Corrosion mitigation of the oil well steels using organic inhibitors – A review

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Abstract

Oil well stimulation, usually done with hot solutions of hydrochloric acid, may induce severe corrosion attack on production tubing, downhole tools and casing. Inorganic, organic and combinations of acids along with surfactants are used in a variety of well stimulation treatments. To reduce the aggressive attack of the acid on tubing and casing materials (N80 steel), inhibitors are added to the acid solution during the acidifying process. The inhibition in oil and gas field is more complicated and requires special eco-friendly inhibitors depending on the area of application such as in refineries, wells, recovery units, pipelines etc. Aggressive gases such as H_2S, CO_2, and organic acids complicate the problem of inhibition in wells. Various factors have to be considered while dealing with corrosion problems of oil and gas industry. The type of reservoir rocks, the acids used for stimulation, the oil well equipments such as tubings and casings and the operating conditions are some of the important factors that affect the corrosivity. Each and every case has to be considered in its totality before a decision is made on the proper materials. No particular material is the cure for all the evils of corrosion. It is imperative to the field operators, pipeline engineers, designers to have corrosion awareness concerning the oil and gas industries in their day to day activities to compact and mitigate corrosion. This work is an attempt in this direction.

Key Words: Well stimulation, N 80 steel, reservoir formation damage, acidization, hydraulic fracturing, eco-friendly corrosion inhibitors.

1. Introduction

The total annual cost of corrosion in the oil and gas production industry is estimated to be $1.372 billion, broken down into $589 million in surface pipeline and facility costs, $463 million annually in downhole tubing expenses, and another $320 million in capital expenditures related to corrosion [1]. It is widely recognized within the oil and gas industry that effective management of corrosion will contribute towards achieving the following benefits:

- Statutory or Corporate compliance with Safety, Health and Environmental policies
- Reduction in leaks
- Increased plant availability
- Reduction in unplanned maintenance
- Reduction in deferment costs

Various factors have to be considered while dealing with corrosion problems of oil and gas industry. The type of reservoir rocks, the acids used for stimulation, the oil well equipments such as tubings and casings and the operating conditions are some of the important factors that affect the corrosivity. Oxygen, which plays such an important role in corrosion, is not normally present in producing formations. It is only at the drilling stage that oxygen contaminated fluids are first introduced. Drilling muds, left untreated, will corrode not only well casing, but also drilling equipment, pipelines and mud handling equipment. Water and carbon dioxide, produced or injected for secondary recovery, can cause severe corrosion of oil well steels. Acids, used to remove scale, readily attack metal. Hydrogen sulphide (H_2S) poses other problems. Handling all these corrosion situations, with the added complications of high temperature, pressures and stresses involved in drilling or production requires the expertise of a corrosion engineer, an increasingly key figure in the industry.

CO_2 and H_2S gases in combination with water are the main cause of corrosion in oil and gas production. In addition, it is normal practice to re-inject production water downhole to maintain the reservoir pressure and stability as well as perform water flooding (using seawater or fresh water sources) to drive oil out of the formation.As field ages, the ratio of watery oil in the produced fluids increases and can reach levels of 95% or higher [2].This rise in water content implies an increase of the corrosion problems. Internal corrosion caused by the produced fluids is the most costly of the corrosion problems in the oil and gas industry since internal mitigation methods cannot be easily maintained and inspected. Therefore, as a field ages, corrosion control becomes more expensive. Approximately 60% of oilfield failures are related to CO_2 corrosion mainly due to inadequate predictive capability and the poor resistance of carbon and low alloy steels to this type of corrosive attack [2].CO_2 can produce not only general corrosion but also localized corrosion, which is a much more serious problem.
From the materials cost point of view, the use of carbon and low alloy steel for tubings and pipelines is the most convenient option [2] and, therefore, big efforts have been made in order to increase their corrosion resistance. When the environment is too aggressive for bare carbon steels, the options to reduce corrosion problems are the use of inhibitors or corrosion resistant alloys.

2. Acidization of oil well
Oil well stimulation, usually done with hot solutions of hydrochloric acid, may induce severe corrosion attack on production tubing, downhole tools and casing .Oil well stimulation is the general term describing a variety of operations performed on a well to improve its productivity. Opening up new channels in the rock for the oil and gas to flow through is called stimulation. Three stimulation treatments are commonly used: explosives to break up the rock, injection of acid to partially dissolve the rock, and hydraulic fracturing to split the rock and prop it open with proppants. Stimulation operations can be focused solely on the well bore or on the reservoir; it can be conducted on old wells and new wells alike; and it can be designed for remedial purposes or for enhanced production. Its main two types of operations are matrix acidization and hydraulic fracturing.
Matrix acidization involves the placement of acid within the well bore at rates and pressures designed to attack an impediment to production without fracturing or damaging the reservoir (typically, hydrofluoric acid is used for sandstone/silica-based problems, and hydrochloric acid or acetic acid is used for limestone/carbonate-based problems). Most matrix stimulation operations target up to a ten foot radius in the reservoir surrounding the well bore. Matrix acidizing is applied primarily to remove skin damage caused by drilling, completion, work-over or well killing fluids and by precipitation of deposits from produced water. Due to the extremely large surface area contacted by acid in matrix treatment, spending time is very short. Therefore, it is difficult to affect formation more than a few feet from the well bore [3].
Hydraulic fracturing (Fig 1&2), which includes acid fracturing, involves the injection of a variety of fluids and other materials into the well at rates that actually cause the cracking or fracturing of the reservoir formation. The variety of materials includes, amongst others: water, acid, special polymer gels, and sand. The fracturing of the reservoir rock and the subsequent filling of the fractured voids with sand ("proppant") (Fig 3) or the creation of acid channels allows for an enhanced conduit to the well bore from distances in excess of a hundred feet.
Fracture acidizing is an alternative to hydraulic fracturing and propping in carbonate reservoirs. In fracture acidizing, the reservoir is hydraulically fractured and then the fracture faces are etched with acid to provide linear flow channels to the well bore. In limestone or carbonate formations, the acid dissolves portions of the

rock in the formation, opening up existing spaces to allow for the flow of petroleum. Fracturing consists of injecting a fluid into the well, the pressure of which 'cracks' or opens up fractures already present in the formation. In addition to the fluid being injected, 'propping agents' are also used. These propping agents can consist of sand, glass beads, epoxy, or silica sand, and serve to prop open the newly widened fissures in the formation. Hydraulic fracturing involves the injection of water into the formation, while CO_2 fracturing uses gaseous carbon dioxide. Fracturing, acidizing, and lifting equipment may all be used on the same well to increase permeability, widening the pores of the formation.
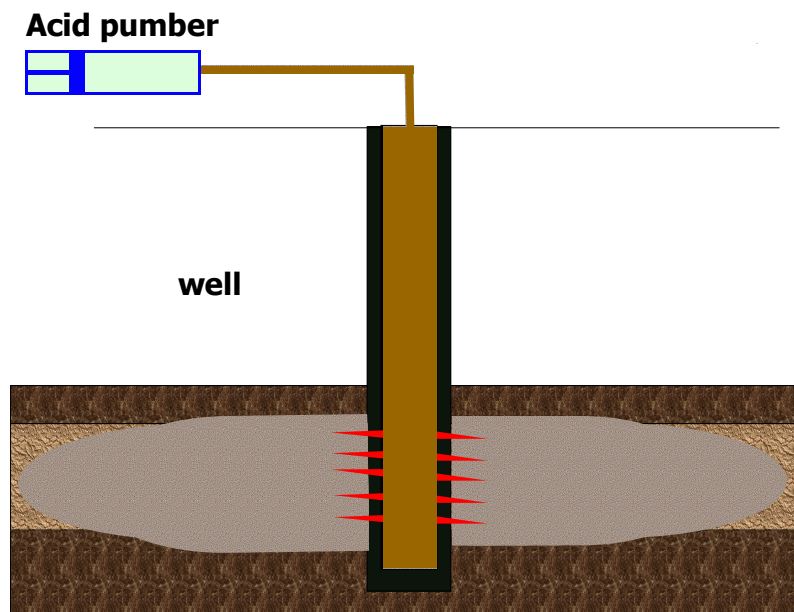

Fig 1: Hydraulic fracturing

A common type of acid employed on wells to stimulate production is hydrochloric acids (HCI), which are useful in removing carbonate reservoirs, or limestones and dolomites, from the rock. Also, HCI can be combined with a mud acid, or hydrofluoric acid (HF), and used to dissolve quartz, sand and clay from the reservoir rocks.
The acid reaction may be represented by the following equation [4].

$$2HCl + CaCO_3 = CaCl_2 + H_2O + CO_2$$

$$CaMg\,(CO_3)_2 + 4HCl = CaCl_2 + MgCl_2 + 2H_2O + 2CO_2$$

In order to protect the integrity of the already completed well, inhibitor additives are introduced to the well to prohibit the acid from breaking down the steel casing in the well. Also, a sequestering agent can be added to block the formation of gels or precipitate of iron, which can clog the reservoir pores during an acid job. After an acid job is performed, the used acid and sediments removed from the reservoir are washed out of the well in a process called backflush.

Starting in the 1860s and used through the 1940s, explosive fracturing used to be the most common method of well fracturing. Explosive fracturing, also known as well shooting, detonated an explosive within the well to break the reservoir rocks. Successful at stimulating production, yet dangerous, explosive fracturing introduced liquid nitrogen into the well via a tin cylinder referred to as a torpedo. The torpedo was lowered into the wellbore and detonated. The explosion created a huge hole that was then cleaned out and completed as an open hole, leaving the bottom of the well open into the reservoir.
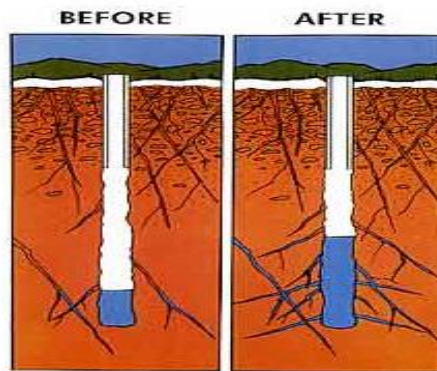
Fig 2: A Well Before and After Fracturing

Fig 3: Different Types of Proppants

2.1 Acids used in well stimulation
Inorganic, organic and combinations of acids along with surfactants are used in a variety of well stimulation treatments. A number of different acids are used in conventional acidizing treatments, the most common are:[5]
• Hydrochloric, HCl
• Hydrofluoric, HF
• Acetic, CH_3COOH
• Formic, HCOOH
• Sulfamic, H_2NSO_3H
• Chloroacetic, $ClCH_2COOH$
Also various combinations of these acids are employed in specific applications. HCl acid used in the field is normally 15% by weight; however acid concentration may vary between 5% and about 35%. HCl will dissolve limestone, dolomite and other carbonates. Acetic acid (HAc) is a weakly –ionized, slow reacting acid. The cost of dissolving a given weight of limestone is greater with acetic acid than with HCl [5]. Acetic acid is relatively easy to inhibit against corrosion and can usually be left in contact with tubing or casing for days without the danger of serious corrosion. Because of this acetic acid is frequently used as a perforating fluid in limestone wells. Other advantages of acetic acid in comparison to HCl are:

1.   Acetic acid is naturally sequestered against iron precipitation.
2.   It does not cause embrittlement or stress cracking of high strength steels.
3.   It will not corrode aluminium.
4.   It will attack chrome plating up to 200^0F. Therefore, acetic acid should be considered when acidizing a well with an alloy pump in the hole.

Formic acid is a weakly –ionized, slow reacting organic acid. It has somewhat similar properties to acetic acid. However, formic acid is more difficult to inhibit against corrosion at higher temperatures and does not have the widespread acceptance and use of acetic acid. Hydrofluoric acid used in oil, gas or service wells is normally 3% HF acid plus 12% HCl. It is employed exclusively in sandstone matrix acidizing to dissolve formation clays or clays which have migrated into formation. Fast reaction time and precipitants make HF acid undesirable in carbonate containing sands having more than 20% solubility in HCl. HF acid should never be used in carbonate formations [5].

Sulfamic acid, a granular –powdered material, reacts about as fast as HCl. The primary advantage of sulfamic acid is that it can be hauled to the location as a dry powder and then mixed with water. Unless sulfamic acid is modified, it will not dissolve iron oxides or other iron scales. Because of its molecular weight the amount of calcium carbonate dissolved sulfamic acid is only about one-third that dissolved by an equal weight of HCl. Sulfamic acid is not recommended for temperatures above 180^0F because it hydrolyzes to form sulphuric acid (H_2SO_4). When H_2SO_4 reacts with limestone or $CaCO_3$ scale, Calcium sulphate ($CaSO_4$) can be precipitated.

2.2 Additives used in Acidization

Surfactants should be used on all acid jobs to reduce surface and interfacial tension, to prevent emulsions, to water wet the formation, etc. Suspending agents are used to prevent settling and bridging of insoluble which can cause blocking in formation pores or fractures. Suspending agents are usually polymers or surfactants. Some suspending particles may prevent emulsions, provide lower surface tension in both raw and spent acid, and water wet the formation [5].

Sequestering agents acts to complex ions of iron and other metallic salts to inhibit precipitation. During acidizing if ferric hydroxide is not prevented from precipitating, this insoluble iron compound may be redeposited near the well bore and cause permanent plugging. Acetic acid is used to maintain a low pH as HCl spends. Citric acid acts as a chelating agent and is particularly useful when higher iron concentration is present.

Sequestered HCl acid is most often used in the treatment of disposal and injection wells. Tubular goods are often coated with iron corrosion products which are soluble in HCl. If iron is in the oxidized condition, it will precipitate when HCl spends in the formation and cause plugging of the rock pores. Other sources of iron that could cause plugging in producing, water flood and disposal wells are iron sulphide and iron carbonate.

Antisludge agents are used to prevent the formation of insoluble sledge when some crude particularly heavy asphaltic crude is in contact with acid .The primary ingredients of a sludge are usually asphaltenes, resins, paraffin waxes, high molecular weight hydrocarbons and formation fines or clays. The addition of certain surfactants can prevent the formation of sludge by keeping colloidal material dispersed. Also these sludge preventing surfactants usually function as emulsion preventers. Sludge is a severe problem with high strength acids.

3. Corrosion inhibition in oil and gas field

Inhibitors are chemicals that are used to protect the surface of metals used in oil and gas industries to prevent corrosion. They protect the surface of metals either by merging with them or by reacting with the impurities in the environment that may cause pollution. The inhibitors are dispersed onto metals from a solution, they then form a thin layer or film on the surface of the metal thereby protecting them. By causing an increase in the anodic and the cathodic polarization behavior an inhibitor prevents and reduces the ions from diffusing with the metallic surface it also helps to create an electrical resistance through its metallic surface.

Factors to consider before using a corrosion inhibitor in the oil and gas industry:

- Toxicity
- Environment Friendliness
- Availability
- Cost

Corrosion Inhibitors used, fall into the following types based on their way of functioning:

- Vapor Phase
- Cathodic
- Anodic
- Passivating

- Film Forming
- Neutralizing and Reactive

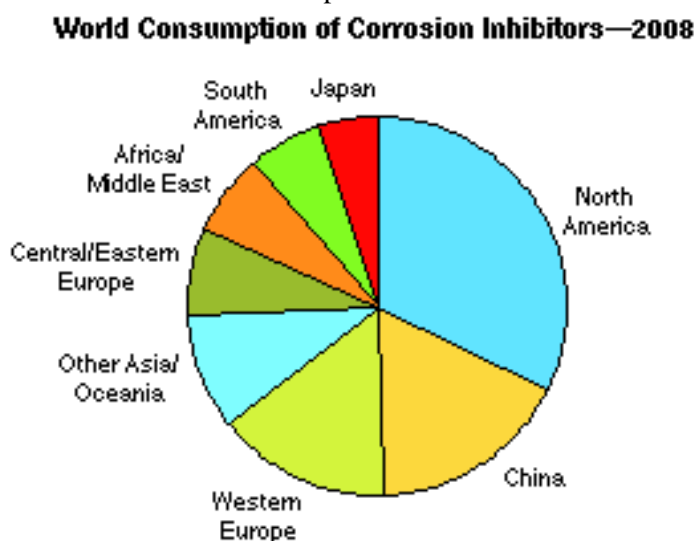The following pie chart shows world consumption of corrosion inhibitors on a value basis [6]:

Fig. 4: World consumption of corrosion inhibitors

3.1 Influencing factors of efficiency of corrosion inhibitors
The corrosion inhibition efficiency of organic compounds is strictly connected with their adsorption properties on the metal surface. The selection of appropriate acid inhibitors mainly depends on the type of acid, its concentration, temperature, velocity, presence of dissolved solids and the type of involved metallic materials. Sometimes, when two or more inhibiting substances (may be organic or inorganic) are added in a corrosive environment, the inhibiting effect is some time greater than that which would be achieved by either of the two (or more) substances individually. This is called a synergistic effect of inhibition. The efficiency of corrosion depends on the following factors.

(1) Inhibitor concentration
It was found that the rate of corrosion decreases with the increase of inhibitor concentration and the inhibition efficiency increases with the increase of inhibitor concentration and tends to approach a maximum value at a certain concentration. It may be due the fact that with increase of the concentration larger no of inhibitor molecules get adsorbed on the metal surface resulting more coverage of the corroded metal surface and make it difficult from further corrosive attack by the electrolyte solution.

(2) Exposure period
It has been found that in general the protectiveness of the inhibitors decreases with the exposure period. The metal dissolution in presence of the inhibitors has been found to increase with exposure period. The fact may be explained as at longer exposure period there may be partial desorption of the inhibitor molecules from the metal surface which previously adsorbed on the surface.

(3) Temperature
The corrosion rate linearly increases with the increase of temperature. In an inhibited acid at an elevated temperature the metal dissolution reaction is complex and causes the following changes:
a)   Desorption of pre-adsorbed inhibitor molecules occur from metal surface
b)   The active area of the metal surface changes because of rapid etching
c)   Decomposition and rearrangement of some inhibitors may take place
d)   Heterogeneous reaction rate increases at uninhibited metal surface

The adsorption and desorption of inhibitor molecules continuously occur at the metal surface. At a particular temperature equilibrium is set up between these two processes. With the increase of temperature due to higher desorption rate, the equilibrium is shifted until the equilibrium is again established at a different value of

equilibrium constant and as a consequence inhibitive protectiveness of the inhibitors decreases with the increasing temperature. Calcott and Wetzel [7] found that the logarithm of the corrosion rate (K) is a function of temperature in between 20^0 to $100\ ^0$C:

$$Log\ K = a + b\ t$$

where 'a' and 'b' are experiment constant and't' is temperature in ^{0}C
 A linear relation between logarithm of corrosion rate and the value of 1/T was found in a moderate range of temperature.

(4) Effect of inhibitor structure
The structural characteristics of the organic inhibitors played key role in the adsorption phenomena and thereby the extent of inhibition. Generally the inhibitor molecule adsorbed on the metal surface through the heteroatom (nitrogen, sulphur, oxygen and even selenium and phosphorous) present in the inhibitor molecule. The electron active center in the organic compound leads to an establishment of adsorptive bond by Lewis acid-base type reaction where inhibitor acts as electron donor and the metal as acceptor. The adsorption bond strength is mainly dependent on the electron density and the polarizability of the reaction centre. It is observed by many authors that the adsorption of surface active organic compounds increase with the increase of molecular weight and the dipole moment. Hammet equation has been employed successfully to correlate the electron density and the inhibition efficiency. The effect of the substituents in the inhibitors molecules has been studied extensively and it was found that the inhibition efficiency is enhanced by the substituent, which increases the electron density of the reaction centre.

3.2 Inhibitors for acidization treatment
Acidization of a petroleum oil well is one of the important stimulation techniques for enhancing oil production. Oil well stimulation, usually done with hot solutions of hydrochloric acid, may induce severe corrosion attack on production tubing, downhole tools and casing. It is commonly brought about by forcing a solution of 15% to 28% hydrochloric acid into the well to open up near bore channels in the formation and hence to increase the flow of oil. To reduce the aggressive attack of the acid on tubing and casing materials (N80 steel), inhibitors are added to the acid solution during the acidifying process. The effective acidizing inhibitors that are usually found in commercial formulations are acetylenic alcohols, alkenyl phenones, aromatic aldehydes, nitrogen containing heterocyclics, quaternary salts and condensation products of carbonyls and amines. However, these inhibitors suffer from drawbacks, they are effective only at high concentrations and they are harmful to the environment due to their toxicity, so it is important to search for new nontoxic and effective organic corrosion inhibitors for oil well steel (N80 steel) – 15% hydrochloric acid system. In this regard, amino acid compounds have a promising alternative for the design of eco-friendly corrosion inhibitors which will satisfy the environmental requirements. In general, organic compounds are more effective than inorganic compounds when used as corrosion inhibitors to protect steel in acidic media [8-13].

The inhibition in oil and gas field is more complicated and requires specialty inhibitors depending on the area of application such as in refineries, wells, recovery units, pipelines etc. Aggressive gases such as H_2S, CO_2, and organic acids complicate the problem of inhibition in wells. Corrosion problems in petroleum refining operations associated with naphthenic acid constituents and sulfur compounds in crude oils have been recognized for many years. It is particularly severe in atmospheric and vacuum distillation units at higher temperatures, 175-400 ^{o}C [14]. Dissolved O_2 is the main species causing corrosion in recovery units. Dry corrosion is of great importance in refinery processes. HCl may form in refineries as a by-product. O_2, CO_2 and H_2S intensify corrosion problems in natural gas pipelines. Wet corrosion in refineries can be controlled by passivating, neutralizing or adsorption type inhibitors. Slag inhibitors are used along with the corrosion inhibitors to reduce deposits. Both water soluble and oil soluble inhibitors are used in pipelines. Adsorption type inhibitors are widely used for preventing internal corrosion of pipelines carrying refined petroleum products. In general, where the operating temperatures and/or the acid concentrations are higher, a proportionately higher amount of the corrosion inhibitor composition will be required. It is preferable to add the inhibitor composition at a relatively high initial dosage rate, about 2000 to 5000 ppm, and to maintain this

level for a relatively short period of time until the presence of the inhibitor induces build-up of a corrosion protective coating on the metal surfaces. Once the protective coating is established, the dosage may be reduced to an operational range, about 10 to 100 ppm [14]. It is known that nitrogen based corrosion inhibitors are relatively ineffective in the high temperature environment. Also, the phosphorus-containing compounds may impair the function of various catalysts used to treat crude oil.

4. Previous studies on inhibition of oil well steels.

Oil industry is facing severe corrosion problem compared to any other industries, the damage from which totals many millions of dollars annually. During acidization different acid mixtures including hydrochloric acid, hydrofluoric acid, acetic acid, formic acid, and chloroacetic acid are used. In these acidic solutions hydrochloric acid is generally used as the basic components to remove plugging in the bore well and stimulate production in petroleum industry because hydrochloric acid is most economical and leaves no insoluble reaction product during acidizing treatment.

Inorganic inhibitors cause severe damage to environment. So a variety of organic compounds have been used as corrosion inhibitors such as nitrogen, oxygen, sulphur containing heterocyclic compounds, quaternary ammonium salts, acetylenic compounds for the protection of steel in acid medium. In general, organic corrosion inhibitors are more effective than inorganic compounds for protection of steels in acid media. A review of literature on high temperature acid corrosion inhibitors revealed that the effective corrosion inhibitors for oil well acidization include acetylene alcohols, quaternary ammonium salts, aldehydes, amines etc

Growcock et al in 1988 [11] reported that 3-Phenyl-2-propyn-1-ol (PPO) effectively mitigates the corrosion of API J55 oilfield tubing in HCl solutions over a wide range of conditions. Product analyses reveal that PPO can undergo hydration on the steel surface or, more slowly, in solution to form β-hydroxypropiophenone (HPP). If adsorbed on the steel, HPP rapidly dehydrates to yield phenyl vinyl ketone (PVK). The latter can oligomerize to form poly (phenyl vinyl ketone). Corrosion kinetics measurements indicate that PPO, HPP (both in protonated form) or PVK can all function as primary inhibitors. The oligomer film serves as a secondary barrier which can bring about an additional reduction of the corrosion rate. A new inhibitor system containing only organic chemicals (ketones, quinolinium salts and formic acid) has been developed to protect oilfield tubular goods to temperatures as high as 400^0F (204^0C) in hydrochloric by Frenier and associates in 1989[12]. The paper describe the synthesis and testing of a series of pyridinium and quinolinium compounds used as part of an inhibitor package that also contains aromatic ketones and aliphatic acids such as formic acid. Quraishi et al in 2000[13] synthesized some selected hydrazides and thiosemicarbazides of fatty acids with 11, 12, and 18 carbon atoms and evaluated as corrosion inhibitors on mild steel and oil-well steel (N80) in boiling 15% hydrochloric acid solution, by weight loss method. Potentiodynamic polarization studies carried out on mild steel and N80 steel at room temperature showed that all the tested compounds are of mixed type. He indicates that effective corrosion inhibitors used during acidization are acetylenic alcohols, alkenyl phenones, aromatic aldehydes, nitrogen-containing hectorocyclics and their quarternary salts, condensation products of carbonyls and amines, and inorganic compounds such as arsenic halides, etc. It is known that condensation products of carbonyls and amines give more inhibition efficiency than constituent carbonyls and amines. In his another paper [15] Quraishi et .al synthesized three fatty acid triazoles, namely, 3-undecane-4- aryl-5-mercapto-1,2,4-triazole (triazole 1), 3(heptadeca-8-ene)- 4-aryl-5-mercapto-1,2,4-triazole (triazole 2), and 3(deca-9- ene)-4-aryl-5-mercapto-1,2-4-triazole (triazole 3) and their corrosion-inhibiting action in 15% hydrochloric acid was evaluated by weight-loss method and electrochemical techniques. Electrochemical polarization studies at room temperature indicated that all the triazoles are mixed-type inhibitors, i.e., they inhibit both anodic and cathodic reactions. In 2001, three long chain fatty acid oxadiazoles namely 2-undecane-5-mercapto-1-oxa-3,4-diazole (UMOD), 2-heptadecene-5-mercapto-1-oxa-3,4-diazole (HMOD) and 2-decene-5-mercapto-1-oxa-3,4-diazole (DMOD) were synthesized by Quarishi et al [16] and evaluated as corrosion inhibitors for mild steel in 15% HCl at 105±2°C by weight loss method. Inhibition tests were also carried out on N80 steel under similar conditions in 15% HCl containing 5000 ppm of UMOD. The results obtained indicated that oxadiazole derivatives are good corrosion inhibitors. UMOD was found to be the best corrosion inhibitor. It exhibited 94% inhibition efficiency for N80 steel and 72% inhibition efficiency for mild steel. In another work, Quraishi et al in 2002[17] studied the influence of three new inhibitors on the corrosion of N80 steel in 15% boiling

HCl was studied. The investigated compounds were dicinnamylidene acetone (DCA), disalicylidene acetone (DSA), and divanillidene acetone (DVA).

Two new organic inhibitors, namely dibenzylidene acetone (DBA) and Di-N-dimethylaminobenzylidene acetone (DDABA), had been synthesized in the laboratory by Athar et al in 2001 [18] and their inhibiting action has been evaluated on corrosion of N80 steel and mild steel (MS) in HCl by weight loss technique. These compounds exhibited the inhibition efficiency of 94.4 per cent and 56.5 per cent for mild steel, whereas for N80 steel these compounds showed inhibition efficiency of 99.7 per cent and 73.8 per cent. The potendiodynamic polarization studies revealed that both the compounds are mixed type inhibitors. The noteworthy feature of the investigation is that inhibition efficiency of both compounds increased on addition of potassium iodide (KI) due to synergism. In 2002, Migahed et al [19] studied the effect of *N*-propyl amino lauryl amide (I) and three of its ethoxylated derivatives (II, III and IV) as corrosion inhibitors of carbon steel in 1 M hydrochloric acid solution. Lopez et al in 2003[2] reviewed and discussed the available information about the effect of microstructure and composition of carbon and low-alloyed steel on corrosion resistance in CO_2 environments. The influence of these parameters on the efficiency of corrosion inhibitors was also discussed the importance of chemical composition and microstructure on CO_2 corrosion of carbon and low alloy steels had been recognized. The chemical composition and the microstructure are not independent variables; the same microstructure can be obtained with different chemical compositions and vice versa. Li and associates in 2003 [20] investigated the de_adsorption behavior of four inhibitors on N80 steel with and without carbonate film by polarization and electrochemical impedance spectroscopy (EIS) techniques. It was found that, for different inhibitors, de_adsorption behavior and adsorbability between with and without carbonate film are different. Furthermore, acidic inhibitor and small size molecule inhibitor shows different inhibition behavior.

Saxena and Goyal in 15th LAWPSP SYMPOSIUM (2004) [10] presented a paper which deals with the preliminary studies carried out at the Indian Institute of Petroleum, Dehradun in the development of acid corrosion inhibitors for high temperature applications and the recent trends in the inhibitor formulations pertaining to such application. A survey of the literature on high temperature acid corrosion inhibitors indicated that various corrosion inhibitors which may be effective either alone or in combination with another normally contain intensifier along with a group of compounds like acetylenic alcohols, cinnamaldehyde derivatives, and organic nitrogen compounds. Most of the commonly known acid corrosion inhibitors contain intensifiers like formic acid, iodides and acid soluble salts of copper, antimony, bismuth and mercury along with the following group of compounds like alpha hydroxy acetylene, alkenyl phenones, and cinnamaldehyde derivatives, organic nitrogen compounds like amines, amides, heterocyclics or quarternary ammonium salts.

Jiang et al in 2005[21] investigated the corrosion inhibitor performance for CO_2 corrosion of N80 steel under static and flowing conditions. Carbon dioxide (CO_2) corrosion of carbon steels is an important problem for oil and gas production and transportation. Inhibitor injection has been and still is the most cost-effective method of solving the problem. But most inhibitor evaluations are generally only based on test results under stagnant or low flow rate (<1 m/s) conditions. This practice may cause the abuse of inhibitors or unexpected inhibitor performance in some actual conditions, because a high flow rate for single phase flow or even a low flow rate for multiphase flow (gas-liquid or sand-containing liquid-solid two-phase flow) probably deteriorate the inhibitor film properties, especially the tenacity of adsorption. Vishwanatham et.al in 2007 [22]had studied the inhibition action of Methoxy phenol (MPH) and nonyl phenol (NPH) on corrosion of N 80 steel in 15% HCl at different exposure period (6 to 24h) and temperature (30 to 110^0C). NPH and MPH had shown maximum efficiency of 83% and 78% at 75mM inhibitor concentration in the acid after 6 h exposure test at ambient temperature. Halogenated salt (HS)-acetylenic compound (AC) mixtures were tested as corrosion inhibitors of 13Cr and 22Cr stainless steel and N80 and P110 carbon steel when exposed to 15 wt.% HCl solutions, at 50°C, 80°C and 100°C by Menezes et al in 2007 [9]. The best corrosion inhibition efficiency is obtained when the concentration of both AC and HS is 1.5 wt. %. Two 2-mercaptobenzothiazole derivatives,*N*,*N'*-bis-(2-thionobenzothiazolin-3-yl-methyl)-*n*-dodecylamine(BTBMDA) and *N*,*N'*-bis-(2-thionobenzothiazolin-3-yl-methyl)-*n*-octadecylamine (BTBMOA), were synthesized under microwave irradiation by Junping et.al in 2007 [23]. Results showed that the two inhibitors could inhibit the corrosion of

N80 steel in simulated solution significantly. Kumar et .al in 2008 [24] investigated the effects of inhibitor mixtures (TVE-3A, TVE-3B and TVE-3C) containing formaldehyde in combination with phenol or cresol on corrosion behavior of N80 steel in 15% HCl solution .The influence of temperature (30-115°C) and time interval (6-24 h) in the absence and presence of inhibitors on corrosion of the steel in the acid has been studied. TVE-3B has shown the maximum inhibition of 68.6% at ambient temperature whereas maximum inhibition shown by TVE-3A and TVE-3C was found to be 62.2% and 65.7% respectively. Khaled et al in 2008 [25] synthesized a new safe green corrosion inhibitor namely N-(5,6-diphenyl-4,5-dihydro-[1,2,4]triazin-3-yl)-guanidine (NTG) and its inhibitive performance towards the corrosion of mild steel in 1 M hydrochloric acid and 0.5 M sulphuric acid had been investigated. These studies have shown that NTG was a very good inhibitor in acid media and the inhibition efficiency up to 99% and 96% in 1M HCl and 0.5M H2SO4, respectively. Jiancum et al in 2008 [26] evaluated the corrosion inhibition of three α,β-unsaturated carbonyl compounds on N80 steel at high temperature and in concentrated acid medium, and proved that both cinnamaldehyde and benzalacetone had an evident anticorrosion effect and could reduce the corrosion of steel effectively in acid medium. Migahed et al in 2008[27] evaluated the effectiveness of the new synthesized compound namely; 6-methyl-5-[*m*-nitro styryl]-3-mercapto-1,2,4-triazine as corrosion inhibitor for mild steel in 12% HCl solution at 50 °C using various chemical and electrochemical techniques. The results showed that anodic dissolution of mild steel was remarkably decreased. Vishwanatham et al in 2009 [28] evaluated the protective ability of mixtures of aniline and phenol as corrosion inhibitors for N80 steel in 15 per cent hydrochloric acid, and reported that synergistic effect of the mixture containing 0.1 per cent AL with 0.7 per cent PH has shown a maximum efficiency (75 per cent at ambient temperature) among other tested combinations in the acid medium.

The inhibition effect of 6-benzylaminopurine (BAP) on the corrosion of cold rolled steel (CRS) in 1.0–7.0 M H_2SO_4 at 25–50 °C was studied by Xianghong Li et al in 2009 [29]. CO_2 corrosion inhibition of N80 steel in liquid single-phase and liquid/particle two-phase flow by 2-undecyl-1-hydroxyethyl imidazoline (HEI-11) and 2-undecyl-1-hydroxyethyl-1-hydroxyethyl quaternary imidazoline (HQI-11) was investigated by Liu et. al in 2009 [29]. The results show that the corrosion rate in the absence and presence of the imidazolines is strongly dependent on the flow condition and presence of entrained sand particles. Chitosan-g-N-carboxymethyl-2-sulfo-4, 5-2H imidazolinone (CSIDZ) with different grafting ratios polymers were synthesized by Zeng et. al in 2009 [30] with 2-bromoacetic acid、Chitosan、2-sulfo imidazolinone as raw materials. The antibacterial activity of the grafted polymer was examined against a series of test microorganism by quantitative suspension method. Yang et.al in 2009 [31] synthesized a corrosion inhibitor with quinoline and benzyl chloride, and then mixed with synergist and dispersant to prepare organic nitrogen quaternary ammonium corrosion inhibitor. Zeng et. al in 2009 [32] developed a new corrosion inhibitor and universal antibacterial reagent,namely,the copolymer of N-isopropylacrylamide (NIPAM) and N-allyl-1-benzoyl-3-phenyl-4, 5-dihydro-4-formamido pyrazole (BPCP).The inhibition efficiency of the copolymer has the maximum value of 90.3% at a inhibitor concentration of 6 g/L. Okafor et al in 2009 [33] studied the inhibition and adsorption behavior of 2-undecyl-1-sodium ethanoate-imidazoline salt (2M2) and thiourea (TU) on N80 mild steel in CO_2-saturated 3 wt.% NaCl solutions at 25 °C, pH 4, and 1 bar CO_2 partial pressure using electrochemical methods. The data suggest that the compounds functioned via a mixed-inhibitor mechanism. A synergistic effect was observed between TU and 2M2. In their another work,[34] the inhibition behavior of 2-undecyl-1-ethylamino-1-methylbenzyl quaternary imidazoline (2UMQI) and KI on mild steel in 1.0 M H_2SO_4 solutions was investigated at 25 °C using electrochemical methods. The results indicated that 2UMQI inhibited the corrosion of mild steel. Zhu et al in 2010 [35] in a self-designed occluded corrosion cavity (OCC) simulated cell, the inhibition mechanism of sodium laurate ($C_{12}H_{23}O_2Na$) to the under deposit corrosion of the N80 steel in a neutral 0·2 mol L^{-1} NaCl solution was studied. The results showed that $C_{12}H_{23}O_2^-$ could form a monomolecular adsorption film on the N80 steel surface in the studied solution, whose adsorption behaviour would follow Flory–Huggins isotherm model, and inhibit both anodic and cathodic processes. $C_{12}H_{23}O_2^-$ displayed good inhibition performance to the under deposit corrosion of the N80 steel in the studied system, which could be mainly attributed to the inhibition to the electrode processes of the bulk cathode and occluded anode, the increase in the resistance of the corrosion deposit layer and the prevention to the autocatalysing acidification effect in OCC. Amosa et.al in 2010 [36] evaluated some selected environmentally benign iron compounds (synthetic magnetite and ferrous

gluconate) as corrosion inhibitors for oil-well steel (N80) in 50 mg/l sulphide concentration at various pH ranging from 5.5 to 11.5 and at High Temperature, High Pressure (HTHP) conditions by the weight loss method. The test temperatures were 150°F, 275°F and 350°F respectively for pressures of 3000 psi, 5000 psi and 6000 psi. The ferrous complex was found to be a better corrosion inhibitor compared to the synthetic magnetite. It exhibited up to 99.2% inhibition efficiency (IE) when the dose of the scavenger was doubled (i.e. when the sulphide to scavenger ratio was 1:2) irrespective of other factors such as pH, temperature and pressure. Whereas, the synthetic magnetite's optimum inhibition efficiency (IE) was observed to be up to 75.1% only when the ratio of the sulphide to scavenger was 1:4 at the lowest pH of the experiment (pH 5.5) which is not desirable for a drilling mud. Yadav et.al in 2011 [8] conducted corrosion inhibition study of two amino acid compounds; 2-amino-*N*-decyl-3-phenyl propionamide (Inh I) and 2-amino-*N*-decylacetamide (Inh II) have been performed for N80 steel in 15% HC. The inhibition efficiencies of the inhibitors followed the sequence, Inh I > Inh II.

Jun et. al in 2010[37] used cigarette butts, one of the most ubiquitous forms of garbage in the world and need to be recycled because their toxicity can kill saltwater and freshwater fish, as corrosion inhibitors for N80 steel at 90 °C in hydrochloric acid. Results show that the inhibition efficiencies arrive at 94.6% and 91.7% in 10% and 15% (wt %) HCl solution, respectively, by adding 5% (wt %) inhibitor. In 20% HCl solution, they show a maximum inhibition efficiency of 88.4% by adding 10% inhibitor. Juantao et.al in 2011 [38] reported that one of effective ways to reduce pollution from cigarette butts is recycling the cigarette butts and inhibitor from recycled cigarette butts shows good inhibition properties .He studied the impact of CuCl on recycled cigarette butts as corrosion inhibitor for N80 steel at 90 °C in 15% HCl. The results show that the inhibition efficiency of water extracts from cigarette butts in the presence of CuCl is higher than in absence of CuCl, and it can reach 95.3% when 9% water extracts with copper added is used.

Sangeetha et al in 2011[39] in their review paper list some extracts of plant materials to replace the environmentally hazardous chromates, several non –chromates that have been used as corrosion inhibitors. The plant extracts are environmentally friendly, non- toxic and readily available. These extracts contain many ingredients. They contain several organic compounds which have polar atoms such as O, N, P and S. They are adsorbed onto the metal surface through these polar atoms; protective films are formed. Xiao et.al in 2011 [40] synthesized 1-phenyl-3-(1-aniline)-1-propene (PAP) by aniline and Cinnamaldehyde, and its inhibitive effect on N80 steel in 15% HCl solution was investigated. The results were shown that, the inhibition efficiency of PAP could exceed 99%.

Evrim Hur et.al in 2011[41] synthesized two novel benzothiazole derivatives (2-[(1, 3-benzothiazol-2-ylamino) methyl]-1-naphthol (1) and 2-{[(6-methyl-1, 3-benzothiazol-2-yl) amino] methyl}-1-naphthol) (2). The potentiodynamic polarization curves indicate that investigated benzothiazole derivatives were acting as anodic inhibitor. Chen et.al in 2011 [42] evaluated the inhibition performance of two imidazolines and their quaternary ammonium salts and the results showed that naphthene-base imidazoline（NI）and lauric acid imidazoline（YUC） had good inhibition efficiency on N80 steel in 15% HCl and 9% mud acid at 60^0C.Okafor et.al in 2011 [43] studied the corrosion and corrosion inhibition of N80 and P110 carbon steels (CS) in CO_2-saturated simulated formation water by rosin amide imidazoline (RAIM) and the results indicate that N80 CS performs better than P110 CS with RAIM at lower temperature and P110 CS at higher temperatures.Liu et.al in 2011[44] evaluated the performance of the selected inhibitors, including thioglycolic acid (TGA), diethylenetriamine (DETA), and naphthene acid imidazolines (IM), on the bare surface of N80 steel and its scaled surface pre-corroded in CO_2-saturated 1%NaCl solution. The results indicate that there is a remarkable difference in inhibition efficiency of inhibitors on the N80 steel with and without pre-corrosion scale. The synergistic effect between inhibitors and corrosion scale not only depends on the size of inhibitor molecules, but also depends on the interaction of the inhibitor with the corrosion scale.

Conclusion

The oil and gas industry has invested heavily in material and personnel to try to tame corrosion and the lines and the component fittings of the lines would undergo material degradation with the varying conditions of wells due to changes in fluid compositions, souring of the wells over the period, changes in the operating conditions of pressures and temperatures. The material degradation results in the loss of mechanical properties like strength, ductility, impact strength etc leads to loss of materials, reduction in thickness and at times ultimate failure. Hence it is imperative to the field operators, pipe line engineers, designers to have corrosion awareness concerning oil and gas industries in their day to day activities to compact and mitigate corrosion and to ensure smooth and uninterrupted flow of oil and gas to the end users. In spite of much advancement in the field of corrosion science and technology, the phenomenon of corrosion remains a major concern to oil and gas industries around the world. Though the serious consequences of corrosion can be controlled to a great extent by selection of highly corrosion resistant materials, the cost factor associated with the same, favors the use of cheap metallic materials along with efficient corrosion prevention methods in many industrial applications. In this aspect, corrosion inhibitors have ample significance. But in spite of the long history of corrosion inhibition; a highly efficient and durable eco-friendly inhibitor that can completely protect iron and low carbon steel in aggressive environments for longer duration is yet to be realized.

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