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Short Review Paper

A review on corrosion problems in context of oil and gas industries and application of suitable corrosion inhibitors

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Abstract

This review paper throws light on ways to combat corrosion of steel. A variety of inhibitors for steels corrosion in the acidic solutions are dealt here. A great emphasis has been made on HCl solutions in drilling and acidizing operations low-grade steels, at high temperatures. A combination of corrosion inhibitors with surfactants, solvents, natural extracts as well as intensifiers in order to improve the strength or we can also say the efficiency of each individual compound at higher temperatures. The aim of this research is to give a pretty good idea about the corrosion problems encountered in drilling and acidizing operations and the inhibition techniques adopted in order to tackle the problem.

Keywords: HCl acidizing, oil and gas industries, Corrosion inhibition, surfactants, acidizing.

Introduction

Corrosion is a very common phenomena which is encountered in the oil and gas industry. The corrosion engineers are mainly concerned with this problem as it occurs in metals from small scale to large scale works and in context of oil and gas industries. Internal corrosion in oil and gas industry is caused by water, carbon dioxide (CO_2) and hydrogen sulfide (H_2S), and also can be aggravated by microbiological activity importantly; the flow regimes of multiphase fluids greatly influence the corrosion rate. For example, at high flow rates, flow induced corrosion and erosion-corrosion may occur, whereas at low flow rates, pitting corrosion is more common. Corrosion is generally related to the amount and nature of the sediments. High-velocity flow tends to sweep sediments out of the pipeline, whereas low velocity allows sediments to settle at the bottom, providing sites for pitting corrosion.

Among the various methods to combat corrosion in oil and gas industry, the use of corrosion inhibitor is one of the best and economical methods. A long list of corrosion inhibitors classified into anodic, cathodic or mixed corrosion inhibitor. There are also various classifications based on the chemical nature, i.e., organic or inorganic. The general mechanism of corrosion inhibition is chemical adsorption (also called chemisorption) of the inhibitor on the surface of the metal and forms a protective thin film which protects the underlying metal from corrosion[1].

Corrosion in the oil industry

As oil and gas industries have very complex nature of demands, several aspects of process pathway are frequently attacked by corrosion. Brondel et al.[2], from Schlumberger have enumerated and described the most probable causes of corrosion. The offshore structures always exposed to rain and seawater, face corrosion at severe rates. In order to tackle this, zinc primers are applied to the parts subjected to moisture etc, which act as sacrificial anodes. Cathodic protection is also used when an opposite current to the corrosion is applied. The drilling pipe equipment used here also has resin based coatings for protection against corrosion as they pass through formation fluids and drilling mud. Drilling muds also act as effective corrosion inhibitors as they are water or oil based. They are non-corrosive and polymer based viscosity modifiers along with a mixture of some more additives reduces the pH and makes the material corrosive. Drilling mud also has a tendency to introduce oxygen and acid gas contaminants which enter via mixing or storage tanks. So here we find that the corrosion engineer has to give prime consideration to the maintenance of pH values so as to be very sure about the extent of corrosion prevention or inhibition.

In addition to this, corrosion finds its way throughout the casings and pipes which are a part of distribution and refining of the hydrocarbon process pathway. Apart from oxygen, CO_2, and H_2S contaminations, the downstream processes also face corrosion problems due to presence of naphthenic acids and aromatic carboxylic acids, in very high temperatures. There are certain units in oil and gas industries that absorb and strip hydrocarbon stream also create corrosion problems which should be given due consideration[3].

The work done in this review sheds light on the most common polymeric structures employed as corrosion busters used in different stages in context of oil and gas processing In even in

the case of oil and gas industries the use of corrosion inhibitors for combating corrosion is very effective since these CIs in required quantities can be applied. The application can be continuous or batch so that the rate of corrosion at the most susceptible areas can be mitigated and there are no chances for a situation to occur where the plant or industry has to be shut down there by affecting the process and operations. Polymeric inhibitors are not widely used but the properties of the macromolecules like better film forming agents. Highly versatile polymers surpass the corrosion inhibition performance of the small molecule inhibitors while keeping the concentration down to a minimum.

Many of the corrosion inhibitors covered under this review are basically polyamine corrosion inhibitors which are modified with carboxylic acid, thiols, disulphides, phosphorus-containing functional groups. Polymerization techniques in CIs can lower down the corrosion rate in highly corrosive mediums found in oil and gas industries[3].

Well acidizing technique

Acidizing technique involves pumping acid into a bore well capable of yielding oil or gas. The main target of acidizing is to improve the bore well's productivity. There are three categories of acid treatments: acid washing; matrix acidizing; fracture acidizing. Limestone formations or sandstone containing carbonates carry large amount of hydrocarbon reservoirs[4]. Well acidizing technique is one of the most important steps in any oil and gas industry.

In well acidizing, the acids(usually a combination of strong and weak) are conveyed at high pressures through the rock formations, where chemical reaction takes place thereby dissolving them (calcite, limestone and dolomite) and enlarging them[5-9]. Acidizing technology is employed in conjunction with fracturing technologies as well as matrix acidizing[8].

Acidizing Techniques: There can be various acids used in acidizing procedure in the process of bore holes made for oil extraction through rock formation.

Use of HCl in acidizing: Once we have a good idea about the type of formation to be acidized and its composition (mineralogy) is critical in order to produce positive results. In case of carbonate formations, the acid job design is based on the use of hydrochloric acid (HCl). Acidizing normally involves pressure introduction of acid (15% conc.) (sometimes in the range of 5% up to 28%)[2,5,10,11]. Standard concentration of 15% acid was simulated in the year 1960 due to insolubility of the arsenic corrosion buster, the primary corrosion controller of that time period, because it was not soluble in conc. higher than 17%. The vast majority of acidizing methods for combating corrosion are carried out 5–28% acid concentration[12].

Reason for using HCl in acidizing procedure: During acidizing procedure, the acid is chemically consumed as well as neutralized as the formation material is dissolved. In case of carbonate formations the reaction is relatively simple. Hydrochloric acid reacts with the carbonate to form a salt, carbon dioxide, along with water. Chlorides show solubility in aqueous phases. Since the time through ages, many acids have been used but didn't prove to be good as compared to HCl. Due to the reason that for example, Sulphates, Nitrates, phosphates showed lower solubility when compared with strong acids like HCl[13].

Combination of HCl as a strong acid with weak acids: The most common conventional acids employed to combat corrosion are HCl, HF, acetic, and formic acids. It has also been noticed that adequate mixtures of these conventional acids with sulphuric, phosphoric, methane sulphonic, nitric, citric as well as chloroacetic acids are employed[2,6,9,10,14-17]. Hydrochloric acid is most commonly employed for boring in carbonate-based reservoirs such as limestone, dolomite etc. Hydrogen Flouride can also be employed alternatively for sandstone rock borings. HCl mixed with Hydrogen flouride, also known as mudacid, is used[5,2]. Three treatment stages are there which are as pre-flush, main-flush, and after-flush. The Pre-flushing, main-flushing is performed with HCl, HF etc. Whereas the after flushing activity is done with the ethylene glycolmonobutyl ether (EGMBE).

Use of organic acids along with hydrochloric acid (inorganic acids): Acetic as well as formic acids in addition to HCl can prove to be good busters for corrosion[18].

Problems encountered while combined application of formic and organic acids: Ali et al.[9] found that formic acids, aliphatic acids of small chain lengths are found highly corrosive as Hydrochloric acid to pipes and other metals but are easy to retard corrosion as compared to HCl[19].

One of the demerits is that carbonate solubility in strong acids is low as compared HCl. Acetic as well as formic acids may also be employed instead of HCl at higher temp[20].

Corrosion problems posed by use of hydrochloric acid and other acids in a refining industry

As HCl is used for dissolving $CaCO_3$ in pickling applications at a lower cost, the faster reaction, the inhibition rates, vary with the Hydrochloric acid conc, which cause threat to the metals. Corrosion problems to steel, tin, or other chrome-plated equipment is faced due to use of HCl which is a great demerit. The acid pumped down in the well is known as live acid and the acid produced from the well after completion of treatment is labelled as spent acid. We can very well have an understanding of this case by just looking into an example of spent acid pilot testing in a lab by taking HCl and thereby mixing it with 150g of dissolved $CaCl_2$ and a pH of 1[4]. For augmenting the acid it should be well maintained[6,7,21].

How to tackle the problem of corrosion in oil and gas pipelines: Now in order to achieve the desired deeper

penetration of the stimulation fluid into the formation, the acid has to be emulsified by using an appropriate agent. In such a manner the acid reaction rate with the rock formation is retarded by a significant although is effective and quantity of spent acid is less thereby allowing deeper penetration through the rock formation (''un retarded'' 15% Hydrochloric acid at temp of 160^0C would permeate only about 10 cm)[19].

Different Materials used in manufacturing of oil wells: Variety of materials is used in making pipelines for oil and gas industries since they have to convey oil and gas from the source to the consumer. One of the basic requirements for a good and durable pipe is it should be resistant from acids thereby causing corrosion. The steels which are employed in well construction come in a broad spectrum from MS of grade N80 of API USA, J55, duplex and chromium steels etc[20,5] One of the properties of metal corrosion resistance is the weld construction acid corrosion phenomena has to be well acquainted by a corrosion engineer[22,23]. Steel metallurgy one of the most important criteria for acidizing the CIs in laboratory testing[22,23]. A small problem sometimes arises because the standard materials which are commonly employed, e.g. API N80 steel, may vary considerably from one manufacturer to another or from one lot to the next, which leads to confusion in comparative corrosion testing.

Many developments took place since last few decades in the development of new corrosion resistant alloys (CRA). From economical point of view many carbon steels are employed[24-27].

A combination of CS along with some special chemical treatments proves to be the most cost cutting method for corrosion control or inhibition[28]. Without the applications of certain chemicals in cases of CIs, carbon steel materials are highly susceptible to corrosion when mixed with certain acids[29]. More corrosion resistant alloys such as austenitic or duplex stainless steels may find a place as good corrosion busters[2]. High-grade alloys are responsible for causing corrosion and also hike the capital costs[20,30]. API N80 CS by American Petroleum Institute is used as the main construction material for down hole tubular, flow lines, and transmission pipelines in the oil industry[7,30-32] and consequently most acid CI data exist for that steel type[33]. API L-80 grade CS tubing is H_2S-resistant steel[7]. A liner for pipes and tubing by the name API G95 was extensively used[19].

Inhibition of steel corrosion

Use of corrosion inhibitors in the acidizing treatments: It is impossible to prevent corrosion completely, however it is possible to control or reduce it[18]. To control corrosion of well tubulars, coiled tubings, etc.[5,20]. A corrosion engineer has to make a good decision regarding the selection of a proper material since corrosion environment vary a lot in context of oil plants and refineries. Corrosion inhibitors of a certain types may be effective for inhibition for a particular material but may prove to be ineffective for the other[34]. Because the mechanism of inhibitors is complex and usually not known i.e. cannot be predicted for its performance Researchers and corrosion engineers face difficulty in understanding the mechanism of a corrosion inhibitor and it's a tough task for them to predict whether a particular CI will be effective for a particular material or not[35].

Compounds employed as Corrosion Inhibitors: Acetylenic alcohols, aromatic aldehydes, alkenyl phenones effectively combat corrosion[16,17,36-38]. Vishwanathan and Haldar[28] also did an experiment in which they found effective inhibition of N-80 Steel in 15 percent Hydrochloric acid.

Common Polymeric corrosion inhibitors: The Long Chain polyamines which are generally derived from long chain fatty acids are good film forming inhibitors[39]. The amines having certain chain lengths and substitution are protection properties of the molecule also prove to be good agents for corrosion mitigation. Several patents[40-42] have explained polyamine chemistry to show how good it is for corrosion inhibition. Some reports drafted for typical polyamines with fatty chain corrosion inhibitors were synthesized by applying equimolar quantities of polyalylene amines, unsaturated diol, as well as organic acids to combat the corrosion problems[41].

Organic acids constitute carboxylic acid, which reacts in the lipophilic group, thereby imparting oil solubility to the inhibitor to form a protective layer for effective inhibition, which if are chemically represented are monocarboxylic acid containing 5-20 Carbon atoms[41].

Use surfactant as corrosion inhibitor: Abiola[43] recorded that some of the derived compounds proved to be effective in preventing evolution of H_2 gas and of Mild steel corrosion in 0.5mol/L concentration and 5mol/Litres Hydrochloric acid at temps of 30^oC. Elachouri et al.[44] used some of very well known surfactants, i.e. some 2 alkyl (C_nH_{n+1}) dimethylamonio) butanol bromides (n=11–15) as CIs for Fe and proved to be effective cathodic type CIs. Their g was augmented by Carbon atoms and CI. Tang et al[45] reported that Napthol based compounds showed fair corrosion busting properties. Moreover, its IE (inhibition efficiency) decreases with increasing temperature. Qui et al.[46] syenthesized 3 compounds as CI and were good enough to combat corrosion.

Green corrosion inhibitors

Although these types of inhibitors are not that effective since its difficult to figure out which inhibitor is responsible for countering corrosion esp in cases of combined use of green corrosion inhibitors, so they have to be used in combination of a strong acid to increase the efficiency and thereby would also prove to be eco friendly. Inhibition performances of some herbs such as (garden cress, coriander, anis, hibiscus and black cumin) were proved as new type of green inhibitors for the protection of steel in acidic medium[47]. Parikh et al.[48] reported the corrosion inhibition efficiency of garlic, onion and bitter gourd by using them as good corrosion inhibitors for mild steel in HCl media.

In a similar fashion, the inhibition activity of quinine and caffeine has been studied for their anticorrosive activity of carbon steel in HCl media[49,50]. The non-toxic corrosion inhibitor for non-ferrous metals, the inhibitive property of Ananas Sativum leaves extract, Pactin from citrus peel[51], *Occiumviridis* extract[52], *Sansevieria trifasciata* extract[53], *Opuntia* extract[54] these natural compounds have been successfully applied as corrosion inhibitors on the surface of aluminium and aluminium alloy in HCl medium. In this context, the corrosion inhibition of aluminium and zinc substrate in HCl medium using Aloevera extract and *Hisbiscus subdariffa* extract were found adequate corrosion inhibitors[55].

Recommendations for testing

Before a corrosion inhibitor (CI) is to be implemented for application at site, a number of laboratory tests are to be conducted in order to assure that the particular CI will be effective or not. The laboratory tests are conducted under the same conditions of temperature as well as pressure by using the same coupon testing material which will be adopted in the field conditions.

Acid volume/sample area ratio: Smith[12] had reported that the major contradictions in which Corrosion inhibition occurred by varying the ratios of the acids and the coupon surface area in respect of their volumes.

Surface preparation and cleaning: Smith[12] also made a claim that and slight differences in the metallurgy of the coupons materials made an effect on corrosion.

Conclusion

This review paper focuses on the corrosion inhibition of steel in acidic medium. A wide spectrum of corrosion controllers for steels in acidic media are represented in this manuscript. Use of hydrochloric acid of known % age at higher temperatures esp. in acidizing procedure is presented. In oil and gas industries, Low grade steel pipes are used because of the fact that it is cheap and easily available. Now the problem of corrosion is very common in such cases which occurs in well acidizing or pickling procedure. So to counteract this severe problem, acetylenic alcohols can act as good corrosion retarders, various surfactants, intensifiers, solvents can be employed. Natural extracts are found less effective as compared to synthetic ones. Physisorption type of adsorption prevents oxidation and rate of corrosion in case of HCl. Nitrate was used in case of oil fields of Saudi Aramco with a pre treatment by using biocides.

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