

Esraa Razaq¹, Shaymaa Abbas Abdulsada^{2*}

^{1,2} Department of Materials Engineering, Faculty of Engineering, University of Kufa, Iraq

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Zastita Materijala X (X)
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Effect of Corrosion Inhibitors on Internal Corrosion in Oil Pipelines: A Brief Review

ABSTRACT

The oil and gas industry primarily relies on pipelines to transport crude and refined petroleum, so transportation of crude oil is mostly handled by pipelines. In view of this, it is impossible to prevent the pipeline surfaces from being continuously exposed to corrosion sources, such as contaminants that contain traces of chromate and sulfur, which can cause corrosion to occur on the pipeline surfaces. It is known that corrosion inhibitors are chemicals that are used in low concentrations for the purpose of reducing or preventing corrosion. The effectiveness of an inhibitor is determined by its ability to react with a metal's surface and produce a protective coating that reduces or prevents corrosion by reacting with the metal's surface. A review of corrosion mechanisms in oil pipelines is presented in this article, along with a description of how corrosion inhibitors can be selected according to the corrosion mechanisms in oil pipelines.

Keywords: Pipelines, Corrosion, Green inhibitors, Carboxylates, Oil.

1. INTRODUCTION

There is a natural tendency for materials, especially metals, to corrode when they react with their environment. Though the mechanisms by which this phenomenon occurs and the consequences that it causes may differ from one another, it is a phenomenon that affects both metallic and non-metallic materials. Corrosion of metallic materials, or rust, is the most common form of corrosion. Iron, in reaction with oxygen and moisture in the air, forms iron oxide (rust). Polymers, for instance, are affected by degradation, which is a type of corrosion. It is important to note that polymers can also degrade if exposed to UV radiation, heat, moisture, and chemicals, in addition to degradation caused by UV radiation, heat, moisture, and chemicals. Even though ceramics are chemically resistant, they may degrade in aggressive environments because of mechanical wear, thermal shock, and chemical attack, despite the fact that they

are chemically resistant. The other type is concrete corrosion, as it is possible for steel reinforcement in reinforced concrete structures to corrode if it is exposed to corrosive chemicals, chloride ions, and carbonation over time. Due to this, the concrete may crack and crumble as a result [1-13]. As mentioned above, the corrosion of metal occurs as a result of chemical reactions between the metal and the environment around it, which causes the metal to slowly disintegrate over time as the environment around it changes [14,18]. As innovative gas fields develop, it is critical that we have the ability to move damp, unprocessed indigenous gases through pipelines and into other inaccessible areas in order to facilitate the advancement of these fields. The importance of understanding corrosion and the methods for preventing it, because of this, cannot be overstated both in terms of safety and economics. Due to the flow of oil inside pipelines, as well as the fact that the pipelines are buried underground, oil pipelines are exposed to internal corrosion as well as external corrosion due to the fact that they are buried underground [18-23].

The use of pipelines for oil and gas delivery is widely recognized as one of the most cost-effective

* Corresponding author: Shaymaa Abbas Abdulsada

E-mail: shaymaa.radhi@uokufa.edu.iq

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and safest methods. It is still necessary to evaluate corrosion and develop the best mitigation techniques for carbon steel pipelines because they are prone to corrosion. As one of the primary means of transporting oil and gas, pipelines have many advantages, including their low operating costs, quick and convenient operations, and capacity to transport large amounts of material. There are a number of pipelines around the world that are unfortunately subject to both internal and exterior corrosion, which could have a significant negative impact both economically and environmentally in the long run [21-26]. Oil pipelines transfer liquid petroleum products from one location to another. There are four types of oil pipelines, (1) gathering pipelines, which transport oil over short distances with pipe diameters ranging from 10.2 to 30.2 cm, (2) feeder pipelines, which transport oil product from oil storage tanks or processing plants to gearbox pipelines and are typically larger than gathering lines. (3) transmission pipelines, in addition to the smaller diameter pipelines, these are also used for transporting oil and natural gas over longer distances; between provinces or countries, and (4) distribution lines can be up to 122 cm in diameter and deliver crude oil from production to ex-

port or consumption points. Corrosion in crude oil pipelines is one of the most serious issues related with the presence of water and contaminants such as chlorides, sulphates, CO_2 , and H_2S dissolved gases. One method for preserving interior oil pipes from corrosion is to use corrosion inhibitors [27-28].

Corrosion inhibitors are one of the methods used to reduce corrosion in petroleum industry. To ensure optimum inhibition, the inhibitors must be supplied at concentrations greater than a particular minimum. There are numerous techniques for combating corrosion, such as cathodic protection, organic coatings, and the use of high-quality corrosion-resistant alloys, but film-forming inhibitors are still widely regarded as the unrivalled method of defence for mild steel in an acid environment. Film-forming inhibitors are used in industries to build a molecular layer directly on the steel surface and an aliphatic tail as a second layer of hydrocarbon to prevent water from touching the steel surface and causing corrosion. All forms of internal corrosion that are anticipated to occur in pipelines are schematically summarised in Fig. 1 to aid in understanding of the various forms of internal corrosion caused by metal loss or cracking mechanism, which will be covered in more detail later [29-43].

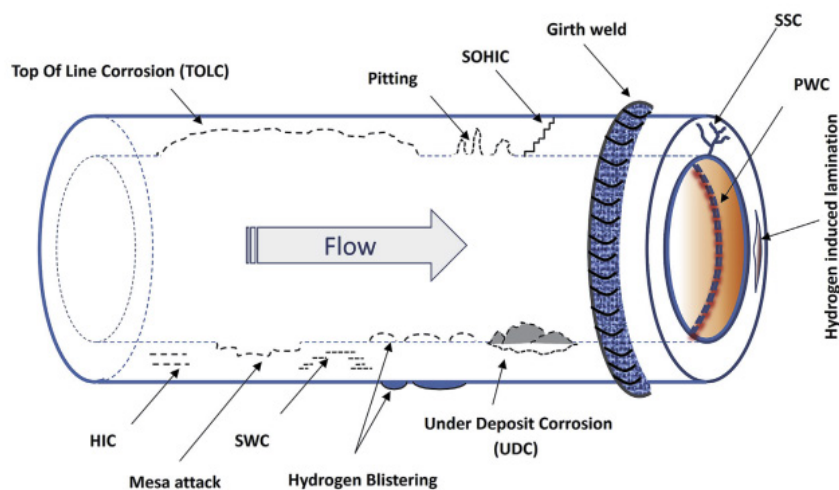


Fig. 1. Various types of internal pipeline corrosion in hydrocarbons [43].

2. CAUSES OF OIL FIELD CORROSION

In oil fields, corrosion can often be traced back to the use of drilling fluids that penetrate into the crude oil that is going to be transported later in the process. These fluids include all of the following [44]:

1. In certain sectors, organic acids are also present, such as acetic acid, which can

cause CO_2 containing devices to corrode faster compared to others. There are hydrocarbon phases; oils with different compositions; and gases like ethane and methane.

2. There are dissolved salts such as calcium carbonate, barium sulphate, sodium sulphate, and sodium chloride in the produced

water, which can induce scaling. Water injection can cause water breakout and souring, as well as scaling due to chemical mixing and hydrogen sulfide generation.

- There are several acids that can dissolve in water and generate corrosive electrolytes, such as carbon dioxide and hydrogen sulphide, which can produce acidic gases.

3. CORROSION MECHANISM IN OIL PIPELINES

Metal corrosion can be considered as an environmental element that is characterised as the unintentional destruction and degradation of working pipelines in an internal or external environment, as a result of chemical, electrochemical, or biochemical contact with the environment. The process of corrosion, which occurs when chemical or electrochemical reactions occur during the interaction between metallic materials and the environment, is a deteriorating attack on metallic materials. Fig. 2 depicts some types of rusting [45].



Fig.2. Different forms of Corrosion [45]

As far as corrosion in oil and gas refineries and related industries is concerned, there are a number of different forms of corrosion that occur in these facilities. These include microbiologically induced corrosion, erosion, stress corrosion cracking, crevice corrosion, oxygen corrosion, sweet corrosion, and sour corrosion [46]. The material of the pipeline has a significant impact on pipeline corrosion as well. The piping material with its varying roughness is shown in Fig. 3. Certain materials, like steel or steel concrete, will increase the rate of corrosion in the pipeline, while other materials, like PVC, stain-

less steel, and some special alloys, can extend the lifespan of the pipeline [47].

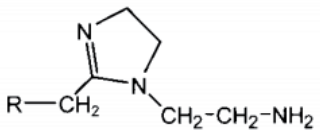
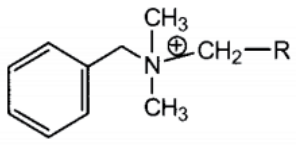
Piping Material	Roughness Factor X
CuNi 90/10	0.9
Steel	1.0
Steel - Old	1.6
Steel - Fouled	2.5

Fig.3. Selection of Piping Materials [47]

4. CORROSION INHIBITORS IN OIL PIPELINES

An inhibitor is a chemical that, when introduced in modest doses, reduces the effective corrosion rate. Inhibitors are classified into four categories based on their mechanism and content. The four categories are barrier layer development, neutralising, scavenging, and environmental change. Temperature and water chemistry are two elements that can influence the blockage of petroleum pipelines [44]. Organic compounds are commonly utilised as corrosion inhibitors in oil field applications, where they are applied in modest amounts (less than 0.1%). Because they adsorb on the steel surface and inhibit both the anodic and cathodic reactions, they are frequently classed as mixed inhibitors. Nonetheless, a lot of inhibitor packages that are sold commercially have a tendency to polarise the steel anodically. Known as filmmaking inhibitors, oilfield corrosion inhibitor chemicals also push adsorbed water molecules away from the surface. For instance, jet fuel, a product with a low water content, uses inhibitor compounds, which only function in this way. Nearly all organic molecules used in oil field corrosion inhibitor packages are strongly polar functional compounds, many of which have a nitrogen basis, such as amines, amides, imidazolines, or quaternary ammonium salts. These compounds also include compounds containing P, S, and O, nitrogen heterocyclics, polyoxyalkylated nitrogen-containing compounds, and salts of nitrogenous molecules with carboxylic acids. It is frequently disputed whether species in the package actually offers protection because, for instance, imidazoline hydrolyzes in water to produce the amide. Some typical molecular structures of inhibitors are illustrated in Table 1 [48].

Table 1: Fundamental chemical structures of inhibitors used in oilfields [48]

Chemical name	Structure
Primary amine	$R-CH_2-NH_2$
Amide	$R_1-CH_2-C(=O)-NH-R_2$
Imidazoline	
Quaternary ammonium ion	
Polyethoxylated amines	$R-N\left(\begin{array}{l} (O-CH_2-CH_2)_n-OH \\ (O-CH_2-CH_2)_n-OH \end{array}\right)$

Inhibitor molecules form a barrier between the corrosive water phase and metal surfaces (Fig. 4) [49].

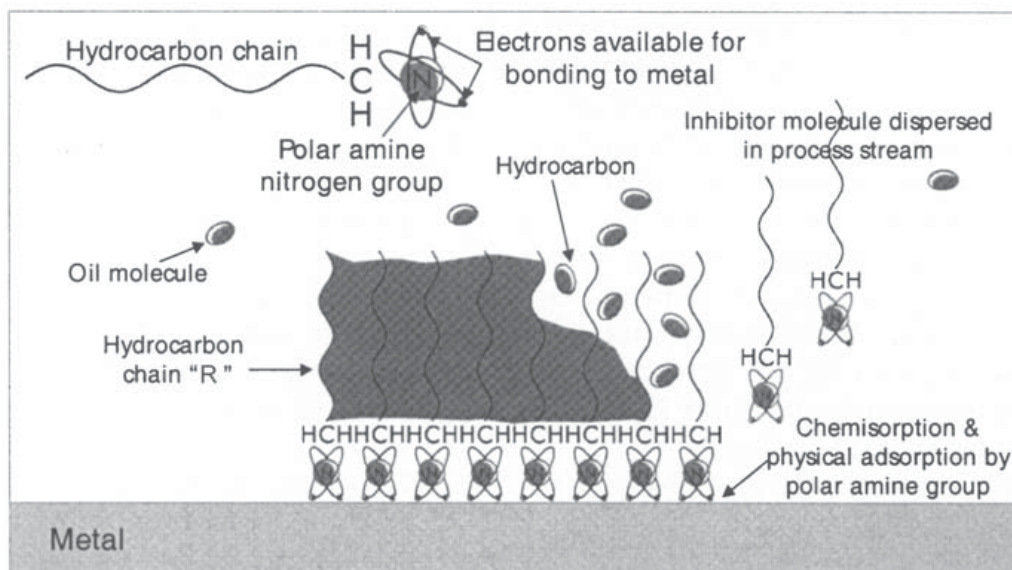


Fig. 4. Schematic illustrating the activity of an oilfield corrosion inhibitor [49].

4.1 Green Inhibitors

Green inhibitors, also known as environmentally friendly inhibitors, are low-cost and renewable. Corrosion inhibitors are derived from natural plant tissues such as fruit and leaf peels. When used at extremely low concentrations, green corrosion inhibitors protect the metal surface from corrosive environments. By changing the anodic or cathodic re-

action kinetics, the plant can speed up the diffusion of hostile ions that contact with the metal surface. Adsorption can also accelerate corrosion on metal surfaces. To form a film layer, progressively increase the electrical resistance of the metal surface. Plant extracts can be easily prepared using low-cost solvents such as water or ethanol. When the extracts have low water solubility, ethanol solvents are used.

To mention a few naturally occurring substances, extracts may include tannins, pigments, steroids, flavonoids, flavones, and essential oils [50].

4.2 Organic Inhibitors

Due to their broad temperature effectiveness, compatibility with protected materials, high solubility, and relatively low toxicity, organic corrosion inhibitors are frequently employed in industry. These substances function as both anodic and cathodic inhibitors. Inhibitors of cathodic corrosion push the corrosion potential down and stop or slow down the cathode's processes (hydrogen evolution and reduction). Anode corrosion inhibitors, on the other hand, work with the metal cation to create an insoluble hydroxide, block active sites on the metal surface, and shift the corrosion potential in the direction of positive values. These actions stop the metal from further oxidising (dissolving), which lowers the rate of corrosion. It is very crucial to use the proper amount of an anode inhibitor, because insufficient concentration to cover all the active sites might lead to localized corrosion which is difficult to detect. Mixed inhibitors offer the most protection since they influence both cathodic and anodic reactions [51].

4.3. Inorganic Inhibitors

Inorganic corrosion inhibitors include salts of zinc, copper, nickel, arsenic, and other metals, with arsenic compounds being the most widely utilised. When these arsenic compounds are combined with the corrosive solution, they scrape the cathode cell on unprotected metal surfaces. The plating reduces the percentage of hydrogen ion interchange due to the creation of iron sulphide between the steel and the acids, which act as an impediment. The reaction between acid and iron sulphide is characterised as a dynamic process. There are advantages and disadvantages to utilising inorganic inhibitors. They have the benefit of working well at high temperatures for extended periods of time and costing less than organic inhibitors. Inorganic inhibitors are more prone to lose their hold in acid solutions stronger than 17% hydrochloric acid, are more difficult to mix, and may produce hazardous arsine gas as a byproduct of corrosion [52].

4.4. Carboxylates

By forming a hydrophobic coating on the metal surface through the adsorption of a carboxylate

group (Lewis base) on Lewis acid, carboxylates can offer corrosion protection. While short-chain fatty acids may encourage corrosion, long-chain fatty acids—like oleic acid, soy fatty acid, TOFA, and polymerized fatty acids—like dimer acids, have long been known to reduce corrosion in a variety of applications. Dicarboxylic acid and its derivatives, known as dicarboxylic ester-acids, have been researched as useful additives for stopping metal corrosion in compositions. Rust development in lubricating oils can be effectively reduced by a synergistic combination of amine derivatives derived from succinic anhydride and tetra propenyl succinic acid. It should be mentioned, though, that the dicarboxylic acids have a propensity to precipitate when Ca^{2+} or Mg^{2+} ions are present, which would negate their ability to prevent rust [53]. However, an outer negative surface can be generated by carboxylates, and it is possible that the amine carboxylate based inhibitors, Fig. 5, could form a film on the steel surface by associating nitrogen with iron atoms. Consequently, a repulsive force between the carboxylate and the chloride in the media or environment is created. The repelling force is significant at low concentrations of chloride and sulphate, but it becomes less at higher concentrations. Therefore, it is probable that sulphate or chloride seeped into the steel, which is why the film's efficiency decreased [54].

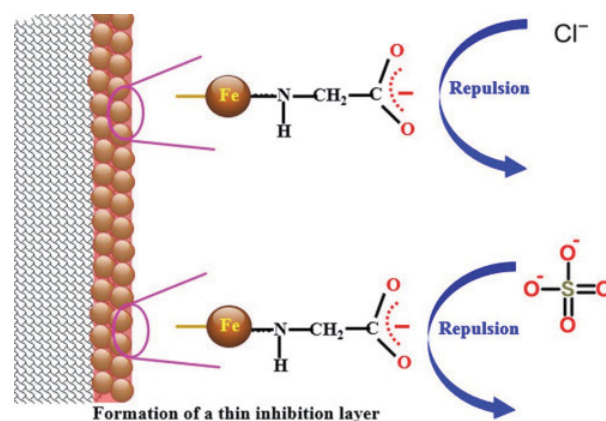


Fig. 5. Proposed mechanisms for the inhibition of corrosion of carbon steel by the investigated amine carboxylate based inhibitors [54].

4.5. Amines

Film-forming amines, or fatty amines, are fatty acid derivatives. These components, which have poor alkaline characteristics, have been neutralised by the use of organic acids in the formulation of the

corrosion inhibitor or by the action of acid gases in the fluid, converting them to cationic components with positive charges. Because electrons are released on the cathode as a result of corrosion, these cationic components are attached to the cathode and form an oily coating on the metal's surface, preventing acid gases from contacting the cathode while releasing hydrogen. Corrosion inhibitors are classified into functional groups with polar heads, such as fatty acids, amines, imidazoline, oxyalkylated amines, oxygen, sulphur, or phosphorus, and quaternary amine salts. Furthermore, corrosion inhibitors with a long chain of hydrocarbons (typically C14-C18) cling well to the surface [55].

5. CONCLUSION

Overall, it can be concluded that corrosion is an issue of great importance in the oil and gas industry, particularly the pipeline industry, where it can lead to economic losses as well as environmental damage. It is critical to ensure pipeline integrity and safety by understanding the mechanisms of corrosion and applying effective mitigation techniques, such as the use of corrosion inhibitors, in order to prevent corrosion in oil pipelines. A variety of corrosion inhibitors are available, including green inhibitors, organic inhibitors, inorganic inhibitors, carboxylates, and amines, and each of them has its own unique protective mechanism for preventing corrosion in pipelines. The key to successful corrosion prevention is selecting the right inhibitor based on the conditions in the environment and the type of system being treated. It is vital that the oil and gas sector uses corrosion inhibitors and follows regular maintenance methods in order to ensure safe and efficient transportation of oil and gas through pipelines.

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IZVOD

EFEKAT INHIBITORA KOROZIJE NA UNUTRAŠNJU KOROZIJU U NAFTOVODIMA: KRATAK PREGLED

Industrija nafte i gasa se prvenstveno oslanja na cevovode za transport sirove i rafinisane nafte, tako da se transport sirove nafte uglavnom obavlja cevovodima. S obzirom na ovo, nemoguće je sprečiti da površine cevovoda budu kontinuirano izložene izvorima korozije, kao što su zagađivači koji sadrže tragove hromata i sumpora, koji mogu izazvati pojavu korozije na površinama cevovoda. Poznato je da su inhibitori korozije hemikalije koje se koriste u niskim koncentracijama u svrhu smanjenja ili sprečavanja korozije. Efikasnost inhibitora je određena njegovom sposobnošću da reaguje sa površinom metala i stvori zaštitni premaz koji smanjuje ili sprečava koroziju reagujući sa površinom metala. U ovom članku je dat pregled mehanizama korozije u naftovodima, uz opis načina izbora inhibitora korozije prema mehanizmima korozije u naftovodima.

Ključne reči: cevovodi, korozija, zeleni inhibitori, karboksilati, nafta.

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The ORCID Ids of all the authors are as follows:

1. Shaymaa Abbas: <https://orcid.org/0000-0001-7006-2950>

2. Esraa Razaq: <https://orcid.org/0009-0008-3963-4349>