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Acidizing Corrosion Inhibitors: A Review

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Abstract

Oil well are periodically acidized for enhancing oil flow. Inhibited hydrochloric acid is used during acidization to prevent corrosion of N80 or J55 steel. In the present work authors have surveyed literature on acidizing corrosion inhibitors and the salient features of research work carried out by the authors have also been highlighted.

Keywords: Acidizing inhibitors, oil wells, HCl, HF

1. Introduction

Acid treatments have been applied to wells in oil and gas bearing rock formations for many years. Acidizing is probably the most widely used work-over and stimulation practice in the oil industry. By dissolving acid soluble components within underground rock formations, or removing material at the wellbore face, the rate of flow of oil or gas out of production wells or the rate of flow of oil-displacing fluids into injection wells may be increased.

2. Conventional Acid Systems

A number of different acids are used in conventional acidizing treatments, the most common are:

- Hydrochloric, HCl
- Hydrofluoric, HF
- Acetic, CH_3COOH
- Formic, HCOOH
- Sulfamic, H_2NSO_3H
- Chloroacetic, $ClCH_2COOH$

These acids differ in their characteristics. Choice of the acid and any additives for a given situation depends on the underground reservoir characteristics and the specific intention of the treatment, for example near well bore damage removal, dissolution of scale in fractures, etc. The majority of acidizing treatments carried out utilize hydrochloric acid (HCl). However, the very fast reaction rate of hydrochloric acid, and other acids listed above, can limit their effectiveness in a number of applications. All conventional acids including HCl, and organic acids react very rapidly on contact with acid sensitive material in the wellbore or formation. Worm holing is a common phenomenon. The rapid reaction means the acid does not penetrate very far into the formation before it is spent. Conventional acid systems are therefore of limited effectiveness in treatments where deep acid penetration is needed. Problems in placing acid are compounded in long horizontal or directional wells. In these wells it is difficult to achieve truly uniform placement of acid along the well-bore, which may be several thousand metres long, let alone achieve uniform stimulation of the surrounding formation. There was an early recognition that it was desirable to delay the rate of reaction of the acid and a variety of techniques have been developed to achieve this. Patents relating to several of these techniques have been issued.

3. Retarded Acid Systems

Methods which have been developed to slow the acidizing process include:

- Emulsifying the aqueous acid solutions in oil (or solvents such as kerosene or diesel fuel) to produce an emulsion, which is slower reacting.
- Dissolving the acids in a non-aqueous solvent.
- The use of non aqueous solutions of organic chemicals that release acids only on contact with water.
- The use of solutions of methyl acetate, which hydrolyses slowly at very high temperatures to produce acetic acid.

In addition to these methods, of which emulsifying the acid is probably the most important, some retardation of the reaction rate can be achieved by gelling the acid or oil wetting the formation solids.

3.a. Gelled Acids

Gelled acids are used to retard acid reaction rate in treatments such as acid fracturing. Retardation results from the increased fluid viscosity reducing the rate of acid transfer to the fracture wall. Use of the gelling agents (normally water soluble polymers) is limited to lower temperature formations as most gelling agents degrade rapidly in acid solution at temperatures above 130°F (55°C). Gelling agents are seldom used in matrix acidizing because the increased acid viscosity reduces injectivity and may prolong the treatment with no net benefit i.e. the slower injection rate counters the benefit of a reduced reaction rate.

3.b. Chemically Retarded Acids

These acids are often prepared by adding an oil-wetting surfactant to the acid in an effort to create a physical barrier to acid transfer to the rock surface. In order to achieve this additive must adsorb on the rock surface and form a coherent film. Use of these acids often requires continuous injection of oil during the treatment. At high flow rates and high formation temperatures, adsorption is diminished and most of these materials become ineffective.

3.c. Emulsified Acids

Emulsified acids may contain the acid as either the internal or the external phase. The former, which is more common, normally contains 10 to 30 percent hydrocarbon as the external phase and 15% hydrochloric acid as the internal phase. When acid is the external phase, the ratio of oil to acid is often about 2:1. Both the higher viscosity created by emulsification and the presence of the oil can retard the rate of acid transfer to the rock surface. This reduction in mass transfer rate, and its corresponding reduction in acid reaction rate, can increase the depth of acid penetration into the rock formation before the acid reacts with the rock or damaging material.

4. Types of Acidizing Processes

Acidizing is used to increase production in many situations. The most important include damage removal, completion and stimulation of horizontal wells, matrix acidizing, fracture acidizing and gel breaking.

4.a. Damage Removal

Damaged wells are those which suffer a restriction in flow rate. This may be due to a number of causes, for example, drilling damage or build up of carbonate scale. Damage may occur at the wellbore face or as a zone of reduced permeability extending several inches or even feet into the formation which severely restricts productivity. If the damage can be removed, very significant increases in production rate can be achieved. Conventional acidizing processes may remove damage up to several inches into the formation but are generally not effective for treatment of deeper damage. Success in treatment of deep formation damage requires the use of highly retarded acids.

4.b. Completion and Stimulation of Horizontal Wells

Horizontal drilling is a technique that has been enthusiastically adopted by the oil industry since about 1988. Because the wellbore has a greater contact area with the oil bearing zone, much higher rates of production are possible compared to conventional vertical wells. Despite higher costs, return on investment is better than for vertical wells in many circumstances. The importance of horizontal wells is likely to increase further. The current trend is towards very long wells which can be up to several km in length. When bringing these wells into production, the effective clean up of drilling fluid damage is needed. This is particularly important in low permeability formations.

4.c. Matrix Acidizing

Matrix acidizing involves the use of acid injected at below fracture pressure. It is normally used for the removal of skin damage associated with work-over, well killing or injection fluids, and by precipitation of scale deposits in tubulars, the wellbore or within the formation. As stated in (4.a.) above, removal of near well bore damage can result in significant stimulation, by say three-fold. Treatment normally involves injecting 15% HCl followed by a sufficient after flush of water or hydrocarbon to clear all acid from well tubulars. A corrosion inhibitor is added to the acid to protect tubulars during exposure to acid. Other additives, such as anti-sludge agents, iron chelating agents, de-emulsifiers and mutual solvents are added as required for a specific formation. Matrix acidizing may also be used to increase formation permeability in undamaged wells. Where damage is thought to exist within the formation, the aim of the treatment is to achieve more or less radial acid penetration deep into the formation to increase the formation permeability around the wellbore. Deep penetration can only be achieved with retarded acid systems.

4.d. Fracture Acidizing

Fracture acidizing, also known as acid fraccing is the most widely used acidizing technique for stimulating limestone or dolomite formations. In an acid fracturing treatment a pad fluid is injected into the formation at a rate higher than the reservoir matrix will accept. This rapid injection produces a build-up in wellbore pressure leading to cracking (fracturing) of the rock. Continued fluid injection increases the fracture's length and width. Acid (normally 15% HCl) is then injected into the fracture to react with the formation and create a flow channel (by etching of the fracture surface) that extends deep into the formation. This allows more reservoir fluid to drain into the wellbore along the new fractures once the well is put back on production. The key to success is penetration of reactive acid along the fracture. This is more difficult to achieve in acid fraccing than in propped fractures (the other main form of fracture treatment). Acid penetration is particularly important in low permeability carbonates, which are frequently subject to scaling where small fractures meet larger fractures.

4.e. Gel Breaking

Acids are used to break acid sensitive gels used in propped fracture applications. The use of acid breakers in open horizontal well compilations has recently been demonstrated.

Acidizing Inhibitors

Around 1895, Herman Frasch [1] conceived the idea of increasing the flow of oil wells in limestone formation based on chemical action. He recommended 30 to 40 wt% hydrochloric acid for acidizing followed by neutralization of reacted acid after the stimulation was completed.

In 1915, J.A. Aupperle [2] was the first to recognize the inhibiting effect of antimony for steel in hydrochloric acid and its accelerating effect on zinc and other metals. He described a method for the quantitative removal of zinc from galvanizing (hot dipped) sheets which was adopted as a standard. According to him antimony accelerates dissolution of zinc metal in hydrochloric acid and it plates out on the steel, preventing acid corrosion to the steel plant.

In 1928, it was claimed by J.A. Gravell [3] that arsenic can be used as an acid corrosion inhibitor for use in storage and transport of acids in steel drums. Arsenic was reported to form a protective coating on the metal surface. He further claimed that metals below iron and above mercury on the electromotive scale had properties similar to arsenic.

In 1945, an aldehyde H_2S reaction product was claimed by W.H. Hill [4] for use in pickling as an acid corrosion inhibitor. The reaction was made under neutral pH conditions.

A. J. Saukaitis and G. S. Gardner [5] in the year 1956 claimed a derivative of rosin amine in which rosin amine and a ketone having a reactive hydrogen atom adjacent to the carbon were reacted with formaldehyde in the presence of hydrochloric acid. The derivatives were effective as inhibitors up to temperatures as high as 302°F.

Mansfield et al. [6] in the year 1959 claimed a hydrochloric acid corrosion inhibitor used in acid baths, made from the reaction product of ammonia or methylamine, formaldehyde and an olefin such as vinyl toluene, α-methyl styrene or α–paradimethylstyrene.

In 1963, Monroe et. al.[7] claimed a major accomplishment in hydrochloric acid corrosion inhibition. They found that the reaction product of an amine or amide (having an active hydrogen atom) excess formaldehyde and a ketone (with an active hydrogen alpha to the carbonyl) in the presence of hydrochloric acid catalyst and excess tall oil fatty acid produced a corrosion inhibitors base. This base when blended with a surfactant and an acetylenic alcohol was claimed to produce a hydrochloric acid corrosion inhibitor equal or superior to arsenic in performance at temperatures 250°F.

Two major advances were made in the years 1964 and 1965 by A. Cizek and J. A. Karlitz [8]. First one includes the crude quinoline benzyl chloride quaternary with an oily substance to include such materials as kerosene, alkyl naphthalenes etc. for oil wetting properties. The second involves the use of formic acid as an intensifier or inhibitor aid. When an intensifier is included in the acid with the corrosion inhibitor the performance properties of the corrosion inhibitor are enhanced. The temperature ranges claimed in the first case was about 200 to 220°F and in the second it was claimed to work in the range of 220°F to 350°F and the pressure was 1000 psi or greater.

F. A. Beale and Oakes [9] were assigned a patent in the year 1966 involving acetylenic alcohol. They claimed synergistic combinations of acetylenic alcohols as corrosion inhibitors for aqueous solutions of non-oxidizing acids.

Lee [10] in the year 1969 evaluated the corrosion inhibiting effect of 7-nitroso-8-hydroxy-quinoline against mild steel in HCl solution. The efficiency was more than 90%.

B. J. Keeney and J. W. Johnson [11] in the year 1973 found that most existing acid corrosion inhibitors used in hydrochloric acid are enhanced when cuprous iodide is combined with the acid inhibitor; temperature was claimed in the range 150 to 450°F. The intensifier was claimed to be effective at high temperatures and low pressure.

McDougall et al.[12] in the same year developed an acetylenic alcohol, amine and/or amine quarternary surfactant, organic solvent and formic acid derivative for use in 15 and 28% hydrochloric acid at elevated temperatures.

A new intensifier in the year 1974 was claimed by T. J. Griffin and F. E. Dollarhide [13] which involved the use of an ionized iodine compound with a corrosion inhibitor consisting of a heterocyclic amine, acetylenic alcohol, a hydrocarbon solvent and surfactant mixture. This inhibitor package was claimed to be effective in mixtures of hydrochloric acid and or mutual solvents. Without the iodide salt as intensifier the same inhibitor was effective only in acid without alcohols and/ or mutual solvents.

In 1977, Sullivan et al. [14] claimed the use of chloromethyl naphthalene quarternary with acetylenic alcohol, surfactants and a formic acid derivative.

A very interesting information was presented by W. R. Dill and B. R. Keeney [15] in the year 1978 which showed that mixtures of formic acid and hydrochloric acid may have particular application as stimulation fluids in very high temperature environments. It was further shown that hydrochloric acid – formic acid mixture are less corrosive than straight hydrochloric acid and such mixtures may be optimized to contain as much as 10% hydrochloric acid and sufficient formic acid to work as an equivalent to 15% hydrochloric acid.

Anderson et al. [16] in the year 1984 examined the effectiveness of 4,7-diphenyl-1,10-phenanthroline in acid medium. They established that the inhibitive action is due to the presence of electrons in the ring.

Frenier et al. [17] in the year 1985 claimed a corrosion inhibitor composition for high temperature wells that consisted of an iodide salt, a formic acid compound, an amine or a quaternary nitrogen compound, and/ or an oxygen containing compound such as phenyl ketone, a phenyl aldehyde, or an alkynol.

Granese and Rosales [18] in the year 1987 elucidated the mechanism of corrosion inhibition of iron and steel in HCl media. Inhibitors effective in corrosion prevention of Iron and steel on treatment with HCl mainly belong to the group of nitrogen containing compounds such as alkyl and aryl amines, saturated and unsaturated N-ring compound, condensation product of amines with aldehydes and ketones and carboxylates amines, nitriles aldoximes, keto-oximes. They observed reduced corrosion by N-containing organic compounds like acridine, hexamethylene, quarternary ammonium sulphate etc. at 85°C. Urotropin a nitrogen containing inhibitor has a wide application in HCl.

An environmental friendly inhibitor was claimed by F. B. Growcock and W. W. Frenier [19] in the year 1988 that consisted of cinnamaldehyde and a surfactant for inhibiting the attack of aqueous corrosive fluids on metals. It was reported for use at low temperature.

Chan et al [20] in the year 1989 evaluated a macrocyclic compound as acid corrosion inhibitor for steel by potentiostatic and impedance methods. It gave 82% efficiency at 25°C in acid chloride environment.in the

Acetylenic alcohols were found by I Hashi Omar and F. Zucchi [21] in the year 1990 to be effective class of inhibitors of carbon steel in 1 N HCl with the help of weight loss measurements and electrochemical data.

The influence of some heterocyclic compounds containing more than one nitrogen atoms in their molecules on corrosion of carbon steel in 1 N HCl was investigated by Trabanelli et al.[22] in the year 1990. With a view to establish correlation between molecular structure and the inhibition efficiency of the various compounds among the examined substances 2.2-Biquinoline, quinoxaline, quinozoline and 2-mercaptopyrimidine showed good inhibiting efficiencies (80%-90%) at temperature 25°C-60°C. The influence of some of the substances on hydrogen penetration into the steel was also studied by these authors.

The inhibitive effect of some substituted phenyl-N-phenyl carbamates on corrosion of iron in 2N HCl was studied by Fonda et al. [23] in the year 1990. They found that inhibition of corrosion occurs by way of adsorption through oxygen atom of phenoxy group and nitrogen atom of –NH group. The inhibitory character of the compound depends upon the concentration of the inhibitor as well as its chemical composition.

In 1991, mercury salts were claimed by A. Cizek [24] for use as an intensifier with an inhibitor. The inhibitor was said to be composed of an acetylenic alcohol, a quarternary ammonium compound, and aromatic hydrocarbon and surfactant.

Granese et al. [25] in the year 1992 studied various heterocyclic N-compounds such as N-hexadecyl derivative of pyridine, quinoline, acridine in HCl by electrochemical and surface analysis and concluded that acridine had the strongest interaction with iron and steel surface while pyridine has the least. According to them the efficiency of these compounds increases with number of aromatic systems and electrons availability in the molecule.

Stupnisek et al. [26] in the year 1992 investigated the inhibiting action of various substituted N-aryl pyroles on corrosion of steel in strong acid solution using electrochemical methods with a view to study the relationship existing between the molecular structure and inhibition efficiency. They found that inhibition efficiency of pyroles was significantly influenced by the type and position of the functional groups. Thus N-pyrole bearing fluorine at ortho position gave better performance than other pyrole derivatives.

Quraishi et al. [27] in the year 1996 synthesized two heterocyclic compounds namely QJ-1 and QJ-2 in the laboratory from indigenous chemicals and their corrosion inhibiting action was evaluated by weight loss method and electrochemical technique in 15% HCl under boiling condition. The performance of the synthesized compound was compared with propargyl alcohol, a commercially available acidizing inhibitor. Both QJ-1 and QJ-2 showed better performance than that of PA for mild steel. In case of oil field steel QJ-2 was found to be as effective as PA.

Quraishi et al. [28] in the year 1997 studied some new triazole derivatives, namely 4-aminobenzylidene-3-propyl-5 mercapto-1,2,4-triazole, 4-aminosalicylidene-3 propyl-5 mercapto-1,2,4,triazole (ACPMT), 4-aminovanillidene-3-propyl-5-mercapto-1,2,4,-triazole, and 4-aminodimethylamino-benzylidene-3-propyl-5-mercapto-1,2,4-triazole (ADPMT) and found their inhibiting action on the corrosion of mild steel in 15% HCl under boiling conditions by the weight loss method. With the exception of ADPMT, all the triazole derivatives tested showed an inhibitor efficiency of 98%. Triazole compounds ACPMT and ASPMT showed an inhibitor efficiency of 99%. Their efficiency was found to be comparable with that of propargyl alcohol.

ABPMT ACPMT

ASPMT VPMT ADPMT

Quraishi et al.[29] in the year 1999 synthesized selected condensation products of aromatic aldehydes and p-phenylenediamine and evaluated as corrosion inhibitors for mild steel and oil-well steel N-80 in 15% HCl at 105°C ± 2°C by the weight loss method. The entire condensation product showed excellent performance. 2,4-dicinnamyledene aminophenylene (DCAP) was found to be the best corrosion inhibitor. It exhibited 99.75% inhibition efficiency for MS and 99.12% for N-80 steel at 5000 ppm of inhibitor concentration. Potentiodynamic polarization studies carried out at room temperature on mild steel in 15% HCl containing 500 ppm of condensation products showed that all the investigated compounds were mixed type inhibitors, whereas 500 ppm DCAP on N-80 steel behaved predominantly as anodic inhibitors.

DCAP

Quraishi et al. [30] in the year 2000 synthesized 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 N-80 in boiling 15%HCl solution by weight loss method. Potentiodynamic polarization studies carried out on mild steel and N-80 steel at room temperature showed that all the investigated compounds are of mixed type. Adsorption studies showed that all the investigated compounds followed Temkin's adsorption isotherm.

Quraishi et al. [31] in the year 2000 synthesized a new N and S containing heterocyclic compound CAHMT and evaluated as corrosion inhibitor for oil-well tubular steel N-80 and mild steel at 105°C ± 2°C by weight loss method. Potentiodynamic polarization measurements were carried out at room temperature for both steels in presence of propargyl alcohol (PA) and CAHMT. Results indicated that CAHMT is a mixed type inhibitor while PA is predominantly cathodic. The adsorption of the inhibitors on N-80 steel and MS surface from 15% HCl obeyed Temkin's adsorption isotherm.

Quraishi et al. [32] in the year 2000 synthesized selected condensation products of aromatic aldehydes and thiosemicarbazide and evaluated as corrosion inhibitors for mild steel and oil-well steel N-80 in 15% HCl at 105 ± 2°C by weight loss method. All the condensation products showed excellent performance. 1-cinnamaldehyde thiosemicarbazone (CTS) was found to be the best corrosion inhibitor. It exhibited 99.67% inhibition efficiency for mild steel and 97.26% for N-80 steel at 5000 ppm of inhibitor concentration. The potentiodynamic polarization studies carried out at room temperature on mild steel in 15% HCl containing 500 ppm of condensation products and on N-80 steel in 15% HCl containing 500 ppm of CTS showed that all the investigated compounds except 1-dimethylaminobenzaldehyde thiosemicarbazone (DTS) are mixed type inhibitors.

DTS VTS

STS BTS

CTS

Quraishi et al. [33] in the year 2001 studied three new organic inhibitors, namely, dicinnamylidene acetone (DCA), disalicylidene acetone (DSA) and divanillidene acetone (DVA) on corrosion of N-80 alloy in boiling hydrochloric acid by the weight loss method. DSA exhibited the best performance, giving an inhibition efficiency of 98.7%. Potentiodynamic polarization studies revealed that all the three inhibitors were mixed-type inhibitors. The adsorption of all three compounds on N-80 alloy followed Temkin's adsorption isotherm.

DSA

DCA DVA

Suroor et al. [34] in the year 2001 synthesized two new organic inhibitors, namely dibenzylidene acetone (DBA) and Di-N-dimethylaminobenzylidene acetone (DDABA), and their inhibiting action was evaluated on corrosion of N-80 steel and mild steel in HCl by weight loss technique. These compounds exhibited the inhibition efficiency of 94.4% and 56.5% for mild steel, whereas for N-80 steel these compounds showed inhibition efficiency of 99.7% and 73.8%. The potentiodynamic polarization revealed that both the compounds were mixed type inhibitors.

DBA DDABA

Quraishi et al. [35] in the year 2001 investigated a new corrosion inhibitor namely, 4-salicylideneamino-3-hydrazino-5-mercapto-1,2,4-triazole (SAHMT), and its influence on corrosion inhibition of oil-well tubular steel (N-80) and mild steel in 15% hydrochloric acid solution under boiling condition was studied using weight loss method. Potentiodynamic polarization measurements revealed that the investigated inhibitor is of mixed type and it inhibits the corrosion of both the steels by blocking the active site of the metal.

SAHMT

Quraishi et al.[36] in the year 2001 synthesized three long chain fatty acid oxadiazoles namely 2-undecane-5-mercapto-1-oxa-3,4-diazole (UMOD),2-heptadecane-5-mercapto-1-oxa-3,4-diazole (HMOD) and 2-decane-5-mercapto-1-oxa-3,4-diazole (DMOD) to evaluate as corrosion inhibitors for mild steel in 15% HCl at 105± 2°C by weight loss method. Inhibition tests were also carried out on N-80 steel under similar conditions in 15% HCl containing 5000 ppm of UMOD. The results obtained indicated that oxadiazole derivatives are good corrosion inhibitors. UMOD showed 94% inhibition efficiency for N-80 steel and 72% inhibition efficiency for mild steel. Potentiodynamic polarization studies carried out at room temperature on mild steel in 15% HCl containing 500 ppm of oxadiazole derivatives and on N-80 in 15% HCl containing 500 ppm of UMOD showed that all the investigated compounds are of mixed type inhibitors.

UMOD HMOD DMOD

Quraishi et al.[37] in the year 2002 discussed the effectiveness of three new organic inhibitors-1-cinnamaldehyde thiosemicarbazone (CTS), 1-benzaldehyde thiosemicarbazone (BTS), and 2-4,dicinnamyldene aminophenylene (DCAP) in controlling the corrosion of carbon steel in hydrochloric acid solution at 60°C. CTS, BTS and DCAP were compared with a standard commercial corrosion inhibitor. Laboratory tests revealed that corrosion protection values of the synthesized compounds were higher than those of the commercial inhibitor.

CTS n=0 BTS n=1

DCAP

Quraishi et al. [38] in the year 2002 synthesized three macrocyclic compounds namely 2,3,9,10-tetramethyl-6,13-dithia-1,4,5,7,8,11,12,14-octaza-cyclotetradeca-1,3,6,8,10,13-hexane (MTAT), 3,4,9,10-tetramethyl-7,12-dithia-1,2,5,6,8,11-hexaazacyclododecane-2,4,7,8,10,12-hexane (MTAD), 3,4,9,10-tetramethyl-7,12-dioxa-1,2,5,6,8,11-hexaazacyclododecane-2,4,7,8,10,12-hexane (MOAD) to study their corrosion inhibitive effect in 5 N HCl by weight loss and potentiodynamic polarization studies. Inhibition studies and corrosion rates of these compounds have been evaluated at three different temperatures ranging from 25° to 70°C.

MTAT MTAD MOAD

Cizek [39] in the year 1994 reviewed literature on acidizing corrosion inhibitors. Various inhibitors and their chemical techniques were discussed. All of them were found to be good acidizing inhibitors for oil well steel and mild steel. The history of the development of oil well acidizing and acid corrosion inhibitors used by this industry was reviewed. As deeper and hotter wells were drilled, stimulation acids were exposed to hotter conditions and the organic inhibitors required intensifiers. High-temperature acid corrosion inhibitors were also discussed.

LI Qian-ding et al. [40] in the year 2008 studied Mannich reaction process, which is involved with the presence of primary amine, formaldehyde, and acetophenone, acetone has been added. By controlling reaction conditions, two hydrogen atoms in amino of the primary amine molecule take the Mannich reaction with acetophenone, acetone, and formaldehyde respectively and thus this new kind Mannich base can be obtained. The results of static corrosion test show that the compound agent has a fine inhibition performance. By adding 1% of the inhibitor to the solution with 20% hydrochloric acid at 90 degrees Celsius, the corrosion rate of N80 steel can be reduced to 0.96 g.

Xiong Nan et al. [41] in the year 2010 studied a kind of Mannich base from benzylamine, acetophenone, and formaldehyde. The optimum synthesizing conditions were determined by the orthogonal test, which were as follows: n (acetophenone) n(formaldehyde) n(benzylamine) = 1:1.5:1.5,reaction time 10 hours, pH value of the reaction mixture 2-3 , and reaction temperature 90℃.

Saxena et al. [42] investigated about some acidizing corrosion inhibitors for oil well equipments. These inhibitors contained intensifiers along with a group of compounds like acetylenic alcohols, cinnalmaldehyde derivatives and organic nitrogen compounds.

Yadav et al. [43] investigated the effect of synthesized amino acid compounds, namely, acetamidoleucine (AAL) and benzamidoleucine (BAL) as corrosion inhibitors for N80 steel in 15% HCl solution was studied by polarization, AC impedance (EIS), and weight loss measurements. It was found that both the inhibitors were effective inhibitors and their inhibition efficiency was significantly increased with increasing concentration of inhibitors. Adsorption of inhibitors at the surface of N80 steel was found to obey Langmuir isotherm.

Frenier et al. [44] studied two model compounds, n-dodecylpyridinium bromide (n-DDPB) and 1-octyn-3-ol, were tested in HCl acid as inhibitors for J55 oilfield stee. This paper describes the kinetic and chemical analyses conducted to arrive at inhibition mechanisms for these model compounds. These studies show that the pyridinium forms a weak bond with the chloride-covered surface an is sensitive to temperature and [HCl]. Octynol, however, chemisorbs and produces a film that contains a reaction product of the acetylenic alcohol.

Migahed et al. [45] studied the evaluation of 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. The strong adsorption ability of this new synthesized compound can be attributed to the presence of multiple adsorption centers of nitrogen as well as π-donor moieties.

Menezes et al. [46] 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. The best corrosion inhibition efficiency is obtained when the concentration of both AC and HS is 1.5 wt. %, which indicates the use of all tested steels in oil well stimulation operated at 50°C and the use of 13Cr, N80 and P110 steels in oil well processing temperatures up to 100°C.

Li et al. [47] combined a Mannich base with propargyl alcohol and organic synergist, that can acquire highly efficient well acidizing corrosion inhibitor, which has not been reported in China so far. Taking the static corrosion rate as evaluation index, the synthetic technological conditions influencing main agent can be optimized by using the orthogonal test method. It was found out that under the experimental conditions, the best synthetic technological condition should be as followings: the total reaction time is 14 hours, the ratio (molar ratio) of reaction materials is 1∶2∶4 for amine, aldehyde and ketone, and the pH value is ranged from 2 to 3. At the same time, the paper has made the preliminary investigation of synergetic effect between main agent and synergist. The results of static corrosion test show that the compound agent has a fine inhibition performance. By adding 1% of the inhibitor to the solution with 20% hydrochloric acid at 90 degrees Celsius, the corrosion rate of N80 steel can be reduced to 0.96 g/(m2·h)

Conclusions

Inhibitors having organic ring and heteroatoms were good acidizing corrosion inhibitors. Potentiodynamic and electrochemical studies also confirmed their efficiency. Synergistic study was effective to study the synergistic mechanism of the different inhibitors.

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