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Inhibition of Corrosion: Mechanisms and Classifications an Overview

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Inhibition of Corrosion: Mechanisms and Classifications an Overview

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Theoretical basis

The Great damage of the corrosion progression have grown into a problematic of global importance, because its reasons plant shutdown, wastage of very important incomes, product corruption, efficiency decreasing, expensive repairs, and costly overdesign. Corrosion also endangers the safety and obstructs the progression of the technology, where corrosion can destroy the substances by reaction with their surroundings.

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The economic costs of corrosion are obviously enormous (Ali *et al.* 2019) [1]. Like another natural risks for example floods, horrible weather, and earthquakes. It can also effect and cause hazardous damages to the infrastructure, waterways, ports, railroads, hazardous materials storage, clean water, drain systems, electricity services, automobiles, boats, aircrafts, refining of the petroleum, defense, gas transmission pipelines and highway bridges. Corrosion also influences the production of pharmaceutical, petrochemical and chemical materials (El Bribri *et al.* 2013) [8].

Therefore, to minimize corrosion of minerals, materials called corrosion inhibitors have been used that can be defined as a chemical material which used to stop or reduce the corrosion when mixed with the minerals in very few amounts and do not react with the environmental components. These substances can be used in any state solid, liquid or gas such as concrete, or paints (as a solid state), solvents, or aqueous solutions (as a liquid state), and water vapor (as a gaseous state) (El-Haddad 2013) [9]. Figure 1 and 2 show corrosion in oil and gas pipeline.

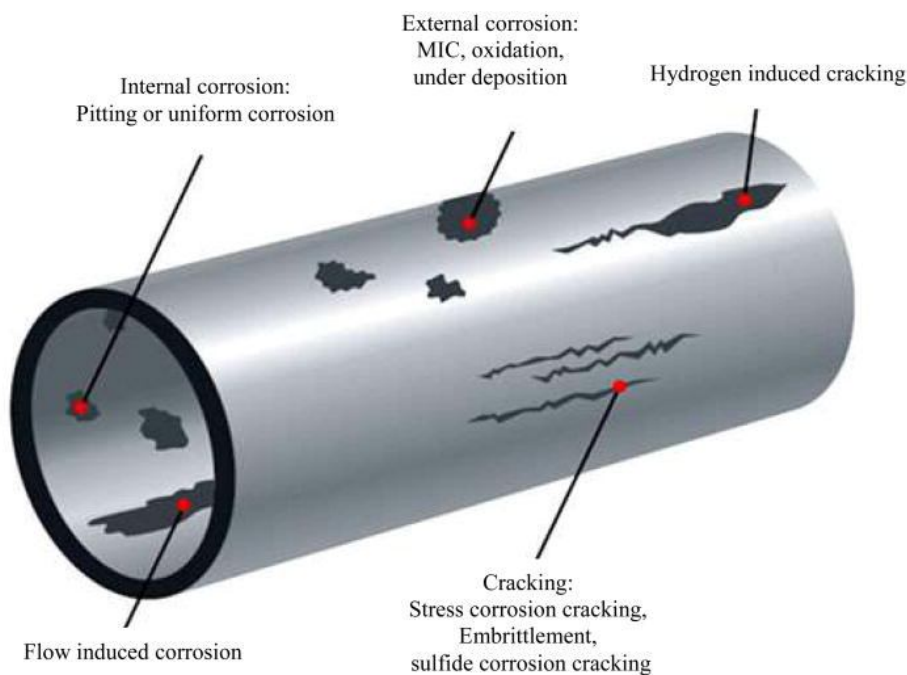


Figure 1. Oil pipeline corrosion (Brien 2014) [5].

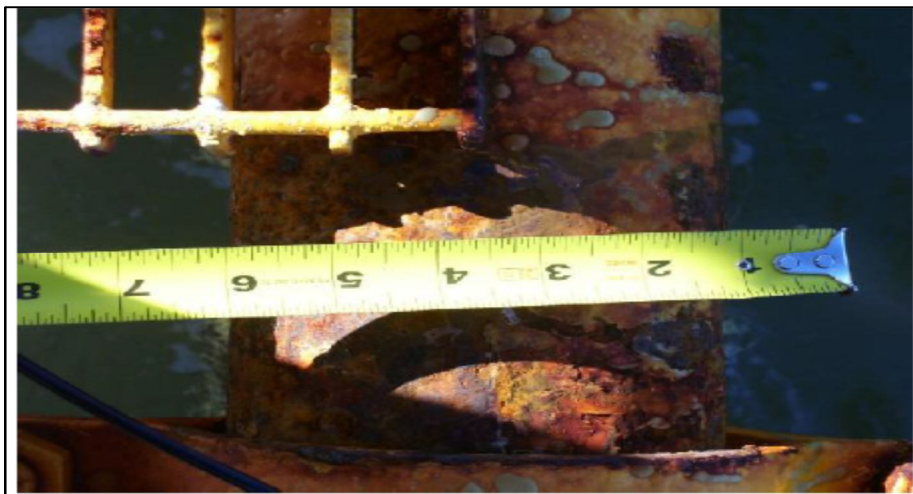


Figure 2. Gas pipeline corrosion (Arsenault 2014) [2].

Classification of Corrosion Inhibitors

The usage of different types of inhibitors to decline the speed of the corrosion progressions is significantly important. As it was mentioned above, corrosion can affect many of life facilities, and then the corrosion inhibitors have been utilized in many of these facilities to reduce the corrosion influences such as petroleum refineries, Water purification plants, additive industries, gas and oil plants, chemical industrial, and heavy industries, (Van Delinder 1984)[17]. There are a large number of studies on the subject of corrosion inhibitors (Hakeem 2016) [10].

Inhibitors can be slowing down corrosion processes by (Boffardi 1987) [6]:

- i. Raising the anodic or cathodic polarization actions (Tafel slopes)
- ii. Decreasing the spreading of ions on the surface of the metals.
- iii. Enhancing the properties of the metallic surfaces by raising their electrical resistance.

Inhibitors have been classified differently depending on various parameters, of them:

1. Classification of inhibitors depending of their chemical functionality

- i. Inorganic inhibitors: it must have the possibility of oxidation of metals, creating a passive layer on its surface that protects it from corrosion, only the negative anions of crystalline salts such as calcium metasilicate, sodium chromate, phosphate, molybdate, and zinc oxide are involved in reducing metal corrosion.

- ii. Organic inhibitors: should be structurally high, have π bonds, have the active center or group. These inhibitors including:
- a. Organic anionic: such as mercaptobenzotriazole, sodium sulfonates, and phosphonates which are utilized normally to make cool water (as antifreeze substances).
 - b. Organic cationic: this type of inhibitors generally has active side as a large aliphatic or aromatic portions with amine groups holding positive charge. They are either in liquid state or solid state like a wax. The most famous organic cationic inhibitors are sodium benzoate, and sodium cinnamate (Milorad 2010) [12].

2. Classification of inhibitors depending of their effects on the electrochemical reactions involved in the corrosion process

Corrosion inhibitors can be divided into three main categories according to their effect on the electrochemical reaction. Some inhibitors influence the cathodic process and others inhibit the anodic reaction. While other inhibitors could affect both the cathodic and anodic processes simultaneously. Anodic and cathodic processes are included in the electrochemical processes of the metallic corrosion. The corrosion inhibitors work mainly by either reduces or stops the anodic or cathodic processes and sometimes both of them. According to that there are three main categories of inhibitors as shown below:

- i. Cathodic type inhibitor: This kind of corrosion inhibitors work by enhancing the cathodic process when adding them to the metals, which lead to the reducing of the cathodic reaction. The negative offset of the corrosion potential process of the conjugated system causes the decreasing of the cathodic reaction rate then that will lead to the decreasing of the corrosion process respectively. Cathodic inhibitor induces the positive ions to move near the cathode and make a shielding layer around it leading to reduce or stop the cathodic reaction by enhancing the polarization process on the cathode. Figure 3 shows the mechanical influence of cathodic inhibitors to stop the corrosion process.

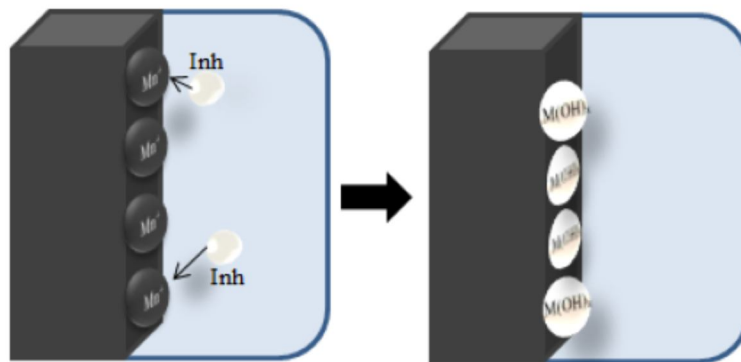


Figure 3. The mechanism of the cathodic inhibitors (Dariva and Galio 2011) [7].

- ii. The second type of inhibitors is the anodic type inhibitor which is work on the same fashion as the cathodic inhibitors but on the anode side. This type of inhibitor works by enhancing the polarization of anodic process and induce the negative ions to move near the anode and encourage passivation which lead to the decreasing of the corrosion amount. Figure 4 shows the mechanism of the anodic inhibitors (Dariva and Galio 2011) [7].

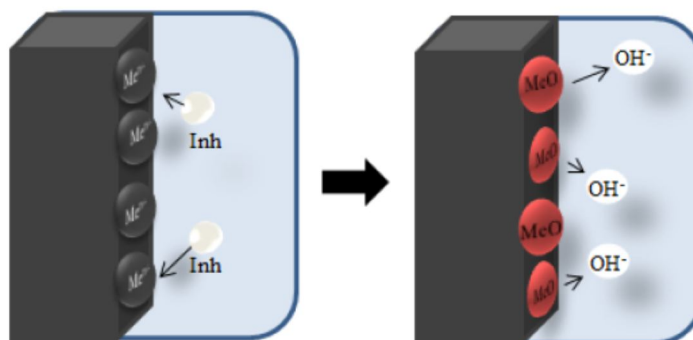


Figure 4. The mechanism of inorganic anodic inhibitor (Dariva and Galio 2011) [7].

- iii. The third type of corrosion inhibitors is the mixed type inhibitors which work by enhancing the polarization for both cathodic and anodic processes follow-on big reducing of the corrosion current (Xiaodong *et al.* 2011) [18].

3. Atmospheric corrosion inhibitors

These inhibitors divided into contact (nonvolatile) and volatile (vapor faze). Contact inhibitors such as substance which is made of metal corrosion protection only in their direct contact with the surface metal. Volatile inhibitors are substances that are relatively easily volatile at normal temperatures, capable for adsorption on the surface of metal, particularly in the gap by protecting it from corrosion. Since the surface of metals under conditions of atmospheric corrosion is always moisture under the membrane that runs corrosion, volatile inhibitors should be able to reduce hygroscopic properties of metal surface or membrane to squeeze out moisture as well as hydrophobic substances.

Inhibitor of the contact number of which is still very big in the industry have found application only nitrites, benzoates, oleate and chromate (Rozenfeld and Persianceva 1985) [14].

Volatile inhibitors are also numerous, and among them are particularly well-known inhibitors based on amines. Of volatile inhibitors are particularly effective nitrite dicyclohexylamine, carbonate and benzoate dicyclohexylamine, monoethanolamine. The duration of the protective effects of volatile inhibitors depends on the tightness packaging. At the appropriate concentration of inhibitor and total isolation from the outside (cellophane and other impermeable material) objects of ferrous metals are not subject to corrosion for 10 years and more (Šluger *et al.* 1981) [15]. The lack of volatile inhibitors is that, their effects cease after removing their steams from the atmosphere surrounding the metal.

Mechanism of Corrosion Inhibition

Inhibition generally outcomes from one or more of the below mechanisms:

- **Adsorption process:** in this mechanism the inhibitors are adsorb on the surface of the metals. The inhibitive process shows typically depends on the amount of inhibitor which covers the metal. The efficiency of adsorbed inhibitors on the metal surface could improve by increasing the coverage area (Thomas 1994) [16].
- **Existence of charge on the metal surface :** in this type of mechanism, the inhibitor adsorbs on the metal surface by electrostatic forces between the charges on the metal surface and dipoles or ions groups of the inhibitor (Raja and Sethuraman 2008) [13].

- **Chemical reaction:** in this mechanism the chemical structure and/or functional group of the inhibitor have an effect. One electron could transfer from the inhibitor to the metal surface to form coordinate bond. Generally, this process is preferred when the metal holds empty electron orbitals of low energy for example transition metals (McCafferty 1989) [11].
- **Interaction between inhibitor and water molecules:** in this mechanism the inhibitors go through replacement reaction with the water on the metal surface resulting elimination of water molecules from the surface of metal. Throughout the inhibitor adsorption, the alteration in interaction energy with water in going from the adsorbed forms to the dissolved form a significant amount of the free energy change on adsorption. That increases the solvation energy of the inhibitor molecules, which is related to the size of the hydrocarbon side in the chemical structure for the inhibitor. Hence the solubility decreases with increasing of the hydrocarbon size which leads to the increasing of adsorption process (Bethencourt 1998) [4].
- **Electrochemical reaction of inhibitors:** Some inhibitors go through electrochemical reduction reaction with the metal surface to form a new compound that exhibits inhibition effect. The inhibitor is added to the metal surface called the primary inhibitor, and the product from the electrochemical reaction called secondary inhibitor. In this type of inhibitive mechanism, the efficiency of the inhibitor might change with the time either enhances or reduces depend to what extend the primary inhibitor effectiveness related to the secondary inhibitor. For instance, sulfoxides ($RS=OR'$) as a primary inhibitor can be reduced to sulfides (S^{-2}) which are more effective as a secondary inhibitor (Bethencourt 1998) [4].
- **Diffusion wall:** in this mechanism the corrosion inhibitor formed a barrier on the surface of the metal and physical prevent any ions or molecules to transfer from and/or to the metal surface and that lead to the decreasing of the corrosion rate. This barrier influences both the anodic and cathodic reactions. Generally, this mechanism works when the inhibitor structure is big such as polysaccharides, proteins, or molecules holding long hydrocarbon chains (Alwash *et al.* 2017) [3].
- **Contribution in the reactions of the electrodes:** Sometimes corrosion reactions include the foundation of adsorbed intermediate compounds with the atoms on the metal surface such as

adsorption of hydrogen in the hydrogen releasing reaction and adsorption of $\text{Fe}(\text{OH})_2$ in the anodic side of iron (Ali *et al.* 2016). The inhibitors might hinder the creation of these intermediates. However the electrode processes may then continue by other pathways by intermediates having the inhibitors. The inhibitors perform as a catalyst in these steps and stay unchanged. Corrosion inhibitors could also delay the speed of hydrogen releasing on the metals by influencing the mechanism of the reaction through increasing the Tafel slopes of cathodic polarization curves. This effectiveness has been detected on iron in the existence of inhibitors for example phenylthiourea, acetylenic hydrocarbons, aniline, benzaldehyde, and pyridinium derivatives (Yousif *et al.* 2015) [19].

Conclusion

Inhibitors are an excellent and easy way to stop the corrosion. They have been used in different application regions because they are easily modified to enhance the inhibition efficiency. This review has focused on the classification of the inhibitors depending on their structure, how the inhibitor could affect on the electrochemical reaction on the metal surface, and atmospheric inhibitors. It also includes mechanism of corrosion inhibition which could help the researchers to choose the best inhibitors for a specific application through deeply understanding the inhibition mechanism.

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