Journal of Petroleum Research and Studies

Open Access
No. 41, December 2023, pp. 78-97

P- ISSN: 2220-5381
E- ISSN: 2710-1096

DOI: http://doi.org/10.52716/jprs.v13i4.707

Corrosion Mechanism and Countermeasures in Oil Refineries - Comprehensive Review

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Received 20/10/2022, Revised 15/03/2023, Accepted 19/03/2023, Published 12/12/2023

Abstract

Due to the international economic growth reliance on petroleum, corrosion is a critical problem for refineries and it has attracted considerable attention in recent times. There is a plethora of knowledge on the prevention of corrosion in petroleum refineries, but it is distributed among several scholarly studies. Therefore, a comprehensive and current analysis of corrosion prevention in refineries is required. Corrosion issues at several refinery units are examined in this paper. In addition, the foundations of the corrosion issue and modern mitigation techniques, like refinery design, cathode safeguard, inhibitors, and covering protection, were investigated. Study concludes by pointing out knowledge gaps, collecting adequate data on refinery facility corrosion, and offering suggestions for future studies.

Keywords: Corrosion risks, environmentally cracking, Crude oil, and Salt formation.

1. Introduction:

The sector of the global economy that deals with oil refining continues to be a priority, and refined products continue to be essential to many different industries as a significant source of energy. This sector is crucial for each region and its surroundings. In spite of these benefits, the refining industry is expected to have a high hazard since refineries are huge, complex operations that carry out a variety of operations while subjected to high levels of heat and pressure. Certain situations increase the risk of corrosion in refineries, which may lead to catastrophic occurrences that block oil flow and have long-lasting effects on staffs, the situation, and the business line [1][2]. Corrosion is an important issue that touches the majority of sectors globally, wreaking havoc on the global economy if left unaddressed [3]. In 2013, the financial losses resulting from corrosion operations and maintenance procedures were between (4 - 5%) of the benefits of global oil output [4]. General corrosion, chloride stress cracking, under-insulation corrosion, and high temperature corrosion are just a few of the kinds of corrosion that may affect refinery equipment if the proper precautions are not followed. The explosion at Venezuela's largest oil refinery in 2012, which killed 26 people, injured 37 others, and shut down production for a long time, was caused by corrosion[5][6], [7]. There is an important need for study and in-depth laboratory investigations to determine the most significant causes and types of corrosion in oil refineries' different operating units. Additionally, research the most effective treatments for decreasing sensitivity to corrosion. The overall amount of research articles on corrosion in refineries demonstrates the scarcity of study in this field. The purpose of this review article is to present the latest information on the concerns and causes of corrosion in oil refineries. One of the future goals of the research is to find ways to stop corrosion and the economic and human losses that come with it.

2. **Petroleum Refinery**

The refinery for petroleum products is a large industrial complex within the confines of which continuous processing equipment is put to work in order to transform crude oil into consumer-friendly goods such as kerosene, gasoline, and diesel fuel[8]. Refineries usually process between 104 - 106 barrels of crude oil every day to make a wide variety of petroleum products. Where, desalters, top evaporation and catalyst fluid allow basic refineries to transform crude oil into marketable products and more valuable[9]. Refineries use polymerization, catalytic reforming, and hydrocracking units as shown in Figure (1). Most oil refinery activities usually are susceptible to corrosion because they include the use of corrosive chemicals, high rates of flow, and high temperatures [10].

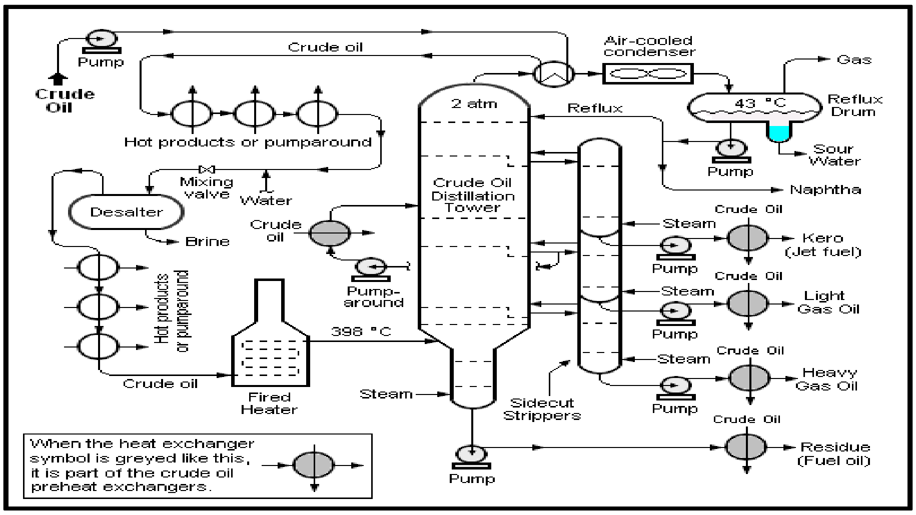

Fig. (1): Crude Schematic flow diagram in petroleum crude oil

3. Corrosion Sources in Refineries

Crude oil is a broad category that encompasses a wide variety of liquid hydrocarbons, both volatile and non-volatile [11]. Some of the impurities in crude oil include corrosive liquids, solids, fumes, or microorganisms. Even while all crude oils have the same basic components, the quantity may vary substantially. Most crude oil consists of water, nitrogen, carbon dioxide, and hydrogen sulphide, all of which may corrode metal at any point in the manufacturing process[12][13]. Hydrogen embrittlement, corrosive environments, stress corrosion, and decomposition corrosion are just a few of the forms of corrosion that may occur on metallic equipment at a refinery due to the presence of these chemicals[14]. The mixture of corrosive gases made up of H_2S and CO_2 that is close to the boiling water inside the desalination unit is the main cause of corrosion on the inside of the steel tubes[15]. The data of corrosion degradation process, cautious material selection, usage of corrosive conditions and corrective measures, detection at an early stage of corrosion positions through checkup programs are essential to ensure the refinery's safe operations[16]. The rate of corrosion in crude oil may be affected by several things; sulphur concentration, acidity, saltiness, hydration, and microbial load are shown in Figure (2)[17].

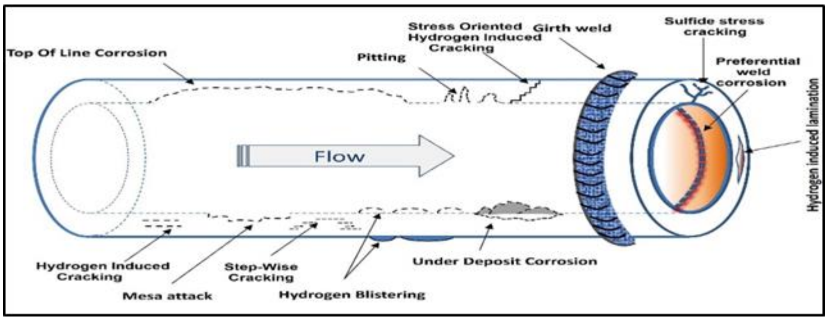

Fig. (2): Significant cracking effects in pipelines [17]

3.1 The unit desalination of crude oil

The crude oil that is delivered to the refinery may include dissolved inorganic ions such as magnesium and chloride, in addition to other inorganic ions. Desalters are devices that clean crude oil of hazardous inorganics such as corrosion and rust[18]. Desalination of water may be accomplished in two ways: chemically and electrically. Salts and other impurities in water may be removed using chemical desalination, which boils a combination of crude oil, water, and degreasers, or through electrical desalination, which uses high voltage to concentrate molecules of suspended water [19]. To reduce the impact of corrosion, chemicals such as ammonia are typically used in one or both of these processes. Most desalting chemicals are known as wastewater demulsifies or pH adjusters[20]. The desalter's water effluent must be maintained acidic to be effective in counteracting the role that sodium naphthenates play in creating disturbances. High crude viscosity and density complicate separation; high salt content and the probability of producing a rag layer raise the risk of fouling, which reduces desalter efficiency. The refinery's crude oil distillation unit processes crude oil by breaking it down into useful product fractions. The most important components for the distillation systems in the oil refinery are pre-flashed drums, heat exchanger systems and atmospheric distillation units [21]. Hydrogen sulphide may damage the tower and condenser if dissolved in the aqueous condensation from the top refluxed barrels of the main fractionation column and water from the vacuum distillation unit. At temperatures ranging from 250 °C to 450 °C, corrosion is often likely to occur in the faster area of the crude distillation unit. Figure (3) shown how these extremely acidic salts may develop a coating on the surface of the crude distillation unit, one of the numerous ways in which corrosion might manifest itself in this apparatus[22].

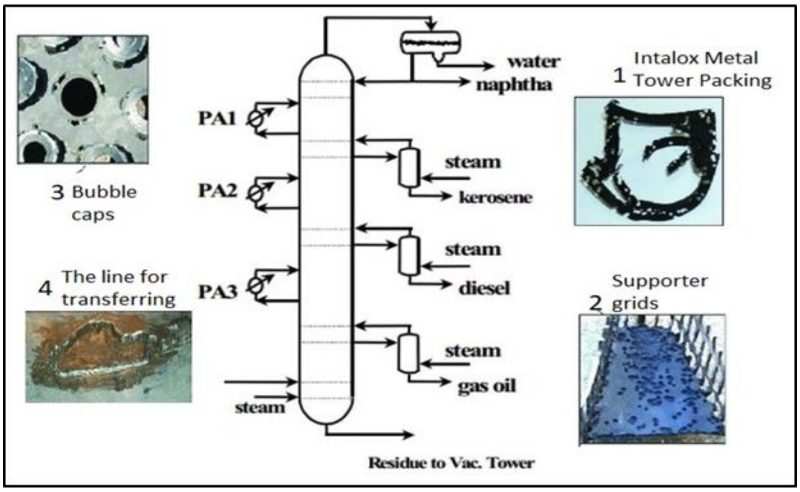

Fig. (3): The damage to the crude distillation unit was due to corrosion [22]

3. Hydrotreatment units

Sulphur and nitrogen removal from petroleum refineries is critical for fraction stability and corrosion avoidance[23]. These impurities, if not eliminated throughout the refining process, have the potential to harm equipment, degrade catalysts, and impair product quality[24]. The fundamental goal of any hydrotreating unit is to remove the Sulphur atoms that are covalently linked to the hydrocarbon molecule. Hydrogen combines with Sulphur and Nitrogen at high temperatures ($325^{o}C$ - $450^{o}C$) and pressures 70 bar in hydrotreating to form H_2S and NH_3[25]. The product is removed from the reactor after cooling and sent to a liquid/gas separator. The abundant sulphur dioxide gas stream is then separated from the H_2S using a gas treatment equipment. Acid salts such as NH_4Cl and NH_4HS may be precipitated from gaseous streams in the hydrotreating unit[26]. Metallurgy fundamentally limits the capacity of hydrotreating systems to handle high-acid crude. Unfortunately, carbon steel, low alloy steels, and titanium are often employed in the building of hydrotreating equipment, and all three of these metals are very corrosive in acid. Carbon steel that is exposed to concentrated NH_4HS quickly rusts, so a cleaning solution will be put into the system. If the NH_4HS flow rate is raised, corrosion may accelerate quickly[26].

4. Fundamentals of Refinery Corrosion

Refinery unit efficiency may be significantly impacted by corrosion of equipment. This is due to the fact that corrosion may disrupt and delay production, cause the release of substances that are hazardous to the natural environment, result in large maintenance expenses, or even lead to plant shutdowns[27]. There are three types of corrosion in refineries and petrochemical plants:

a) At temperatures below 100 °C, this kind of corrosion takes place when electrolytes are present. Dissolved corrosive gases or salts might trigger this form of corrosion, and it is a risk. Therefore, it's important to choose elements that won't react in a solution together.

b) Oil refineries and chemical plants cause soil, air, and water contamination.

c) Corrosion phenomena include acid dew point corrosion, condensation corrosion, and steam generator corrosion.

A. Corrosion at low temperatures

An electrochemical process is responsible for corrosion taking place at temperatures below 100 °C. Acidic, alkaline aqueous solutions are all conducive to the formation of corrosion. The organic acids in hydrocarbons may erode the distillation systems' top portions[28]. Inorganic chemicals, rather than processed hydrocarbons, cause this kind of corrosion. The most common sources of corrosive elements include impurities found in crude oil (including air, NH_3, water, and H_2S) and chemicals that are employed in various processes, like solvents, neutralizers, and catalysts. Constant exposure to sulfone in petrochemical facilities might lead to the development of harmful corrosion products (acids)[29]. Also, treating amines in an aqueous phase could cause acidic gases to build up inside the unit operations, which would lead to the formation of corrosive salt.

B. Corrosion at high temperatures

High-temperature corrosion occurs when a material is subjected to a chemical assault at temperatures greater than 400°C, generally from gases, solid or molten salts, or molten metals. Corrosion resistance is not a sufficient criterion for selecting materials for use in high-temperature service[30]. In addition to that, you have to take into consideration their creep strength and structural stability. High temperature corrosion issues are significant in refineries. Breakdowns in machinery may have catastrophic repercussions since high-temperature operations sometimes entail high pressures. There is always the danger of fire and toxic material discharges when a hydrocarbon stream ruptures[31]. Besides having a significant negative effect on the environment, they might cause serious harm to persons, severe property damage, and even death[31]. Fortunately, many of the Sulphur compounds contained in crude oil are also major contributors to high-temperature refinery corrosion. Over the years, a lot of research has been done to figure out how different kinds of high-temperature sulphide corrosion work. Because of the link between corrosion rates and how long things last, it is possible to make very accurate predictions about how long they will last [30].

C. Corrosion caused by naphthalene

Naphthenic acid, one of the most frequent corrosive agents in crude oil, is one of the most aggressive and has a variety of additional impacts on refinery equipment [32]. To combat the erosion caused by naphthenic acid, it is necessary to first comprehend the structure and behavior of these compounds. As an oil field ages, biodegradation sets in, and with it, a changed naphthenic acid structure. However, as they progress in sophistication, they grow more belligerent. Naphthenic acid causes corrosion in carbon steel between 210oC - 240°C, with the maximal activity temperature occurring at 370°C [33]. Because naphthenic acid decomposes at high temperatures, corrosion is limited to a maximum of 430oC. Naphthenic acid corrosion has been shown to take place solely in the liquid state [34]. It has also been suggested that the amount of Sulphur and naphthenic acid in crude oil has an effect on the rate of corrosion. It has been the subject of extensive research in a number of studies, as shown in Figure (4) [35]. Predicting how naphthenic acid will corrode is hard because of the complex interactions between the type of crude oil, temperature, flow rate, type of alloy, surface state and Sulphur contented [36].

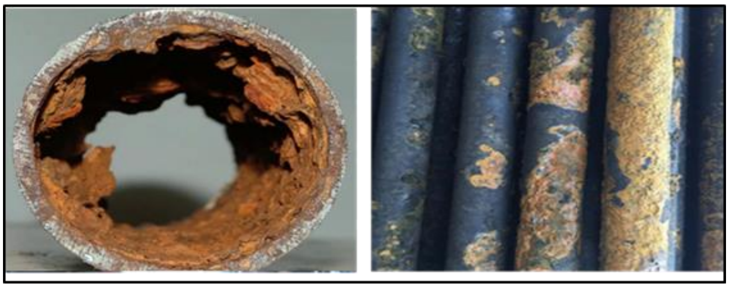

Fig. (4): Example parts of naphthalene corrosion in refinery units [35]

D. Corrosion caused by H_2S

Despite the fact that both CO_2 and H_2S are dissolved in water inside natural gas, the quantity and concentrations of both chemicals may vary substantially depending on the sample. When carbon dioxide is the source of corrosion, a condition identified as " uniform corrosion" develops. Acid corrosion is the condition that occurs when H_2S causes corrosion[37]. H_2S corrosion induces a breach in the metal, releasing H_2S gas into the surrounding surroundings and inflicting substantial environmental harm as well as health dangers to site employees. Temperatures and pressures in equipment are crucial in avoiding corrosion[38]. High temperatures accelerate hydrogen sulphide corrosion; when the distillation unit reaches 210 °C or higher, the quality of the distillate starts to degrade, and the consequences are particularly visible in drilling pipelines used in the oil industry. Pressure lowers the acidity of H_2S, improves its solubility in water, and lessens the danger of H_2S corrosion by slowing the rate of heat loss[39]. Temperature, flow rate, exposure length, H_2S partial pressure, salt levels, metallurgy, and the kind of deposits on the mineral surface have all been identified as factors that inspiration rate and performance of H_2S corrosion in refinery. Figure (5) shown H_2S corrosion in several of the components. Because the different components that influence hydrogen sulphide corrosion are interrelated, it is impossible to isolate the effect of any one component on this occurrence[40]. However, the oil and gas industry has conducted extensive studies on H_2S corrosion [41].

Fig. (5): Corrosion pipe caused by H_2S [40]

E. CO_2 corrosion

Carbon dioxide corrosion is common form corrosion in the petroleum industry, and is responsible for more than 62% of failures. Investments in CO_2 erosion prevention represent 10%-30% of the total budgets of refiners and fossil fuels[42]. The CO_2 corrosion process includes the following stages that have been extensively studied in order to gain a comprehensive understanding of it. The first stage is the dilution of CO_2 with the water content of the crude oil producing carbonic acid. As for the second stage, it is dissolving the metal surface, releasing iron ions and creating hydrogen gas, and it is called (anodic and cathodic reactions)[43]. Changes in temperature, CO_2 partial pressure, and type of flow affect the corrosion properties of carbon-dioxide and the carbonate layer in it[43].

F. Ammonium disulfide corrosion (NH_4HS)

If nitrogen is present in the feed phases, NH_3 can be given as neutralizer or generated in the reactors. Since NH_3 reacts with H_2S to form NH_4HS, it must be added to the mixture to neutralize the product[44]. Carbon steel has prevalent metal in oil refinery, and is also the most displayed to NH_4HS corrosion, which can cause significant corrosion at many points around the refinery, but will primarily damage corrosion and water treatment tools[45]. It has been seen that every 1% increase in the concentration of NH4HS makes carbon steels more likely to rust badly. Figure (6) shows that increasing the speed from 3.4 m/s - 6.4 m/s increased the wear rate of carbon steel by 40% - 64%, which poses a threat to worker safety. Bubbles on the tape surface are one of the most visible indicators of NH_4HS[46].

Carbon steel can only be taken out of NH_4HS after it has rusted and broken up. At that point, water must be forced through the exit because there is no solid chemical treatment available at the moment. Once the protective coating is stripped away, there are a few things that need to be rectified before any more treatment can be done to lessen the environmental damage caused by NH_4HS[47].

Fig. (6): Corrosion caused by NH4HS [46]

G. Ammonium chloride-induced corrosion (NH_4Cl)

One of the most common reasons for the breakdown of machinery and pipes in the modern petroleum refining sector is corrosion caused by ammonium chloride. Corrosion caused by NH_4Cl has a catastrophic impact on refineries because of the associated expenses of equipment, operation, and maintenance[48]. Corrosion can also mess up the refinery's structure and make it harder for equipment to work as it should. Corrosion caused by NH_4Cl may be seen on pipes and other metal components in places like drainage and water treatment plants, ore distillation tower devices, and fractionation stages for heat exchange units[49]. Under the combined action of chlorides and sulfides, the usage of steel materials has already had inconsistent results, with some studies indicating that stress corrosion cracking and breaking have occurred. So far, only nickel alloys have shown good results in these areas because ammonium chloride contains hydrochloric acid and a weak base (NH_3). It is classified as acid salt, and its corrosion is worse near the condensation point of water, when NHCl concentrations are very high[50]. An indication of corrosion cracking brought on by the NH_4Cl layer is viewed in Figure (7), where, carbon steel formed after 12 hours of immersion in (10%, 20%) NH_4Cl resolutions, respectively[51]. The main key elements must be addressed for NH_4Cl corrosion:

- The temperature and concentration of NH_3 and HCl.

- Based on NH_3 and HCl concentrations, NH_4Cl salts may condense from increasing streams as they cool and harm tubes and devices above the water's boiling point.
- Due to the fact that NH_4Cl salts are very acidic and rapidly absorb water, even minute quantities of water may result in severe corrosion.

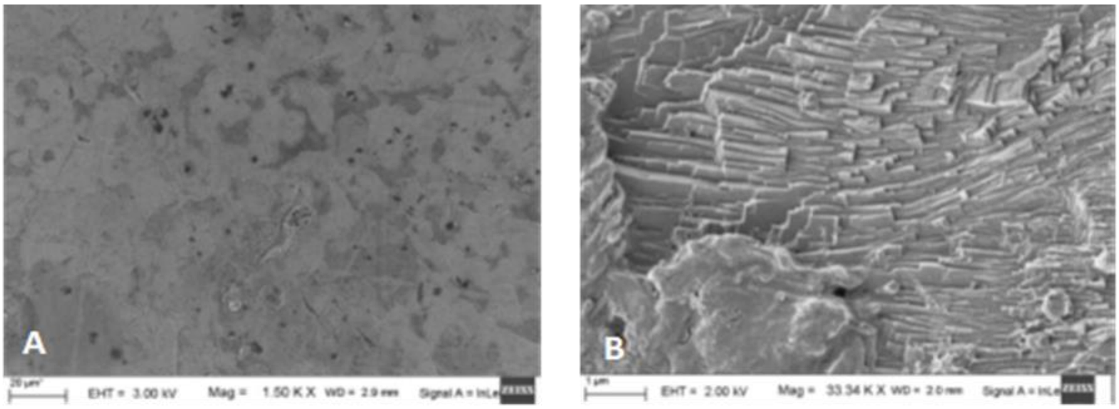

Fig. (7): Carbon steel corrosion after 12 hours of immersion in (10%, and 20%) NH4Cl solutions [51]

5. Corrosion Treatment Methods

Implementing corrosion mitigation measures, such as coating or injecting corrosion inhibitors, into refinery design is essential to safeguard metallic equipment from corrosion in a harsh environment[52]. Especially as the market continues to push up demand for oil and as many oil fields approach the middle and late phases of development, the materials and composition of crude oil have a direct impact on the types of corrosion that may occur and the wear that can occur on oil refining equipment. Deteriorations in crude oil quality, Sulphur content, salt content, heavy metal content, and acid value have all contributed to a rise in equipment corrosion. When you include in evident and observable material losses, it's easy to see why metal corrosion is such a concern throughout the globe[53]. Furthermore, due to metal corrosion's impact on the human element, which may result in severe injuries and even death, cost-effective and efficient protective solutions have become an absolute need. Corrosion prevention methods may be broadly categorized as follows:

5.1 The refinery designs

Corrosion-causing elements should be taken into account during strainer design. By analyzing the geometry of the apparatus, one can regulate the flow rate of the fluid and prevent buildups of acidic water. Additionally, it is crucial to choose a construction material that can withstand the severe conditions inherent to refinery operations. Polymeric materials and compounds are widely used in the refining industry. The strong chemical resistance of these materials is seen in their ability to withstand exposure to many different gases and solvents. It is often believed that polymers lack both the heat resistance and mechanical characteristics. Polymers chemically breakdown at high temperatures and become brittle when cooled to low ones. As a consequence, the goals of the refinery's processes dictate the kind of polymeric materials and groups that are used. A corrosion monitoring system, such as electrical resistance sensors, must be deployed at various points around the refinery to show the corrosion condition in real-time[54].

5.2 Coating

Metals that have been painted or coated with organic compounds may be more resistant to corrosion from the effects of atmospheric gases[55]. Coatings may be sorted into several categories depending on the polymer that was used to make it. Corrosion is stopped dead in its tracks by the coating's ability to regulate electrochemical properties or establish a buffer zone between the metal part and the environment. Since it is resistant to heat, wear, pitting, and erosion, it may be employed under figure (8) shown crude oil conditions[55].

Fig. (8): Corrosion protection by coatings

The following are examples of organic coatings that are often used:

- Coatings consisting of alkyds and epoxy esters that, once dry, encourage the formation of an insulating layer.
- Coatings made of two components urethane.
- Rubber coatings consisting of polymer compositions of vinyl or polystyrene.
- Water soluble coatings.
- Coatings with high solid content.
- Powder coatings.

5.3 Cathodic

During the cathodic protection process, the surface of the metal is changed so that it becomes the negative electrode of the electrochemical cell[56]. This eliminates the possibility of corrosion of the metal in the first place. This technology is used more often in petroleum refineries so that pipelines or underground tanks can be protected from potential hazards[57]. Carbon steel, stainless steel, and aluminum are just some of the metallic materials that might benefit from cathodic protection. Refineries often employ above-ground storage tanks to hold petroleum products, and these tanks are coated with a cathodic protective coating to prevent corrosion as shown in figure (9). Pure hydrocarbon liquids, as a rule, do not contribute to corrosion, which means that the internal surfaces do not need protection against corrosion[58].

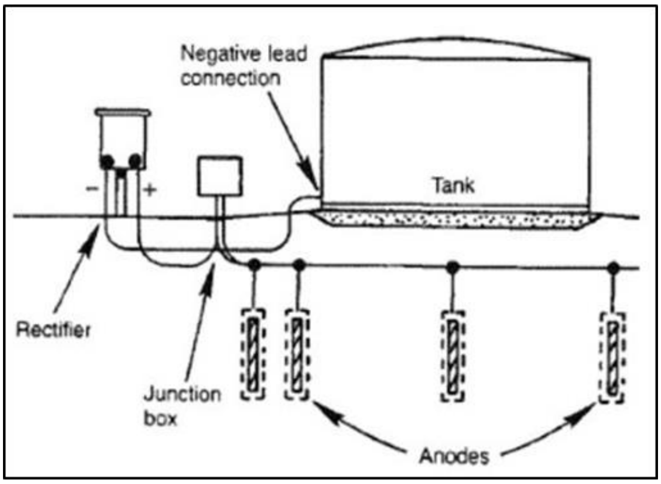

Fig. (9): Anode bed installation

5.4 Inhibitors

Corrosion inhibitors prevent a metal's decomposition when they come in touch with corrosive metal or air[59]. It is possible that the inhibitors work by absorbing themselves on the surface of the metal and creating a protective layer there. Dispersion methods can be used to apply these compounds either as a solution or as a protective layer, both applications are possible[60]. The ability of the inhibitor to reduce corrosion is contingent upon the following factors:

- Altering the conductivity of the anodic or cathodic polarization state.
- Reducing the amount of ionization that occurs at the metal's surface is the goal.
- Bringing about an increase in the external resistance value of the metal.

Refineries, drill rigs, chemical factories, and water treatment plants are some of the largest consumers of corrosion inhibitors. Corrosion inhibitors are helpful because they may be applied directly to metals in the field to stop rusting and corroding in their current locations[61].

6. Conclusions:

Corrosion expenses account for about 25% of the overall breakdown costs in the global petroleum sector. Consequences will worsen without management, causing significant damage to industry and the economy. Refinery units, the physical and chemical principles of corrosion in refinery units, causes of corrosion, corrosion processes, and corrosion mitigation strategies are all described in this article. According to the study's findings, corrosion in refineries is a problem that has been given less attention in the scholarly literature than other forms of corrosion in the petroleum sector. Novel nanomaterials, ultra-hydrophobic coatings, and efficient heat-resistant corrosion inhibitors are all areas in need of more research, as is the development of reliable corrosion prediction models for refineries.

The Critical Gaps in Research:

1. Refineries have challenges when it comes to obtaining quantitative wear data, correlating it with operational and process parameters, and accurately predicting the position of wear in real time[62].
2. Experiments conducted in the lab provide the basis for the vast majority of today's prediction models; nevertheless, these results may not be an accurate reflection of circumstances in the field.
3. Future research should focus on developing efficient corrosion inhibitors that are safe for the environment, include no harmful compounds, and are naturally degradable in light of many rules set in place by the government governing the usage of hazardous materials.

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