these properties. All coatings can be divided into three main groups depending on the nature of the base material used: organic, inorganic, and metallic [5]. Fig. 13 shows the coating groups with some examples. In refineries, all three types of coatings are used to protect tanks, pipes, columns, and other equipment from natural gas, water, and the environment [5].

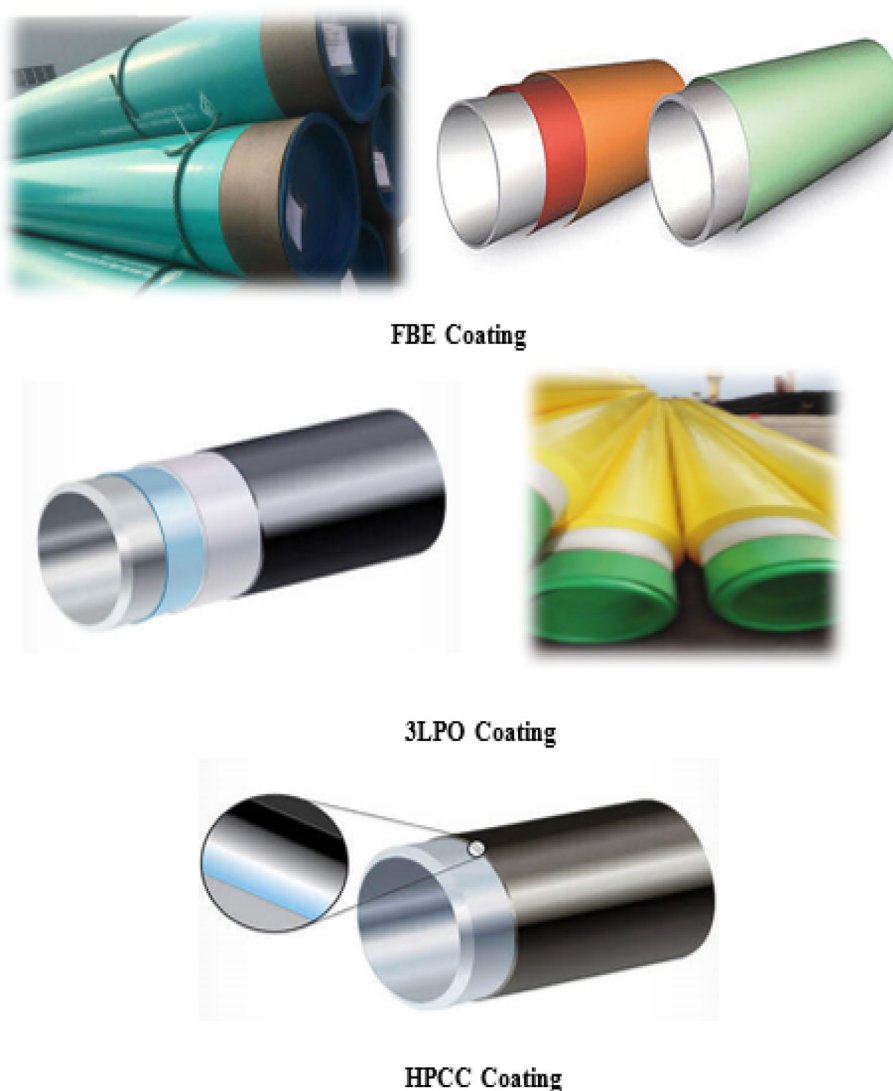
Many coatings have been developed in recent years to meet the demanding and diverse needs of the oil and gas industry. These types improve operational safety while also providing opportunities to improve the efficiency of various processes in refineries. The most commonly used external anti-corrosion coating systems are fusion-bonded epoxy (FBE) and a three-layer polyolefin (3LPO) (polyethylene (PE) or polypropylene (PP)). Single-layer FBE is the most popular in North America, Saudi Arabia, and the United Kingdom. While dual-layer FBE coatings are popular in Australia, 3LPO coatings dominate the rest of the world's pipe coating market [40]. The high performance composite coating system (HPCC) is a cutting-edge composite system that represents

the most recent advancement in anti-corrosion coating systems. The HPCC is a single layer, powder-coated multicomponent coating system composed of an FBE base coat, a medium density polyethylene outer coat, and a tie layer containing a chemically modified polyethylene adhesive. All materials of the three components of the composite coating are applied using an electrostatic powder coating process. The tie layer is a blend of adhesive and FBE with a gradation of FBE concentration. The HPCC system provides excellent pipe surface adhesion with inherent shear resistance properties, flexibility at low temperatures, impact and cathodic disbandment resistance, and very low moisture permeability [94]. Fig. 14 shows FBE, 3LPO, and HPCC coating system that protect oil and gas pipelines from corrosion.

Several studies on various types of coatings have shown that they are effective in protecting various types of steels in crude oil environments [94–97].

##### 5.5. Cathodic protection

Cathodic protection (CP) is a corrosion-control technique that involves converting a metal surface into the cathode of an electrochemical cell [9]. Cathodic protection can help prevent stress corrosion cracking in some cases. This method is widely used in oil and gas refineries to protect buried pipelines and



**Fig. 14** FBE, 3LPO, and HPCC coating system that protect oil and gas pipelines from corrosion.

storage tanks. The philosophy behind the use of CP is that applying organic coatings to metal structures is the primary method for controlling corrosion, and cathodic protection is used in conjunction with it to reduce defects that occur during application and service [5]. In many cases, combining CP and coatings is the most cost-effective solution.

The CP is applied to the inner and outer surfaces of the aboveground storage tanks used in refineries (oil products and/or water). Pure hydrocarbon fluids are usually non-corrosive, so internal surfaces do not need to be protected from corrosion. Internal corrosion may, however, occur in aboveground storage tanks with internal surfaces exposed to sediments, water, and other contaminants, according to experience [98].

The CP only works when all four basic components are present: anode, cathode, electrolyte, and complete electrical circuit. If any of these four components is missing, the cathodic

protection activity is halted. It should be noted that the corrosion rate of metal structures exposed to CP is never zero, but it is extremely low and suitable for use without risk of corrosion. Different metals and alloys, such as carbon steel, ductile iron, cast iron, stainless steel, aluminum, and brass are effectively protected by CP [5].

CP system includes two types [5,9,40]:

- Sacrificial (or galvanic) anode cathodic protection (SACP),
- Impressed current cathodic protection (ICCP).

In the sacrificial anode (SACP) method, an active metal such as Al, Zn, and Mg are attached to the metal structure. This active metal corrodes and releases current to the metal structure under protection. As the current flows, all corrosion occurs on the anode, which sacrifices itself to protect the metal structure from corrosion. Impressed current (ICCP), on the



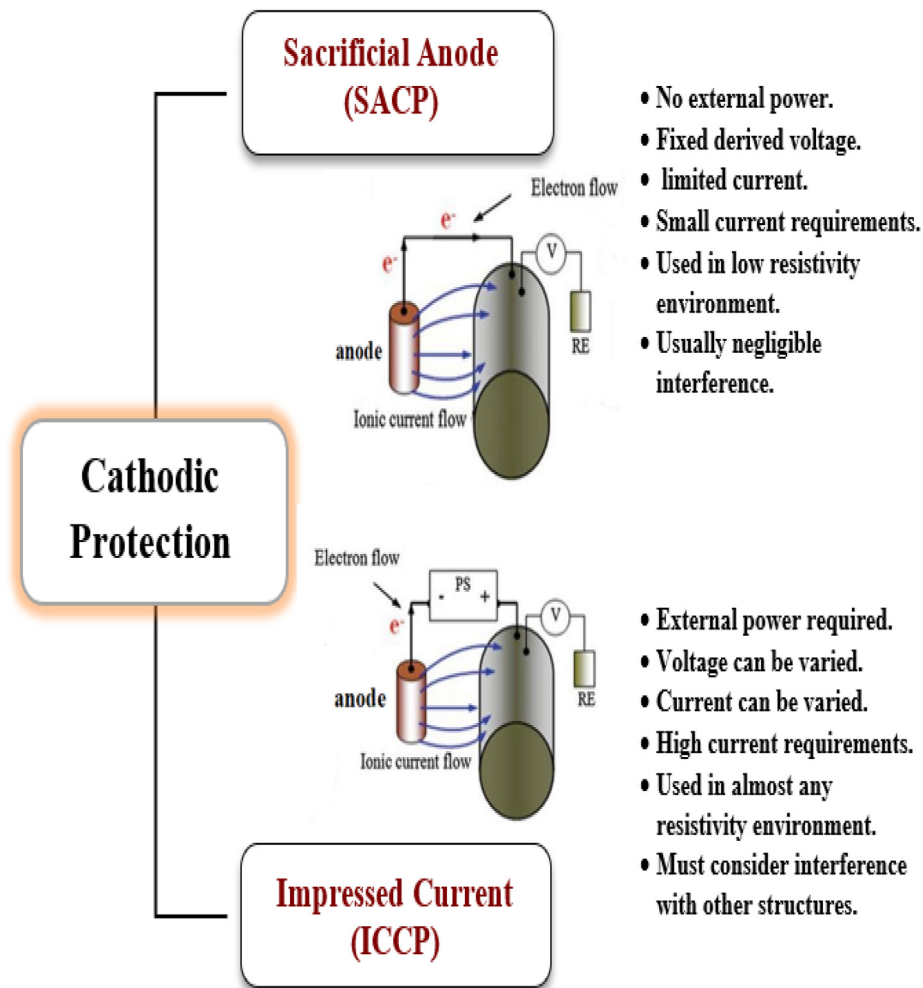


Fig. 15 Cathodic protection (CP) systems used to protect metal structures from corrosion in refineries.

other hand, uses an anode that is connected to a DC power source. The anode, which can be made of graphite, mixed metal oxides, or high silicon cast iron, is either inert or has a low consumption rate and can be surrounded by carbonaceous backfill to increase efficiency and lower costs [5,9,40]. The difference between the two CP methods is depicted in Fig. 15.

### 5.6. Corrosion inhibitors

Internal corrosion is one of the most dangerous types of corrosion that can occur in refineries because there is no cost-effective way to maintain and inspect it. To avoid costly alloy upgrades, one economically viable option is to control internal corrosion with corrosion inhibitors. Corrosion inhibitors are substances that, when used at low concentrations in a corrosive medium, reduce the rate of corrosion by forming a film that prevents the corrosive substance from coming into contact with the exposed metal surface [8]. There is no universal classification for corrosion inhibitors, but they can be classified as shown in Fig. 16 based on their mechanism of composition and action. Some literature [99,100] has gone into great detail about the different types of inhibitors found in oil and gas facilities based on this classification.

Substances considered as potential corrosion inhibitors in the oil and gas industry should have the physical and chemical properties listed below [101]:

- stability;
- inability to precipitate in the form of residue; and
- inability to form emulsion.

Corrosion inhibitor, possibly applied in the oil industry, should possess sufficient solubility in hydrocarbons.

The selection of a suitable corrosion inhibitor for specific industrial applications is an extremely complex issue [102]. Among other things, the effectiveness of a specific agent is determined by [101]:

- The type of material which interacts with the inhibitor;
- The aggressiveness of the environment (for example, the presence of redox species and pH of the environment);
- The place where the inhibitor is applied (refinery, drilling equipment, gas and oil pipelines, etc.);
- The type of transferred or stored fuel.

Different organic compounds containing -N, -S, -O, -P, -Si, or other substances are used as corrosion inhibitors. In petro-

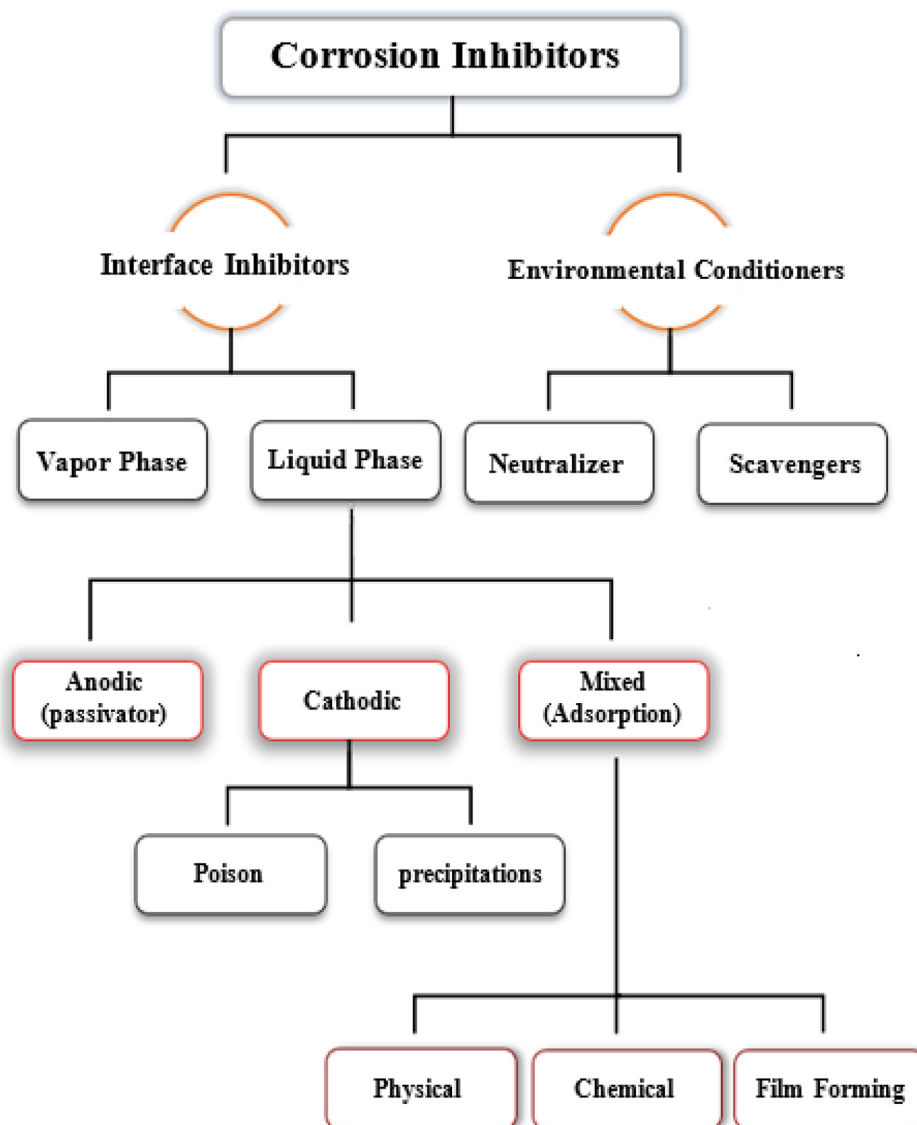


Fig. 16 Classification of corrosion inhibitors.

leum refineries, nitrogenated-containing compounds, such as amine and ammonium salts, quaternary ammonium salts, imidazole and their derivatives are mainly used [101,103]. Because there are so many corrosion inhibitors in the market, it is important to figure out which one to use based on the corrosive media and operating environment. When NA corrosion becomes a problem, some organic corrosion inhibitors are effective at temperatures above 200 °C. Acidic corrosion inhibitors such as alkyl phenol, organic polysulfide, fatty acid amine, thiazolidine, and thiophosphate have been claimed to be effective in refineries. While high-temperature acidic corrosion inhibitors have been used successfully, the effect of catalyst deactivation has been documented. A low concentration corrosion inhibitor is continuously injected into the process stream to mitigate high-temperature corrosion [13]. Refineries, for example, use phosphate ester-based corrosion inhibitors at critical locations in the overhead distillation process to reduce the effect of NA corrosion. Because the inhibitor is highly corrosive to alloy steel and even stainless steel, it is dosed with injection quills [9].

Inorganic corrosion inhibitors, on the other hand, contain salts of copper, zinc, arsenic, nickel, and other metals, with arsenic compounds being the most commonly used. When using inorganic inhibitors, there are benefits and drawbacks. The advantages are that they work exceptionally well at high temperatures for longer periods of time and are less expensive than organic inhibitors. Inorganic inhibitors are more likely to lose their effectiveness in acid solutions that are stronger than 17% HCl and may release toxic arsine gas as a byproduct of corrosion [104]. Polymeric (naturally occurring and synthetic) materials tend to be the focus of study in the hunt for a perfect alternative for inorganic corrosion inhibitors. Polymers are made up of long chains of monomers that can have a variety of structures, including linear chains, branched, hyperbranched, rotaxanes, comb-like, dendrimeric cross-links, and so on. Polymers have better film-forming capabilities, multifunctionality, solubility, flexible viscosity, increased number of attachment points to metal surfaces, cost effectiveness, and eco-friendliness when compared to the more widely used small molecule corrosion inhibitors, in addition to the inherent

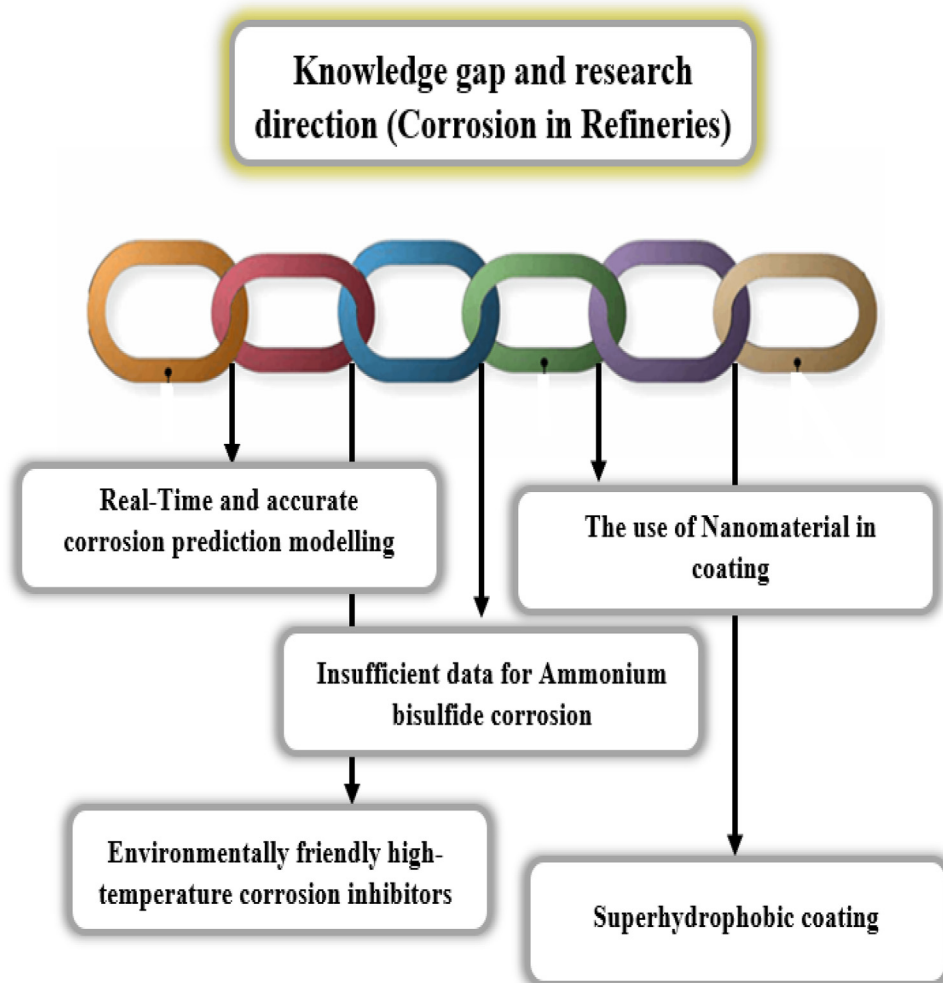


Fig. 17 Knowledge gaps and research direction for corrosion in refineries.

stability [105,106]. Polyvinylamide derivatives, polyamino acids, polyanilines, polycarboxylates/polycarboxylic acids, polysulfides, and polysaccharides (for example, hydroxyethylcellulose, carboxymethylcellulose, guar gum, and polygalactomannans) [106], are some examples of polymers used as corrosion inhibitors in the oil and gas industry. These polymers can also be modified and used as corrosion inhibitors in the refinery.

The use of “green” corrosion inhibitors is becoming more popular. Because they must be evaluated from a safety, health, and environmental standpoint, there is no clear and acceptable definition of “green” corrosion inhibitors. Corrosion inhibitors should have a low toxicity (preferably non-toxic), be biodegradable, and contain no harmful elements or substances. In other words, the corrosion inhibitors currently in use must meet all equipment’s safety and risk requirements, as well as reliability and quality assurance assessments [26].

In the next section, we will discuss the existing knowledge gaps and future research directions that will help advance research in corrosion mitigation approaches in refinery operations.

## 6. Knowledge gaps and future research direction

Governmental regulations as well as the critical gap in research and needed technologies, will guide future research directions. The development of green corrosion inhibitors and coatings has piqued researchers’ interest in light of recent safety and environmental concerns [8]. As a result of the several governmental restrictions on the use of toxic materials, there has been an increase in the number of papers devoted to the development of effective corrosion inhibitors that are environmentally friendly, non-toxic, and biodegradable. Future research should also concentrate on the development of effective high-temperature catalysts for the conversion of NA [89]. The lack of quantitative corrosion data and its correlation with operating and process conditions as well as the ability to predict the corrosion site in real time and with high accuracy, are all challenges that refineries are facing these days. The majority of current prediction models are based on laboratory experiments, which may or may not accurately reflect field conditions. The use of a long-lasting superhydrophobic smart coating is another highly anticipated method of mitigation [107]. Recent research has focused on the development of a smart coating that responds automat-

ically when exposed to an aggressive environment. They will extend the life of the equipment and lower maintenance costs [10,11]. Fig. 17 summarizes the most important points that must be considered as knowledge gaps and future research trends when studying corrosion in refineries.

#### 6.1. Real-time and accurate corrosion prediction modelling

Predicting the rate of corrosion for refinery equipment is difficult because several factors can influence the rate of corrosion. Observations and laboratory testing are required to obtain corrosion rate data for refinery equipment. While there are corrosion prediction models for laboratory settings, these models may not accurately represent actual field conditions [107]. Real-time corrosion modeling is conceptually similar to real-time corrosion monitoring, where the purpose is to provide on-time and accurate information about the corrosion rate. Using laboratory data, empirical correlation, and field experience, multiple industries collaborated on research that resulted in numerous corrosion prediction models [108]. These models were useful in the upstream oil and gas industry, but due to the significant complexity of potential interactions between various process parameters and chemical reactions, they were deemed insignificant for refinery applications [107].

#### 6.2. Environmentally friendly high-temperature corrosion inhibitors

In an acidic environment, it is critical to find corrosion inhibitors that work at high temperatures. The majority of corrosion inhibitors that have been used in the past and are effective at high temperatures no longer meet environmental regulations. Thermal decomposition causes some corrosion inhibitors to lose their effectiveness at high temperatures. High-temperature corrosion inhibitors are a cost-effective option to metallurgical upgrade using corrosion resistance alloys. Current corrosion inhibitors, on the other hand, have significant drawbacks. Obot et al., [56] have published a detailed review on high-temperature sweet corrosion and inhibition in the oil and gas industries. This study looked at corrosion inhibitors for high-temperature sweet corrosion of steel in the scientific literature. The most commonly reported inhibitors for high-temperature sweet corrosion of steel were nitrogen-based chemistries such as amines, amides, and imidazolines, according to the review. At temperatures ranging from 90 to 150 °C, reported inhibition efficiencies were greater than 80%. At temperatures below 100 °C and CO<sub>2</sub> partial pressures below 10,000 psi, however, most corrosion inhibitors perform well. According to the findings, there are numerous knowledge gaps on corrosion inhibitors for sweet corrosion at high temperatures. These findings can also be applicable to refinery at low to medium temperatures.

#### 6.3. Insufficient data for ammonium bisulfide (NH<sub>4</sub>HS) corrosion

There is insufficient corrosion data to predict the corrosiveness of NH<sub>4</sub>HS over a wide range of concentration and

velocity, as evidenced by the literature. Corrosion data for other metals and alloys are scarce than for carbon steel. Since the effects of temperature, pH, partial pressure of H<sub>2</sub>S, and NH<sub>3</sub> on the corrosiveness of NH<sub>4</sub>HS are yet to be quantified, more research is needed. The refinery's predictability of NH<sub>4</sub>HS corrosion will be improved by collecting all of these data [66].

#### 6.4. The use of nanomaterial in coating

Nanomaterial-containing coatings offer much better material and processing properties than conventional coatings (for example, increased indentation resistance, high elasticity, fast drying, no expansion after contact with water, high water vapor permeability). Graphene, among nanoparticles, has exceptional thermal, mechanical, and electrical properties due to its 2-dimensional atomic structure, and these properties are advantageous for coating applications. A review of the literature revealed that graphene, graphene oxides, and other similar derivatives could provide a significant barrier to through-coating transport of chemical diffusion (for example, OH<sup>-</sup>, Cl<sup>-</sup>, and O<sub>2</sub>), potentially improving corrosion mitigation and control of metallic structures [109–111]. Despite the efforts and progress made in this field, the existing literature on graphene coating characterization focuses primarily on electrochemical properties. As a result, a more thorough characterization of the coatings, such as ultimate strain (ductility), tensile strength, abrasion properties, and long-term performance, could be extremely beneficial in gaining a thorough understanding of graphene-based coatings [112]. Therefore, more research for use of nanomaterial in coating will pave the way for the development of new types of coatings that are effective at repelling water and preventing rust [113]. Nanoparticles are also being used to create superhydrophobic coatings to protect metal surfaces in harsh environments. A clear mechanism for developing such advanced coatings, on the other hand, will necessitate more fundamental and applied research [11].

#### 6.5. Superhydrophobic coating

Corrosion resistance has improved owing to the use of superhydrophobic coatings. The concept of superhydrophobicity can be found in some plants, which have water-repellent leaves. Water droplets can easily roll off their leaves due to these repelling qualities, keeping the surface clean [11]. Superhydrophobic coatings can be viewed as a low-cost solution to corrosion and fouling in pipelines and equipment, and they are frequently used over a variety of substrates [114]. Other advantages of using superhydrophobic polymer coatings include properties such as self-cleaning, anti-icing, oil–water separation, and viscous-drag reduction [115]. The two important factors that must be considered in fabricating superhydrophobic surfaces are surface chemistry (surface energy) and surface geometry (surface roughness). Low surface energy materials such as fluoroalkyl silane and micro/nanostructure surface geometry are the most common parameters utilized in achieving superhydrophobicity. When silver nanoparticles are used to create superhydrophobic surfaces, they are reported to be very resistant to microorganisms. Shape-memory polymers



have also recently been used in the fabrication of superhydrophobic surfaces for self-healing functionality [116].

Future research should focus on developing new, smart, superhydrophobic coatings that incorporate corrosion inhibitors and self-healing capabilities that can repair their anti-corrosion, antibiofouling, and self-healing functions independently or with minimal interference from external agents such as UV light. More environmentally friendly and cheap superhydrophobic coatings must be developed in the future, with an emphasis on their widespread or industrial application. In recent studies, the anti-corrosion performance of many superhydrophobic coatings has been evaluated for only a short period (maximum two months). As a result, there will be a future demand for superior superhydrophobic coatings that can withstand severe corrosive conditions for an extended period of time. New superhydrophobic coatings must be developed to protect industrial grade carbon steel (for example, X80 and X90) which is primarily used to transport crude oil at high pressure and temperature [116].

## 7. Conclusion

Corrosion in the refinery operations cost the petroleum industry billions of dollars to manage and control. In the work, we conducted a comprehensive review on the corrosion challenges in the petroleum refinery operations. Important areas such as refinery units, physicochemical basics of corrosion at the refinery units, sources of corrosion, mechanisms of corrosion, current state of the art mitigation methods (engineering design, cathodic protection, the use of corrosion inhibitors and metal coating) were reviewed. The review concludes that corrosion in the refinery has not received wide attention in the scientific literature like other corrosion issues in the petroleum industry. Critical knowledge gaps such as inaccurate prediction models, collection of insufficient data regarding ammonium bisulfide ( $\text{NH}_4\text{HS}$ ) corrosion, the need for the development of smart coating and environmentally friendly high-temperature corrosion inhibitors were discussed. We submit that future research directions should focus on accurate prediction models for refinery corrosion, development of novel nanomaterials and superhydrophobic coatings, effective high-temperature corrosion inhibitors ( $> 100\text{ }^\circ\text{C}$ ) and more data should be obtained for ammonium bisulfide, ammonium chloride and hydrogen sulfide (sour) corrosion.

## Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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