

Review on Corrosion Inhibitors for Oil and Gas pipelines in petroleum industries

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Abstract

The pipeline system in the oil and gas industry is the main tool for transportation of crude and refined petroleum. Therefore, continuous exposure of the pipeline surfaces to sources of corrosion such as impurities that contains sulfur and chromate is totally unavoidable. Employment of commercial corrosion inhibitors are compounds used in low concentration to minimize or prevent the corrosion process. The effectiveness of an inhibitor depends on its ability to react with the surface of a metal to form a protective film which take apart in reducing or providing protection against corrosion. Using of commercial corrosion inhibitors to minimize the corrosion is being restrained due to toxicity towards the environment. The appearance of “green” chemistry has led to the use of plant extracts and fruit and vegetable wastes which have proven by researcher to be good corrosion inhibitors. In the last decade development of ionic liquids (IL) has attracted researcher's attention due to their interesting properties, considered as green and sustainable candidates to replace the traditional volatile corrosion inhibitor. In this review the main focus is dedicated to the different types of corrosion inhibitors, such as the type of chemicals and their application through a novel and comprehensive classification of the inhibitors. Finally, the methods of corrosion inhibitors application are evaluated, and implications in introducing novel corrosion inhibitors are explored aims to provide information for further investigation and research to discover more efficient inhibition measures for protection of oil and gas pipeline in petroleum industry.

Key words: corrosion, Inhibitors, oil and gas industry, pipe lines, toxicity, green, commercial, ionic liquid (IL)

1. Introduction

Corrosion is more than just an inevitable natural process; it is also one of the most serious engineering problems in modern society.(El-Enin and Amin 2015) Corrosion is deterioration of materials by chemical or electrochemical reaction within the working environment. The term corrosion is sometimes also applied to the deterioration of plastics and other non-metallic materials, which are susceptible to swelling, crazing, cracking softening, etc., is essentially rather than electrochemical in nature (Perry and DW 2007) .Among the various methods to avoid or prevent destruction or degradation of metal surface, the corrosion inhibitor is one of the best know methods of corrosion protection and one of the most useful on the industry. This method is following stand up due to low cost and practice method.(Al-Otaibi, Al-Mayouf et al. 2014)

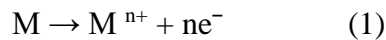
Important researches have being conducted with government investment mainly in large areas such as development construction of new pipelines for shale gas and growth in construction. The focus of these researches has being the inhibitors applications in water and concrete for the protection of metals. (Dariva and Galio 2014). Metal Pipes and casings play an essential role in the production of oil and gas. Sustainable production from a reservoir is highly dependent on the integrity of these downhole strings. One of the significant threats to any well's integrity (based on NORSOK D-010 and ISO 16530) standards is corrosion, which can lead to production shut-down, explosion, and high-risk incidents, as well as the high cost for the wells' workover in case of lack of proper identification, control, and monitoring of corrosion. Many industrial accidents, as well as human and environmental disasters, have been reported as a result of tube or pipes corrosion and poor performance of tubing, further emphasizing the importance of this issue.

In this review we have focused on the chemical inhibition of carbon steel casing and tubing in different media, including completion fluid, acidizing and stimulation fluid, and the production stream. This approach covers the all possible and latest advancements of corrosion inhibitors and their inhibition mechanism have been reviewed from the scientific point of view. Also, their injection, application, and testing have been discussed from the operational and industrial viewpoint. This review also bridges the research findings and the application of pipe line corrosion

inhibitors. To provide a better understanding of the objectives, for the initial parts of this review, corrosion mechanisms and different mitigation methods have been briefly discussed.

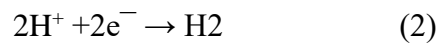
The chemistry of corrosion includes the surface of all metals (except for gold) in air is covered with oxide film. When such metal is immersed in an aqueous solution, the oxide film tends to dissolve. All corrosion reactions are electrochemical in nature. The rate of corrosion process depends on the two conjugate reactions at the metal surface:

A) Anodic reaction:



The anode is the site at which metal is corroded. The metal is dissolved and transferred to the solution as metal ions positively charged. The electrons flow, as electrical current, to the cathode where they are consumed.

B) Cathodic Reaction:



The cathode is the site at which the electrons react with some reducible component of the electrolyte and detached from the metal. The rate of the anodic and cathodic reactions must be equivalent according to Faradays' Laws, being determined by the total flow of electrons from the anode to cathode which is called the "corrosion current", I_{corr} . Since the corrosion current must also flow through the electrolyte by ionic conduction, conductivity of the electrolyte will be influenced by the way in which corrosion cells operate. (Abdel Hamid, Ghanem et al. 2005)

Types of corrosion	Description
Uniform corrosion	Deteriorates the whole surface of the metal and makes the surface thin.
Galvanic corrosion	Occurs with an electrolyte with metals having different value of electrical potentials.
Pitting corrosion	Occurs because of random attacks on particular parts of the metals surface to form pits. The pit acts as the anode ,while the undamaged part of the metal is the cathode.

Stress corrosion cracking	A complex form of corrosion which arises due to stress and corrosive environment.
Corrosion fatigue	A combination of cyclic stress and corrosion.
Intergranular corrosion	Corrosion occurs on or near the grain boundaries of a metal.
Crevice corrosion	Concentration cell corrosion due to the trapping of corrosive liquid between the gaps of the metal.
Filiform corrosion	Concentration cell corrosion on metallic surfaces coated with a thin organic film.
Erosion corrosion	Flow- assisted corrosion which is due to the movement of corrosive liquids on metal surface.
Fretting corrosion	A form of erosion-corrosion which shows the combined effect of corrosion and fretting of metal.

(Chigondo and Chigondo 2016)

2. Types of corrosion in Oil and Gas Industry

2.1 Sweet corrosion (CO₂ corrosion)

Carbon dioxide (CO₂) corrosion has been a recognized problem in oil and gas production and transportation facilities for many years. CO₂ is one of the main corroding agents in the oil and gas production systems. Dry CO₂ gas is not itself corrosive at the temperatures encountered within oil and gas production systems but is so when dissolved in an aqueous phase through which it can promote an electrochemical reaction between steel and the contacting aqueous phase. CO₂ will mix with the water, forming carbonic acid making the fluid acidic. CO₂ corrosion is influenced by temperature, increase in pH value, composition of the aqueous stream, presence of non-aqueous phases, flow condition, and metal characteristics and is by far the most prevalent form of attack encountered in oil and gas production. At elevated temperatures, iron carbide scale is formed on the oil and gas pipe as a protective scale, and the metal starts to corrode under these conditions. CO₂ corrosion can appear in two principal forms: pitting (localized attack that results in rapid penetration and removal of metal at a small discrete area) and mesa attack (a form of localized CO₂ corrosion under medium-flow conditions). Various mechanisms have been postulated for the

CO₂ corrosion process but all involve either carbonic acid or the bicarbonate ion formed on dissolution of CO₂ in water. (Mohamed, A. and Oyekola, P., 2020)

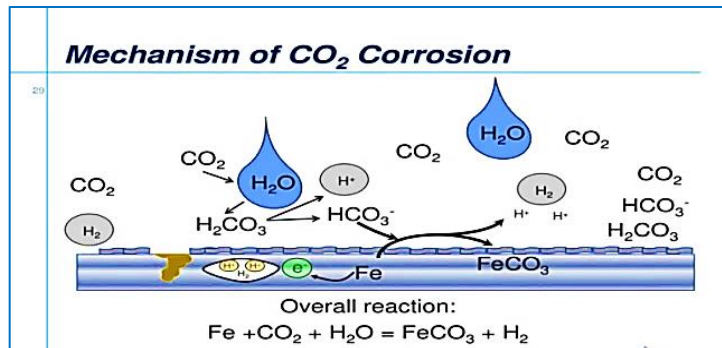


Fig.1 Mechanism of CO₂ corrosion

2.2 Sour corrosion (H₂S corrosion)

Hydrogen sulfide is known to be very harmful in the corrosion of metals or alloys, regardless of its application in oil and gas. In a matter of fact, hydrogen sulfide can be the root of sulfide stress corrosion cracking (SSCC) failure in pipelines. However, hydrogen sulfide is only corrosive when it is dissolved in water, where its solubility is relatively higher than that of carbon dioxide and oxygen. The deterioration of metal due to contact with hydrogen sulfide (H₂S) and moisture is called sour corrosion which is the most damaging to drill pipe. Although H₂S is not corrosive by itself, it becomes a severely corrosive agent in the presence of water leading to pipeline embrittlement. Hydrogen sulfide when dissolved in water is a weak acid, and therefore, it is a source of hydrogen ions and is corrosive. The corrosion products are iron sulfides (FeS_x) and hydrogen. Iron sulfide forms a scale that at low temperature can act as a barrier to slow corrosion. The forms of sour corrosion are uniform, pitting, and stepwise cracking. (Rosenfeld and Marshakov 1964) (Tamalmani and Husin 2020)

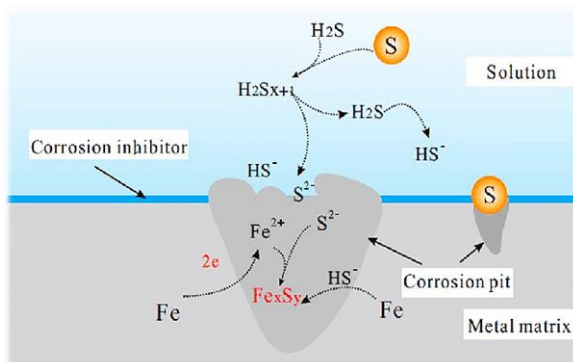


Fig.2 Mechanism of H₂S corrosion

2.3 Crevice corrosion

It's a form of localized corrosion that occurs in holes, fissures, cracks, and other shielded areas on metal surfaces that are exposed to corrosive environments. It happens in areas where metals come into contact with metals or metals come into contact with non-metals, such as gaskets, couplings, and joints. Small amounts of stagnant solution caused by holes, gasket surfaces, Lap joints, surface deposits, and crevices under bolt and rivet heads are all common sources of attack. (Uygunoğlu and Gunes 2015).

Crevice corrosion is a common form of corrosion to which Active passive metals are particularly sensitive. Crevice corrosion is generally observed where small amounts of standing electrolyte solution occur, for example, between flanges, bolts, nuts, and so on (Fig. 3).

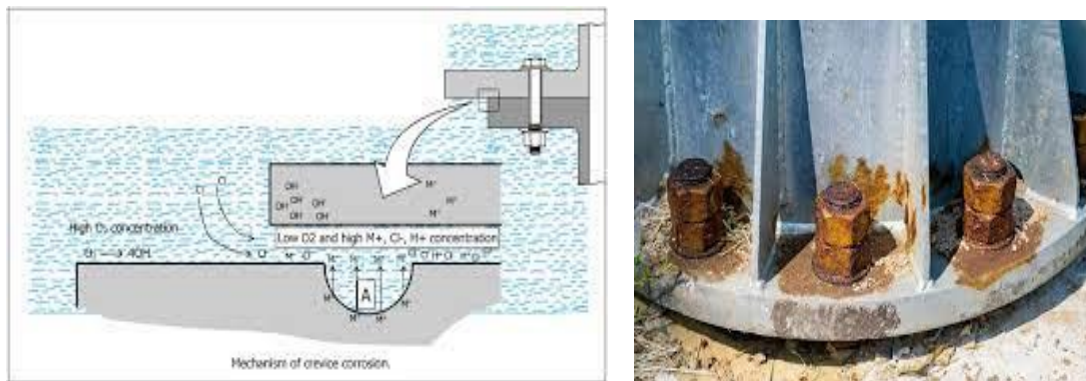
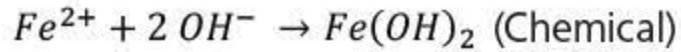
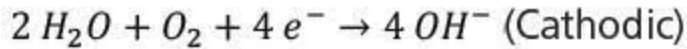
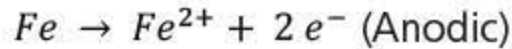


Fig. 3 crevice corrosion between flanges, and bolts.

Crevice corrosion can also occur underneath corrosion products and other deposits and is then known as under-deposit corrosion. The presence of chloride ions is highly conducive to crevice corrosion. The crevice must be wide enough to admit moisture and narrow enough to ensure a standing medium.

The mechanism is represented as follows:

Take, for example, two metal plates (M), which are riveted together and are located in aerated seawater (pH $\frac{1}{4}$ 7). The overall reaction consists of the dissolving of metal M and the reduction of oxygen to hydroxide ions:



Initially, these reactions occur over the entire surface area, also inside the crevice (Fig. 3). After some time, the oxygen inside the crevice will have been consumed due to the absence of flow.

The dissolution process of metal M, however, continues inside the crevice (Fig. 4).

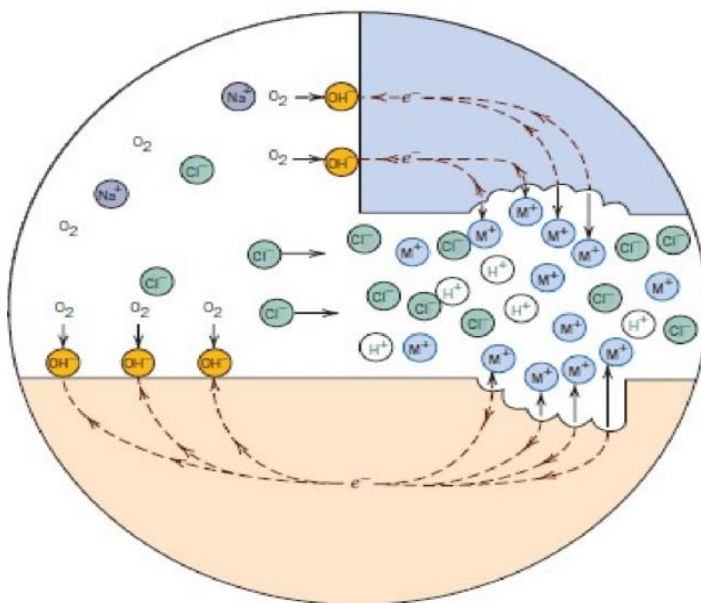


Fig.4. schematic illustration of the mechanism of crevice corrosion

2.4 Erosion corrosion

The erosion corrosion mechanism increases corrosion reaction rate by continuously removing the passive layer of corrosion products from the wall of the pipe. The passive layer is a thin film of corrosion product that actually serves to stabilize the corrosion reaction and slow it down. As a result of the turbulence and high shear stress in the line, this passive layer can be removed causing the corrosion rate to increase. The erosion corrosion is always experienced where there is high turbulence flow regime with significantly higher rate of corrosion and is dependent on fluid flow rate and the density and morphology of solids present in the fluid. High velocities and presence of abrasive suspended material and the corrodents in drilling and produced fluids contribute to this

destructive process. This form of corrosion is often overlooked or recognized as being caused by wear. (Okonkwo and Mohamed 2014)

2.5 Microbiologically induced corrosion

This type of corrosion is caused by bacterial activities. The bacteria produce waste products like CO₂, H₂S, and organic acids that corrode the pipes by increasing the toxicity of the flowing fluid in the pipeline. The microbes tend to form colonies in a hospitable environment and allow enhanced corrosion under the colony. The formation of these colonies is promoted by neutral water especially when stagnant. Numerous reports of the presence of microbes in reservoirs had been published. It was found that found abundant microbial flora indigenous in oil field formation waters, which included species of Bacillus, Pseudomonas, Micrococcus, Mycobacterium, Clostridium, and Escherichia. Escherichia is reported to contain hydrogenase, an enzyme that utilizes molecular hydrogen and may be associated with cathodic hydrogen depolarization, causing corrosion of steel casings and pipes in the oil field. Bacteria that form slime (some form of polysaccharides), such as Achromobacter species, Flavobacterium sp., and Desulfuricans sp., will adhere to each other, forming a large mass. They also adhere to the walls of the pores, causing severe plugging problems at injection wells. Microbiologically induced corrosion (MIC) is recognized by the appearance of a black slimy waste material or nodules on the pipe surface as well as pitting of the pipe wall underneath these deposits. (Videla and Herrera 2009) add ref.

2.6. Stress corrosion cracking

Stress corrosion cracking (SCC) is a form of localized corrosion which produces cracks in metals by simultaneous action of a corrodent and tensile stress. It propagates over a range of velocities from 10⁻³ to 10 mm/h depending upon the combination of alloy and environment involved. SCC is the cracking induced from the combined influence of tensile stress and a corrosive medium. The impact of SCC on material seems to fall between dry cracking and the fatigue threshold of that material. SCC in pipeline is a type of environmentally associated cracking. This is because the crack is caused by various factors combined with the environment surrounding the pipe. The most obvious identifying characteristic of SCC in a pipeline is high pH of the surrounding environment, appearance of patches, or colonies of parallel cracks on the external of the pipe. (Videla and Herrera 2009)

2.7 Sweet and Sour Corrosion

High pressures during the transportation of crude oil increase the concentration of dissolved gases. In sweet corrosion, carbon dioxide dissolves in water to form carbonic acid, which then reacts with the iron in the metal work to form iron carbonate. This causes pitting in the metal work and it is this corrosion that subsequently weakens the system. In some crude oils the presence of sulphate reducing bacteria leads to the formation of hydrogen sulphide gas, which is the cause of sour corrosion. Although this type of corrosion is not as common as sweet, when it is present in a system it is more destructive. Hydrogen sulphide reacts with the steel surfaces to produce iron sulphide, leaving pitting in the steel work. Moreover, hydrogen gas is produced and collects on the surface, causing hydrogen blistering and further weakening of the pipework. (Ren, Liu et al. 2005)

3. Corrosion Inhibitors

Controlling corrosion is a big challenge in the oil and gas industry. Easily accessible oil reserves have been depleted resulting in an ever-increasing requirement to explore more isolated locations, under harsher conditions. The presence of water, acids, acidic gases, high levels of oxygen and brine all provide the perfect environment for corrosion. This corrosive environment is further complicated by flow conditions, operating temperatures and pressure changes. Corrosion inhibitors are surfactants which give them properties allowing them to partition between the oil and water phase. The hydrophilic group adsorbs onto the metal surface, which leaves the hydrophobic group to form a water-resistant organic film on the surface. It is this film that prevents the corrosive species from coming into contact with the metal surface. (Al-Janabi, 2020)

3.1 Inhibitors classifications

Inhibitors are substances or mixtures that in low concentration and in aggressive environment inhibit, prevent or minimize the corrosion.(Obot, Obi-Egbedi et al. 2009) The corrosion inhibitors can be chemicals either synthetic or natural and could be classified by: • the chemical nature as organic or inorganic;

- The mechanism of action as anodic,
- Cathodic or a anodic-cathodic mix and by adsorption action, or;

- As oxidants or not oxidants.

In general, the inorganic inhibitors have cathodic actions or anodic. The organics inhibitors have both actions, cathodic and anodic and the protective by a film adsorption. This chapter is subdivided in according to the classification of the inhibitors shown on the Figure 5.

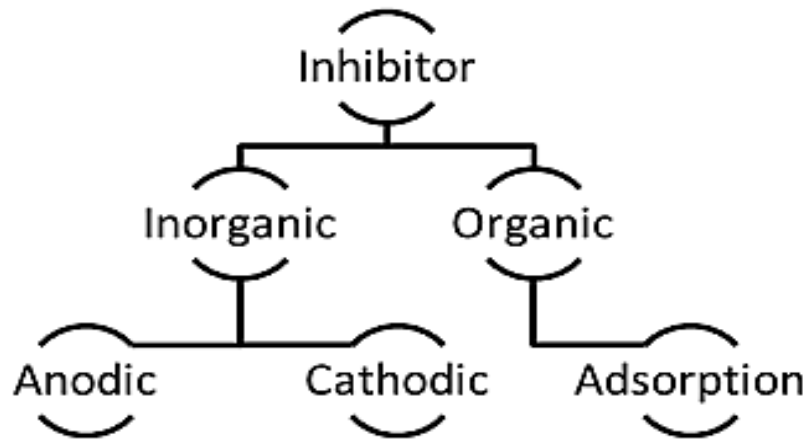


Fig.5 Classification of inhibitors

3.1.1 Inorganic inhibitors

A- Anodic inhibitors

Anodic inhibitors (also called passivation inhibitors) act by a reducing anodic reaction, that is, blocks the anode reaction and supports the natural reaction of passivation metal surface, also, due to the forming a film adsorbed on the metal. In general, the inhibitors react with the corrosion product, initially formed, resulting in a cohesive and insoluble film on the metal surface. (Mainier, Guimarães et al. 2003) Figure 6, shows a potentiation polarization diagram of a solution

with behavior inhibitor anodic. The anodic reaction is affected by the corrosion inhibitors and the corrosion potential of the metal is shifted to more positive values. As well, the value of the current in the curve decreases with the presence of the corrosion inhibitor.

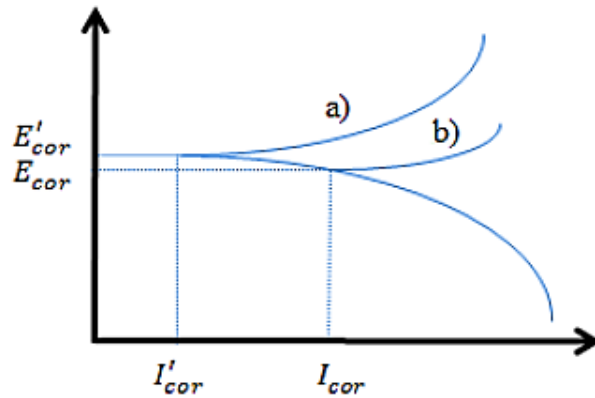


Fig.6 Potentiation polarization diagram: electrochemical behavior of a metal in a solution with anodic inhibitor a) versus without inhibitor (b).

The anodic inhibitors react with metallic ions Me^{n+} produced on the anode, forming generally, insoluble hydroxides which are deposited on the metal surface as insoluble film and impermeable to metallic ion. From the hydrolysis of inhibitors results in OH^- ions. Figure 7 shows how is the mechanism of the anodic inhibitory effect.

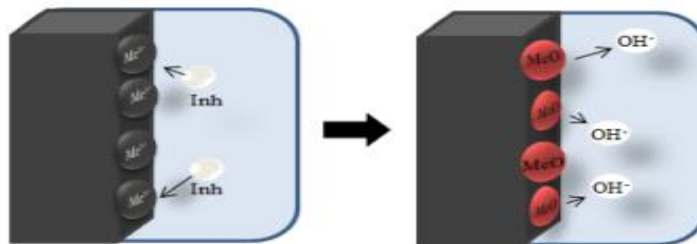


Fig. 7 Illustration of anodic inorganic inhibitors effect and their mechanism of action

When the concentrations of inhibitor becomes high enough, the cathodic current density at the primary passivation potential becomes higher than the critical anodic current density, that is, shift the potential for a noble sense, and, consequently, the metal is passivated. (Bardal 2004) For the anodic inhibitors effect, it is very important that the inhibitor concentrations should be high enough in the solution. The inappropriate amount of the inhibitors affects the formation of film protection, because it will not cover the metal completely, leaving sites of the metal exposed, thus causing a localized corrosion. Concentrations below to the critical value are worse than without inhibitors at all. In general, can cause pitting, due reduction at the anodic area relative to cathodic, or can accelerate corrosion, like generalized corrosion, due to full breakdown the passivity. Some examples of anodic inorganic inhibitors are nitrates, molybdates, sodium chromates, phosphates, hydroxides and silicates.

B- Cathodic inhibitors

During the corrosion process, the cathodic corrosion inhibitors prevent the occurrence of the cathodic reaction of the metal. These inhibitors have metal ions able to produce a cathodic reaction due to alkalinity, thus producing insoluble compounds that precipitate selectively on cathodic sites. Deposit over the metal a compact and adherent film, restricting the diffusion of reducible species in these areas. Thus, increasing the impedance of the surface and the diffusion restriction of the reducible species, that is, the oxygen diffusion and electrons conductive in these areas. These inhibitors cause high cathodic inhibition. Figure 8, shows an example of a polarization curve of the metal on the solution with a cathodic inhibitor. When the cathodic reaction is affected the corrosion potential is shifted to more negative values.

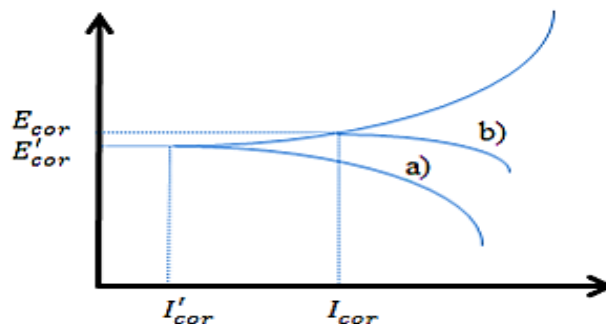


Fig.8 Potentiation polarization diagram: electrochemical behavior of the metal in a cathodic inhibitors solution (a), as compared to the same solution, without inhibitor (b).

The cathodic inhibitors form a barrier of insoluble precipitates over the metal, covering it. Thus, restricts the metal contact with the environment, even if it is completely immersed, preventing the occurrence of the corrosion reaction. Due to this, the cathodic inhibitor is independent of concentration, thus, they are considerably more secure than anodic inhibitor.

Figure 9, shows the illustration of mechanical effect of cathodic inhibitors to restrain the corrosion process.

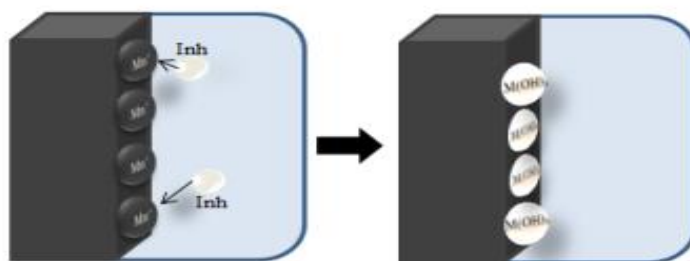


Fig.9 Illustration has shown the mechanism of actuation of the cathodic inhibitors.

Some examples of inorganic cathodic inhibitors are the ions of the magnesium, zinc, and nickel that react with the hydroxyl (OH^-) of the water forming the insoluble hydroxides as ($\text{Mg}(\text{OH})_2$, $\text{Zn}(\text{OH})_2$, $\text{Ni}(\text{OH})_2$) which are deposited on the cathodic site of the metal surface, protecting it. Also can be cited polyphosphates, phosphonates, tannins, lignins and calcium salts as examples that presents the same reaction mechanism. (Dariva and Galio 2014)

3.1.2. Organic inhibitor

Organic inhibitors are forming a film over the corroded surface. They form a hydrophobic layer on the surface of the metal to prevent dissolution of metal. The efficiency of these inhibitors depends upon their chemical composition and their molecular structure as well as their affinity with the metal. Organic compounds used as inhibitors, occasionally, they act as cathodic, anodic or together, as cathodic and anodic inhibitors, nevertheless, as a general rule, act through a process of surface adsorption, designated as a film- forming. Naturally the occurrence of molecules exhibiting a strong affinity for metal surfaces compounds showing good inhibition efficiency and

low environmental risk. (Yaro, Khadom et al. 2013) These inhibitors build up a protective hydrophobic film adsorbed molecules on the metal surface, which provides a barrier to the dissolution of the metal in the electrolyte. They must be soluble or dispersible in the medium surrounding the metal.

In the Figure 10, that shows a theoretical potentiostatic polarization curve, it can be seen that the effect of the solution containing organic inhibitor on the metal presents an anodic and cathodic behavior. After the addition of the inhibitor, the corrosion potential remains the same, but the current decreases from I_{cor} to I'_{cor} .

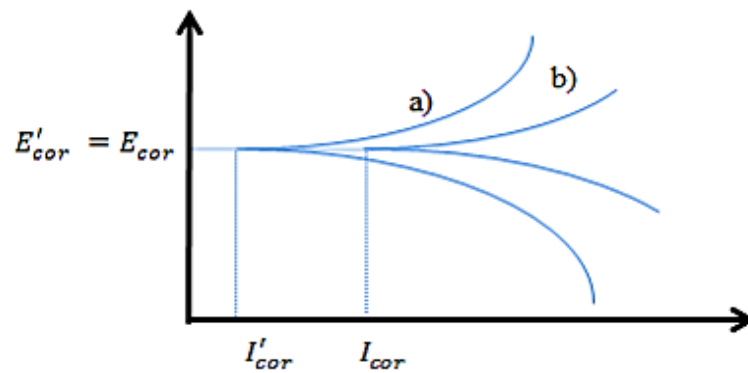


Fig.10 Theoretical potentiostatic polarization diagram: electrochemical behavior a metal on a solution containing a cathodic and anodic inhibitor (a) compared to the same solution without the inhibitor (b).

Figure 11, showed in the mechanism of actuation of organic inhibitors, when it is adsorbed to the metal surface and forms a protector film on it.

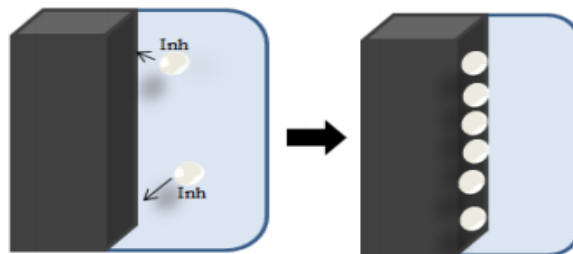


Fig.11, Illustration of the mechanism of actuation of the organic inhibitor: acting through adsorption of the inhibitor on the metal surface. Where the *Inh* represents the inhibitor molecules

The efficiency of an organic inhibitor depends on the following categories:




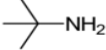


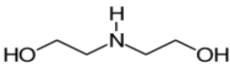

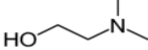
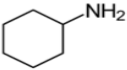
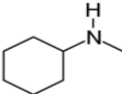
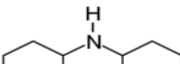
- **chemical structure**, like the size of the organic molecule;
- **aromaticity** and/or conjugated bonding, as the carbon chain length
- **type and number of bonding** atoms or groups in the molecule (either π or σ);
- **nature and the charges of the metal surface** of adsorption mode like bonding strength to metal substrate;
- **compactability**: ability for a layer to become compact or cross-linked,
- **capability to form a complex** with the atom as a solid within the metal lattice;
- **type of the electrolyte solution** like adequate solubility in the environment.

The efficiency of these organic corrosion inhibitors is related to the presence of polar functional groups with S, O or N atoms in the molecule, heterocyclic compounds and pi electrons, generally have hydrophilic or hydrophobic parts ionizable. The polar function is usually regarded as the reaction center for the establishment of the adsorption process. The organic acid inhibitor that contains oxygen, nitrogen and/or sulfur is adsorbed on the metallic surface blocking the active corrosion sites. Although the most effective and efficient organic inhibitors are compounds that have π -bonds, it present biological toxicity and environmental harmful characteristics. (El-Haddad 2013). Some examples are amines, urea, Mercaptobenzothiazole (MBT), benzotriazole e toliotriazol, aldehydes, heterocyclic nitrogen compounds, sulfur-containing compounds and acetylenic compounds and also ascorbic acid, succinic acid, tryptamine, caffeine and extracts of natural substances.

There is another type of inhibitors available now a day there are still some inhibitors that act in vapor phase (volatile corrosion inhibitor). Some examples are: dicicloexilamônio benzoate, diisopropylammonium nitrite or benzoate, ethanolamine benzoate or carbonate and also the combination of urea and sodium nitrite. (Mainier, Guimarães et al. 2003)

Table 1:

Molecular structures of some commercial corrosion inhibitors in oil fields (R. Heidersbach, 2018)

Number	Inhibitor	Abbreviation	Structural formula
1	Propylamine	PA	
2	iso- Propylamine	i-PA	
3	Butylamine	BA	
4	Tert-Butylamine	t-BA	
5	Hexylamine	HA	
6	Ethylenediamine	EDA	
7	Diethanolamine	DEA	
8	3-Amino-1-propanol	3-AP	
9	2-Dimethylethanolamine	2-DEA	
10	Cyclohexylamine	CHA	
11	N-Methylcyclohexylamine	N-MCA	
12	Dicyclohexylamine	DCHA	

3.1.2.1 Adsorption inhibitors

These represent the most widely used class of inhibitors. In general, they are organic compounds which get adsorbed on the metal surface and provide a blanketing effect over the entire surface, that is, both in cathodic and anodic cases. Generally they effect both cathodic and anodic reactions equally, but in many cases the effect may not be equal. These are commonly used in the acid pickling of hot rolled products in order to remove the black mill scale and are thus known as pickling inhibitors. Examples: fig-12, Compounds containing lone pairs of electrons such as nitrogen atoms in amines, quinolines, sulfur atoms in thio compounds and oxygen atoms in aldehydes.(Geethamani, Narmatha et al. 2019)

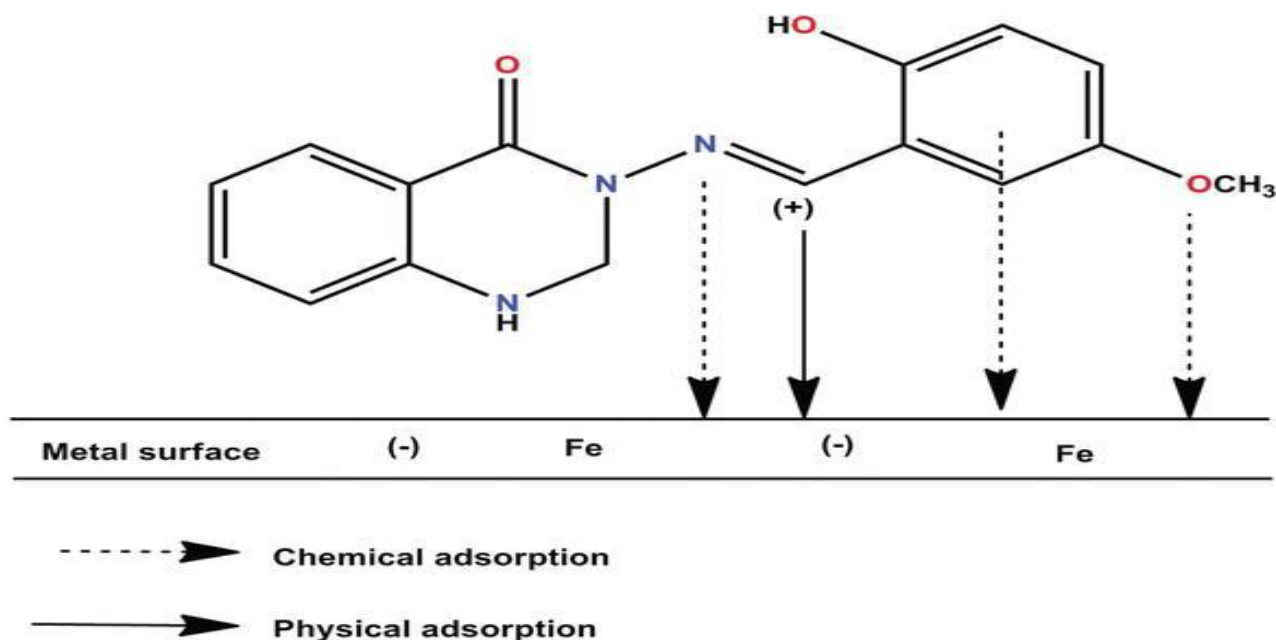


Fig. 12, corrosion inhibitor and adsorption

3.2 Toxic Inhibitors:

The salts such as, Sodium Tungstate (Na_2WO_4), Vandates (NaVO_3), Nitrites (NaNO_2), Silicates ($\text{Na}_2\text{Si}_2\text{O}_5$), and chromates (NaCrO_4) were used to protect both ferrous and non-ferrous metals. The applications of nitrites and chromates are diminishing due to their toxic nature. For the environmental protection, molybdate salts or rare earth metals replaced chromates as corrosion inhibitors for open recirculating cooling water system, but these compounds are very expensive.(El-Enin and Amin 2015)

3.3 Eco Friendly corrosion Inhibitors:

The current trend for inhibitor usage is towards more environmentally friendly green chemicals. For environmental protection, the scientific efforts have increased to study the inhibiting power of natural products like peels, seeds, fruit. shells and leaves that contain different organic compounds, (e.g. amino acids, alkaloids, flavonoids, pigments, tannins,....etc.) which suppress the dissolution reaction of metals and prevent the environmental pollution.(El-Enin and Amin 2015). Researches have been carried out on the use of eco-friendly corrosion inhibitors, which are obtained from low cost and sustainable source. Cashew nut shell liquid (CNSL), a by-product of the cashew nut industry, and the residue of its distillation (R) were evaluated as

corrosion inhibitors for API P110 carbon steel in 15% HCl. The study reveals the importance of sustainable assets, such as cashew nut residues, that when properly purified and formulated may exhibit high corrosion inhibition efficiency, even under aggressive conditions found in the offshore oil and gas industry. Fig.13

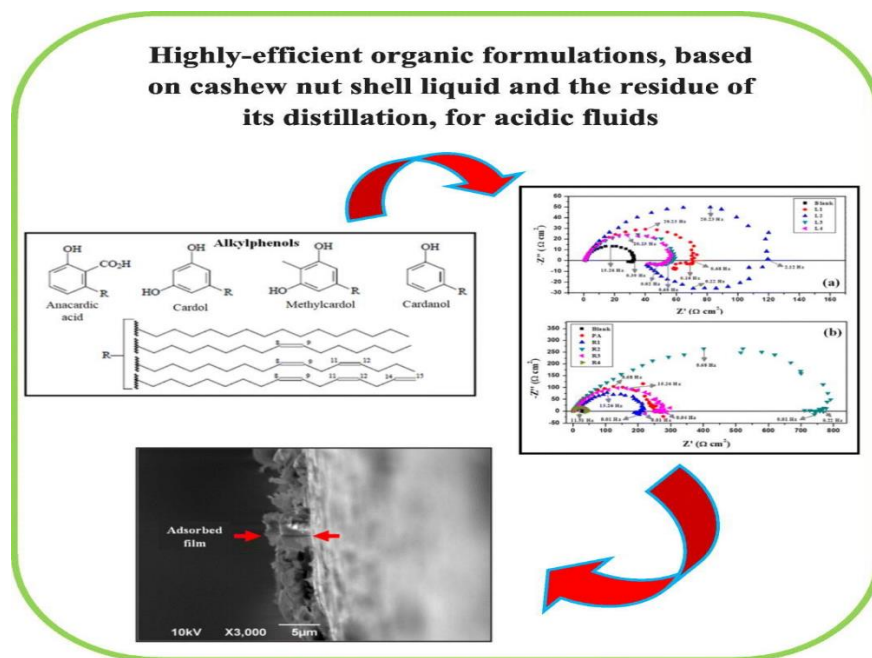


Fig.13. Eco-friendly corrosion inhibitors based on Cashew nut shell liquid (CNSL) for acidizing fluids

3.4 Green corrosion inhibitors:

Green chemistry which is a relatively new and rapidly growing area of chemistry that involves Designing of products and processes that reduce the use and production of toxic substances is very essential. Recently, worldwide growing ecological awareness and strict environmental protocols do not permit the synthesis and utilization of hazardous traditional volatile corrosion inhibitors. In this regard use of multi component reactions (MCRs) in combination with ultrasonic (sonochemical) and microwave irradiation is one of the best alternative synthetic strategies toward “green synthesis.

Therefore, there is vital need for improvement in the synthetic and engineering chemistry either by environmentally friendly starting materials or proper designing for synthesis using non-classical energy sources such as ultrasound and microwave heating. Recently, scientists are trying to develop plant extracts and drugs as green corrosion inhibitors due to their natural and/or biological origins and non-toxic nature. However, extraction and purification of plant extracts is very tedious, laborious, extremely expensive, time consuming and requires large number of organic solvents (figure 14). Therefore, there is need to develop “ green inhibitors ”by proper designing of the synthesis that can be achieved either by using cheap and environmental friendly starting materials or by synthesizing them from one step MCR reactions .(Verma, Ebenso et al. 2018)

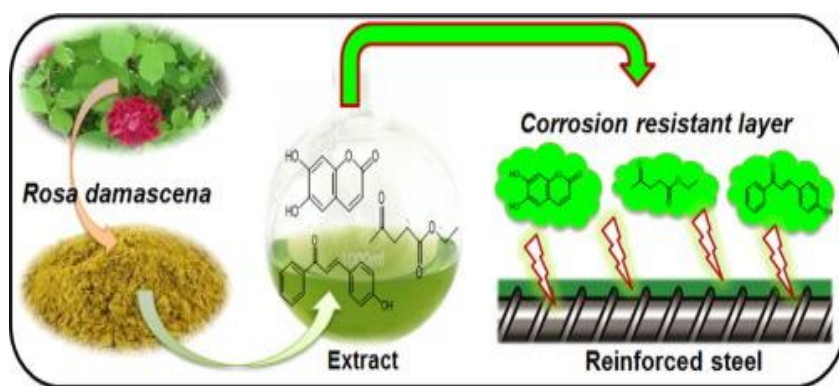


Fig.14. Green corrosion inhibitor.

Development of green and sustainable technologies for the corrosion prevention is highly desirable due to increasing ecological awareness and strict environmental regulations. In the past two decades, the research in the field of green corrosion inhibitors has been addressed toward the goal of using cheap effective molecules at low or zero environmental impact. These compounds include purine and adenine, which have been tested for copper corrosion in chloride (M. Scendo,2007, M. Scendo,2008), sulfate (M. Scendo,2007), and nitrate solutions (M. Scendo, et al.,2008).

Ionic liquids (ILs) are molten salts with melting points at or below ambient room temperature, which are composed of organic cations and various anions. Ionic liquids possess a large number of physicochemical properties (H. Zhao, et al., 2006, T. Tsuda,2007), mainly, good electrical conductivity, solvent transport, and a relatively wide electrochemical window (T. Tsuda,

et al.,2007). Configuration of ILs consists of an amphiphilic group with a long chain, hydrophobic tail, and a hydrophilic polar head. Usually, ILs have nitrogen, Sulphur, and phosphorus as the central atoms of cations, such as imidazolium, pyrrolidinium, quaternary ammonium, pyridinium, piperidinium, sulfonium and quaternary phosphonium. It was found that the action of such inhibitors depends on the specific interaction between the functional groups and the metal surface, due to the presence of the $-C=N-$ group and electronegative nitrogen in the molecule. Ionic liquids and different types of surfactants base inhibitors are well known to have a high activity in acid medium (S. Caporali et al.,2008, G. Yue, et al.2009) and therefore are used in oil field to minimize carbon dioxide-induced corrosion (A. Inglese, et al.,1998, P. Zhao, et al., 2008). Metallic corrosion inhibition using ionic liquids has shown a considerable interest due to their interesting properties such as low volatility, non-inflammability, non-toxic nature, high thermal and chemical stability and their ability to adsorb on the metallic surface. The ionic liquids are promising, noble, green and sustainable candidates to replace the traditional volatile corrosion inhibitors and can be effectively adsorb on metallic surface. Several ionic liquids have been used successfully as corrosion inhibitors for mild steel. (ChandrabhanVermaaEto.etl, 2017). The mechanism of ionic liquid adsorption on steel pipe wall is illustrated in the **fig. 15**.

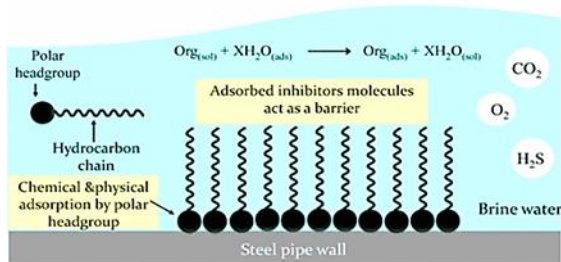


Fig.15 Ionic liquids act as corrosion inhibito

4. Inhibitor efficiency

The inhibition efficiency is defined as where and are the corrosion current density values without inhibitor and with different inhibitors, respectively.

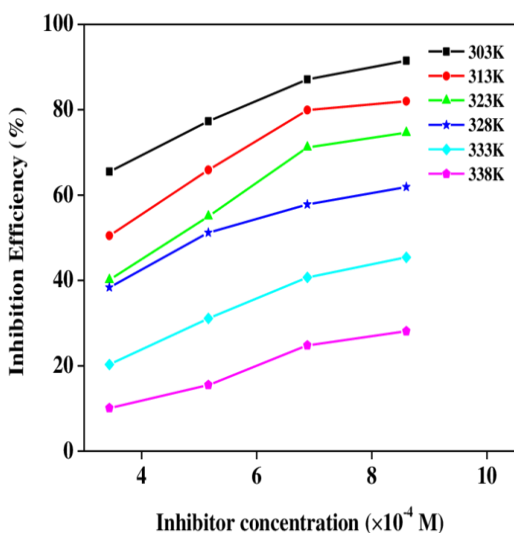
The inhibitor efficiency could be measured by the follow equation:

$$\text{Efficiency of inhibitor} = \frac{(\text{Weight loss without inhibitor} - \text{Weight loss with inhibitor})}{\text{Weight loss without inhibitor}} \times 100$$

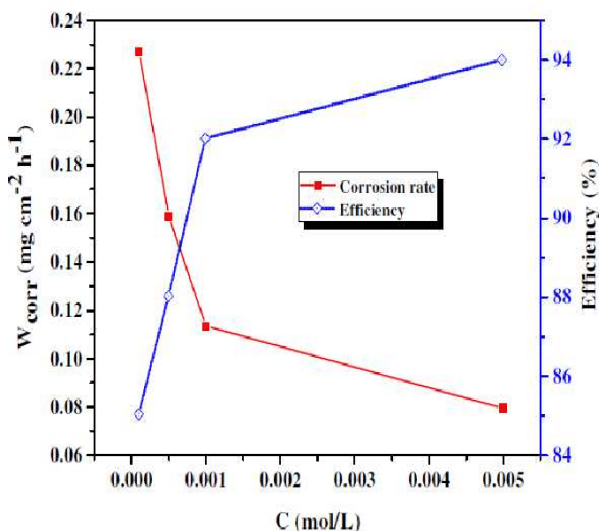
$$\text{Corrosion Rate} = \frac{534 \times \text{Weight loss (g)}}{\text{Density} \times \text{Area (cm)} \times \text{Time (hr)}}$$

$$\text{Surface Coverage } \theta = \frac{((\text{Weight loss without inhibitor}) - (\text{Weight loss with inhibitor}))}{\text{Weight loss without inhibitor}}$$

The traditional approach to evaluate the viability of corrosion inhibition combines an assessment of corrosion inhibitor efficiency and availability. It is often assumed that an inhibited rate of 0.1mm/year can be achieved and focus is given to the desired availability. Therefore, achieving a high inhibitor efficiency is key to project delivery and integrity risk management. Extensive inhibitor testing data has been reviewed across a range of environmental conditions. The influence of environmental parameters (including corrosivity, temperature, brine salinity and hydrodynamics) on inhibitor performance has been analyzed. The effect of the parameters and relative criticality to achieving acceptable inhibitor performance has been defined and a matrix has been developed to enable assessment of the likelihood of achieving successful inhibition. In general, the efficiency of an inhibitor increases with an increase in inhibitor concentration, e.g. a typically good inhibitor would give 95% inhibition at a concentration of 0.008% and 90% at a concentration of 0.004%. (H.A. Sorkhabi,et.al.2000, X. Li, S. Deng,et. al.2009)



(A)



(B)

Fig-16,

(A) relation between corrosion inhibitor concentration and inhibitor efficiency at different temperatures.

(B) relation between inhibitor concentration and corrosion rate and inhibitor efficiency

A close look at the figure 16 B, reveals that the corrosion rate decreases as the concentration of inhibitor increases, while the inhibitor efficiency increases with the increase in the inhibitor concentration. This means that the inhibitor efficiency decreases with increase in the temperature but inhibitor efficiency increases with increase in the inhibitor concentrations for all the temperature ranges studied as shown in Figure 16 A.

5. Mechanisms of actions of inhibitors

Generally, the mechanism of the inhibitor is one or more of three that are cited below:

- the inhibitor is chemically adsorbed (chemisorption) on the surface of the metal and forms a protective thin film with inhibitor effect or by combination between inhibitor ions and metallic surface. The inhibitor leads a formation of a film by oxide protection of the base metal illustrated in fig.17. (Luana B.2019)

- the inhibitor reacts with a potential corrosive component present in aqueous media and the product is a complex. (Ju, Kai et al. 2008)

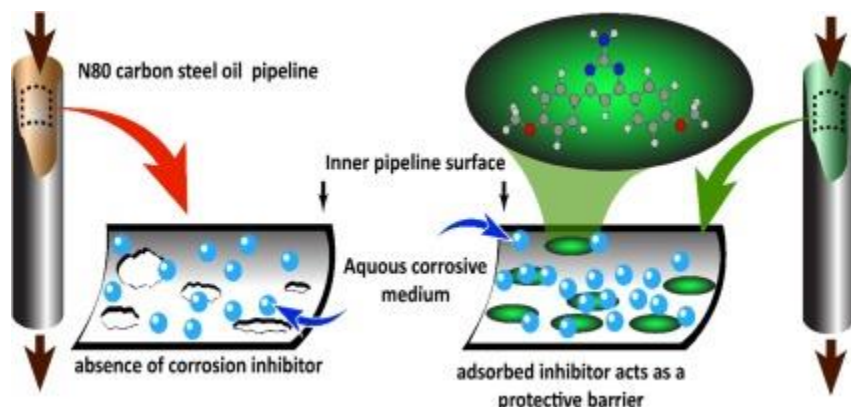


Fig.17. mitigation of corrosion in petroleum pipe line using pyrimidines as corrosion inhibitors

The corrosion process was investigated by means of scanning Kelvin probe force microscopy (SKPFM), in situ atomic force microscopy, and scanning electron microscopy coupled with energy dispersive spectroscopy. Employment of the high-resolution and in situ techniques results in a deep understanding of the details of the physical chemistry and mechanisms of the corrosion processes. The applicability of the SKPFM for mechanistic analysis of the effect of different corrosion inhibitors is demonstrated for the first time. The inhibitors under study show sufficient hindering of the localized corrosion processes especially in the case of pitting formation located around the intermetallic S-phase particles. A detailed mechanism of the corrosion process and its inhibition is proposed based on thermodynamic analysis. (Kiryl A., et.al.2006)

6. Conclusions

Corrosion is a natural process which reduces the binding energy in metals and degrades the useful properties of materials it is observed as one of the main reasons for the failures of oil and gas infrastructure. The corrosion issue is unavoidable for the oil and gas industry, creating a similar impact to those of natural disasters. Therefore, completely stopping this issue is not possible, but taking preventative measure to inhibit the metal surface from corroding is more economical. In this review different types corrosion inhibitors, has been consolidated to aid in mitigating the corrosion in general and specifically in oil and gas pipeline.

The use of conventional and commercial corrosion inhibitors has long been in practice. Nonetheless, applications of commercial inhibitors have been restrained over time. This is due to their toxic properties that contribute negative impact to the environment. Therefore, with the aim of preventing environment and work knowledges towards concerning more with the green (plant- and fruit-based) corrosion inhibitors. Development of ionic liquids has attracted researcher's attention due to their interesting properties such as low volatility, non-inflammability, non-toxic nature, high thermal and chemical stability and their ability to adsorb on the metallic surface. Hence further research themes for accurate inhibition efficiency measurement are still under investigation. Inhibitors are a great method of preventing corrosion and are easy to apply. Has application in a wide range of sectors of petroleum oil and gas industries.

The knowledge of the method of the action, facilitates the choice of the inhibitors, improves efficiency, avoids the process is impaired and side effects. It is important in the choice of inhibitor, ascertain the subsequent effects of this towards the environment. The search for environmental friendly inhibitors has shown excellent results, outperforming conventional inhibitors.

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