Review

Progress in the development of sour corrosion inhibitors: Past, present, and future perspectives

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ABSTRACT

Metallic pipelines and gathering tanks play a vital role during oil and gas exploration, production, transmission, and processing. These facilities are usually attacked by corrosion. The use of corrosion inhibitors is one of the most economical and reliable approaches to control the corrosion of oil and gas metallic facilities. This paper looks at the progress made in the development of sour corrosion inhibitors from early 1900 to date. Scientific literatures were reviewed. The review identified four classes of organic corrosion inhibitors for sour environments, namely, amine-based, imidazoline-based, polymer-based, and Gemini-surfactant-based inhibitors. The strengths and weaknesses of these inhibitors were highlighted. The review revealed that the patronage of amine-based chemistries has declined, and the current technology is based on imidazoline and quaternary salt chemistries. The existing knowledge gap and the future research direction in the area of sour corrosion inhibitors development have been highlighted.

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Contents

Introduction

The oil and gas exploration and production industry is a driving sector of the global economy and presently contributes 2–3% to the global economy, with a total revenue of 2 trillion USD [1]. It is forecasted that crude oil and natural gas will remain the fuels with the largest shares of over 27% and 25%, respectively, by 2040 [2]. The sector is challenged with serious corrosion problems during production, transportation, storage, and processing [3]. A leading oil and gas operating company spent $1.372 billion a year on corrosion-related problems according to a recent study [4]. According to this study, about $589 million was spent on surface pipelines and facilities, $463 million on downhole tubing, and $320 million on capital expenditures related to corrosion [4]. The corrosion problem is not only limited to the oil and gas industry but is also endemic and challenges both the global economy and human life.

Sour corrosion is a longstanding problem in the oil and gas industry and was first reported in the 1940s in the Louisiana and Texas oil wells [5,6]. Sour corrosion is defined as the corrosion of metals in aqueous environment containing acid gases (H_2S/CO_2), but with H_2S concentration sufficiently higher than that of CO_2 to dominate the corrosion behaviour and corrosion products [5]. According to NACE, the partial pressure of hydrogen sulphide should be higher than 0.30 kPa (0.05 psi) [7]. The NACE MR 0175 has identified three corrosion domains for H_2S/CO_2 systems [8] (Fig. 1). Region 0 is characterized by a trace amount of H_2S [8]. Region 1 is a mild sour corrosion domain where the concentration of H_2S is slightly higher than the threshold value [8]. Region 2 is an intermediate sour corrosion domain and is affected by the slightest change in the partial pressure of hydrogen sulphide gas (pH_2S). Region 3 is a severe sour corrosion domain that has very high H_2S concentration and low *in situ* pH [8]. The following rule applies for ascertaining the dominant corrosion phenomenon in H_2S/CO_2 systems: H_2S corrosion dominates in an environment with $pCO_2/pH_2S < 20$ while CO_2 corrosion is prevalent when $pCO_2/pH_2S > 500$ [8]. An environment with $20 \leq pCO_2/pH_2S \leq 500$ exhibits mixed CO_2/H_2S corrosion [8]. The presence of H_2S can enhance CO_2 corrosion by acting as an accelerator of anodic dissolution through sulphide adsorption or suppress CO_2 corrosion by virtue of protective sulphide scale formation [8].

Globally, the number of producing oil and gas wells is estimated at 950,000 [9]. One-third of these wells are sour [10]. Fluids produced from the sour wells are corrosive, and the main cause of corrosion is the dissolution of acid gases (CO_2 and H_2S) in the water cut [11]. The higher the water cut in a produced fluid, the more corrosive the fluid. A dry produced fluid containing less than 1% water cut is less corrosive than a wet fluid containing greater than 20% water cut [12]. Unfortunately, the ratio of water cut to oil in produced fluid increases as an oil well ages [11] and can reach a level as high as 95% [11] depending on the age of the well. Apart from the natural water content in produced fluid, it is common-practice to re-inject production water downhole to maintain pressure and stability in the well [4]. In addition, water flooding is performed using seawater to drive oil out of formation [4]. These practices increase the water content of the produced fluid, and the implication is an associated increase in the corrosion risk.
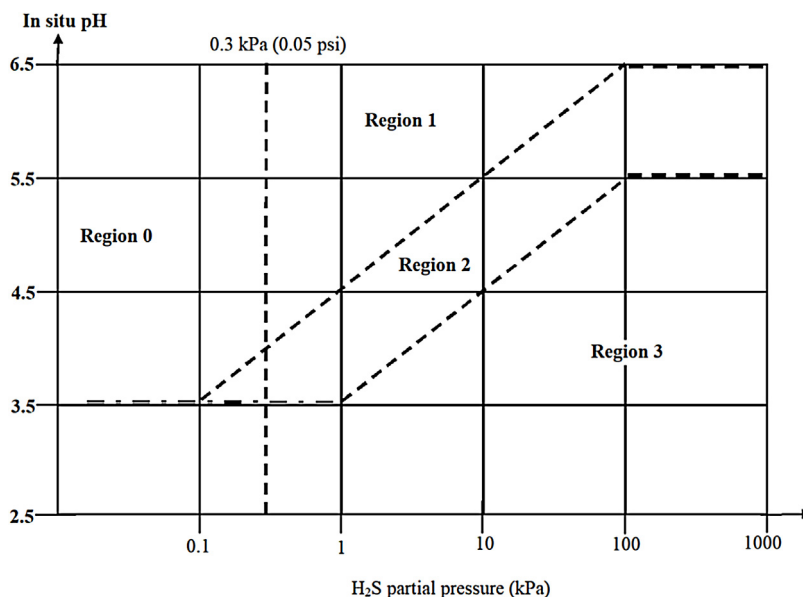

Fig. 1. NACE MR0175/ISO 15156 "region of service" for sour conditions [31].

Internal corrosion is one of the worrisome forms of corrosion in the oil and gas industry owing to the fact that its corrosion control is cost ineffective because mitigation techniques cannot be easily maintained and inspected [4,11]. This form of corrosion is very common with multiphase transportation pipelines [13]. When H_2S gas is present in produced fluid, at low temperature, iron sulphide film is formed as a dense and protective corrosion product [13]. Localized corrosion with very high corrosion rate can occur when the corrosion product film fails to offer sufficient protection [13]. This is one of the most feared types of corrosion attack in oil and gas pipelines. Fig. 2 illustrates typical debris from sour crude gathering and transportation systems [14].

The majority of localized corrosion problems in sour environments manifest as under-deposit corrosion (UDC) [15,16]. UDC initiates at a break in the protective FeS films or underneath of sludge deposits [15,16], which typically consists of sand particles, clays, corrosion products such as iron sulphide and iron carbonate. The film ruptures and breakdowns could be caused by the intrinsic transition of iron sulphide corrosion product from one thermodynamic state to another. The corrosivity of the system can as well be aggravated by bacterial growth and co-deposition of wax or paraffin materials onto the surface deposits [16]. At present, there is no inhibitor specifically designed for UDC in sour environments [16]. According to Alanazi [16], the development of a corrosion inhibitor for such an application would be a very challenging task in terms of inhibitor diffusion, and adsorption by deposits and because no laboratory standard procedure is available for testing the effectiveness of UDC corrosion inhibitors. This review looks at the progress made in the development of sour corrosion inhibitors.

Degradation mechanism of carbon steel in sour environment

The use of carbon steel and low alloy steel for tubing, injection lines, flowlines, trunk lines/interfield lines, export or loading lines, transfer lines, gathering lines, disposal lines, and subsea pipelines remains a convenient option because of its low cost and excellent mechanical properties. Carbon steel is susceptible to corrosion and can degrade in a sour environment at an alarming rate.

The mechanism of H_2S corrosion is still not fully understood. The controversies revolve mostly on the formation and transition of mackinawite [17] as this product is affected by factors like temperature, concentration of the acid gases, length of time, *etc.* [17]. Nevertheless, Wen et al. [18], recently provided an insight into the mechanism of carbon steel corrosion at low temperatures and low H_2S pressure. The sour corrosion process begins with the
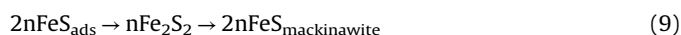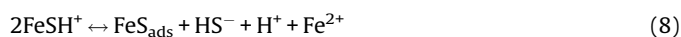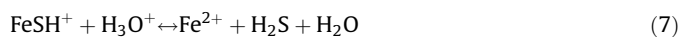

Fig. 2. Typical debris in a sour crude gathering and transportation system [39].

dissolution of the gas in water cut and the dissociation of $H_2S_{(aq)}$ to produces H^+ and HS^- ions according to Eqs. (1) and (2) [18,19]:

$$H_2S_{(g)} \xrightarrow{K_{H_2S}} H_2S_{(aq)} \tag{1}$$

$$H_2S_{(aq)} \xrightarrow{K_1} H^+ + HS^- \tag{2}$$

$$HS^- \xrightarrow{K_2} H^+ + S^{2-} \tag{3}$$

where K_{H_2S} and K_i (i = 1, 2) denote the solubility constants and ionization constants for H_2S, respectively. The secondary ionization of the bisulphide (HS^-) (Eq. (3)) leads to the formation of H^+ and S^{2-} ions [18]. Suleimenov et al. [20,21] and Kharaka et al. [22] had derived three nonlinear equations for the estimation of the solubility constant (K_{H_2S}), primary and secondary ionization constants (K_1, K_2), respectively. The equations were verified experimentally [23] and the numerical value for K_{H_2S}, K_1, and K_2 given as 0.097 [20], 1.052×10^{-7} [21], and 8.710×10^{-18} [22], respectively.

The degradation of carbon steel proceeds according to the following anodic reactions [24–26]:

$$Fe + H_2S + H_2O \leftrightarrow FeSH_{ads}^- + H_3O^+ \tag{4}$$

$$FeSH_{ads}^- \leftrightarrow Fe(SH)_{ads} + e^- \tag{5}$$

$$Fe(SH)_{ads} \leftrightarrow FeSH^+ + e^- \tag{6}$$

$$FeSH^+ + H_3O^+ \leftrightarrow Fe^{2+} + H_2S + H_2O \tag{7}$$

$$2FeSH^+ \leftrightarrow FeS_{ads} + HS^- + H^+ + Fe^{2+} \tag{8}$$

$$2nFeS_{ads} \rightarrow nFe_2S_2 \rightarrow 2nFeS_{mackinawite} \tag{9}$$
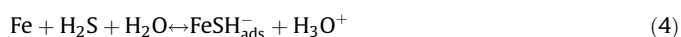
where $FeSH_{ads}^-$ and $FeSH_{ads}$ are adsorbed mesophases and FeS_{ads} the adsorbed amorphous FeS. The hydrolysis of the $FeSH_{ads}^-$ mesophase facilitates the formation of Fe^{2+}.

In the cathodic site, series of depolarization processes involving H_2S, HS^-, and H^+ take place (Eqs. (10)–(12). The H^+ ions generated by the ionization of H_2S are reduced to H_2 [18].

$$H_2S + e^- \rightarrow H + HS^- \tag{10}$$

$$HS^- + e^- \rightarrow H + S^{2-} \tag{11}$$

$$H^+ + e^- \rightarrow H \tag{12}$$
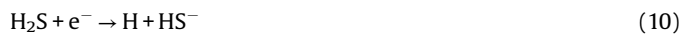
In summary, the general mechanism of H_2S corrosion involves the gradual desorption of metallic Fe, the formation of FeS (mackinawite) in the anodic region and the simultaneous reduction of H^+ ions to H_2 in the cathodic region (Fig. 3). As previously mentioned, the controversies on the mechanism of sour corrosion revolve on the metastable nature of mackinawite. Ning et al. [27] reported that gregite and pyrite were the main corrosion products at 60 °C and at pH_2S of 7.75 mbar and 3.5 mbar, respectively. Bai et al. [28] reported that troilite was the final

Fig. 3. General mechanism of iron oxidation in an H_2S environment.

corrosion product at 50 °C after 96 h exposure duration. Sardisco and Pitts [29] summarized the sequence of the reaction products with time at low temperatures as: mackinawite → cubic FeS → troilite → pyrrhotite → greigite → pyrite.

Factors affecting sour corrosion of carbon steel

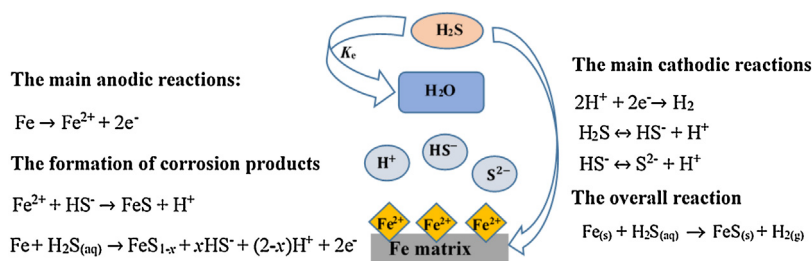A number of factors influence H_2S corrosion, including H_2S partial pressure, flow velocity and regime, temperature, exposure duration, steel chemistry, oxygen ingress, surface deposits (*e.g.,* corrosion products, scales, and wax), concentration of dissolved salts and organic acids (*i.e.,* sodium chloride and ethanoic acids), and fluid chemistry (*e.g.*, water chemistry, pH, water cut, organic acids, phase ratios, and oil wettability). These factors are interdependent; understanding the effect of a single parameter on sour corrosion is somewhat impossible. For instance, the effect of temperature on sour corrosion will be complicated by factors such as the metal surface deposits, concentration of the acid gases, and even the exposure duration. Nevertheless, numerous research works have been devoted to understanding the influence of these parameters on sour corrosion.

Tang et al. [30] studied the effect of H_2S concentration on the corrosion behaviour of steel and concluded that an increase in H_2S concentration enhanced hydrogen evolution reaction that in turn caused hydrogen induced cracking to the steel. Taheri et al. [31] observed that mackinawite film became unstable at H_2S concentrations of up to 0.035 mol/L and at temperatures higher than 80 °C. These findings are consistent with those of Brown et al. [32] that in a mixed H_2S/CO_2 environment where H_2S concentration is very low (<10 ppm) in the gas phase, rapid and significant reduction in the CO_2 corrosion rate was observed but the trend was reversed at higher H_2S concentrations.

Mackinawite is a polymorph of FeS and the first one to form during sour corrosion. It is a metastable compound but can remain the dominant phase for prolonged period as long as the temperature is kept below a certain limit. Stability depends on factors such temperature, partial pressure of H_2S, and pH [33]. It was hypothesized [34,35] that in a wet sour environment, mackinawite formation is rapid and occurs through a heterogeneous chemical redox reaction of H_2S with iron on steel surface. The mackinawite forms a dense film on steel surface and this film acts as a diffusion barrier for all species involved in the corrosion reaction. This film undergoes a cyclic process of growth, cracking, and delamination to develop the corrosion product layer. The amount of FeS retained on the metal surface depends on the layer formation rate and the layer damage rate and this, to some extent, controls the corrosion rate. Sardisco et al. [36] reported that at H_2S partial pressure ranging from 0.001 to 4 psi, a significant amount of mackinawite was formed relative to other FeS species and the corrosion rate was very high. It was concluded that the Mackinawite film formed was non-protective and porous.

Based on experimental [37,38] and theoretical [39,40] studies, at an initial exposure time, the corrosion rate of carbon steel in an H_2S environment increases with rising temperature. Nevertheless, because the formation of a protective iron sulphide layer is favoured at elevated temperatures, the corrosion rate decreases more rapidly at very high temperatures, and at a longer exposure times. Sun and Nesic [39] reported that the dependence of corrosion rate on temperature was very weak at short immersion times and the effect disappeared at long immersion durations.

The flow rate has been found to have a noticeable influence on the corrosion behaviour of carbon steel in H_2S environment [39,40]. A higher flow rate results in an accelerated corrosion rate due to mass transport processes [39] and equally affects the formation and precipitation of the protective iron sulphide [39,40]. Sun and Nesic [39] examined the influence of flow rate on the corrosion rate of low carbon steel by varying the rotation speed of a cylindrical metal specimen up to 8000 rpm. It was found that the corrosion rate increased with velocity, and the effect was quite pronounced at shorter exposure times. Sun and co-workers noted that at longer exposure times, the corrosion rate declined considerably due to FeS build-up. By comparing the scaling tendency in stagnant and hydrodynamic conditions, the scaling tendency decreased by almost 60% under flowing conditions relative to stagnant conditions, which indicates that the FeS scale was lost under flowing conditions due to hydrodynamic stresses induced by flow. The influence of fluid chemistry on sour corrosion has also been studied [41–44].

Based on studies of the factors influencing sour corrosion [41–44], the following generalizations can be made:

i The uniform corrosion rate of carbon steel is lower in an H_2S dominated environment than in CO_2 dominated environment. This is due to the formation of protective iron sulphide scale.
ii The uniform corrosion rate decreases as the exposure time increases due to iron sulphide formation.
iii Breakdown of iron sulphide film increases the susceptibility of carbon steel to localized and pitting corrosion.
iv Sour corrosion is less sensitive to temperature compared to sweet corrosion.
v Increase in pipe wall shear stress increases the vulnerability of carbon steel to uniform, localized, and pitting sour corrosion.

Sour corrosion inhibitors

As metal corrosion is inevitable, scientists and engineers have constantly developed strategies to reduce the rate of corrosion to a minimum. The use of corrosion inhibitors is one such strategy and is always the technique of choice for controlling internal corrosion in oil and gas pipelines. Corrosion inhibitors are applied by either injection or batch treatment methods. In continuous injection, inhibitor concentration in the range of 10–1000 parts per million (ppm) is required, whereas 1–20 vol. percent may be used in a batch treatment approach [45], with the goal to reduce the corrosion rate to less than 4 mpy (0.1 mm/year) [45].

The market for metal corrosion inhibitors has witnessed significant growth, particularly in the 21st century, with organic corrosion inhibitors leading by almost 70% [46]. For instance, the forecasted demand for corrosion inhibitors in the USA for the 2017 to 2022 period is estimated to be 4.1% per year and a volume demand of 1.7 billion pounds [46]. The corrosion inhibitor market is characterized by product innovation through continuous research and development (R&D). In this section, the evolution of sour corrosion inhibitors from inception to date is analysed by assessing the trend of published research articles, conference articles, scientific disclosures and inventions, and other scientific information.

Sour corrosion has been a long-standing problem. By searching the keywords "sour corrosion inhibitors, corrosion inhibition of H_2S corrosion, and H_2S corrosion inhibitors" in search engines such as Google Scholar and OnePetro, approximately 10,700 results, excluding patent information, were obtained. Of this information, 5905 were conference information, while journal information accounted for approximately 933. In addition, by searching the keywords "sour corrosion inhibitors and hydrogen sulphide (H_2S) corrosion inhibitors" on various patent databases [47–52], approximately 12,955 results were obtained. A plot of the number of scientific publication in the area of sour corrosion and inhibition per decade is shown in Fig. 4. It reveals a steady increase, which may be due to one of two reasons: either sour corrosion is a more serious issue than envisaged or more insight into the corrosion mechanism has been gained.

The 1900s were dominated by the use of inorganic corrosion inhibitors for the protection of carbon steel against sour corrosion [53,54]. Nevertheless, it is on record that an organic corrosion inhibitor was discovered as early as 1945. Menaul and Dunn [55] reported that 125 and 259 ppm formaldehyde decreased the corrosion rate of mild steel in sour environment from 0.92 lb. per sq. ft. per year to 0.113 and 0.105 lb. per sq. ft. per year, respectively. It was believed that the formaldehyde reacted with hydrogen sulphide gas to form an intermediate compound that further reacted with iron surface to form the protective layer. This publication seems to mark the beginning of the use of organic compounds as sour corrosion inhibitors and may have been the bedrock to the patent granted to Moyer et al. [56] in February 7, 1950. In the disclosure, Moyer et al. claimed that solutions of

formaldehyde and an organic compound containing at least one amino reactive group (alkyl amines, alkanol amines, arylamino phenols, and alkyl amino phenylene diamines) markedly inhibited the corrosive actions of oil well brine. In 1947 [57] and 1949 [58], rosin amine D acetate was reported as the first amine corrosion inhibitor for flood waters containing H_2S and CO_2 gases. Thereafter, many alkyl and aryl high molecular weight amines were explored as sour corrosion inhibitors [59–62].

The middle of the 1900s witnessed an evolution of another class of organic compounds as sour corrosion inhibitors — imidazolines. In a report that seems to be the first on imidazolines as sour corrosion inhibitors, a United States patent 2, 466, 517 was granted to Blair et al. [63] on April 5, 1949. In the granted patent, Blair disclosed a family of substituted imidazolines in which the imidazoline molecule contained at least one aliphatic or cycloaliphatic hydrocarbon group having 8–32 carbon atoms, as a corrosion inhibitor in corrosive environment containing acidic gases. Thereafter, Bennett [64] concluded in 1955 that high molecular weight compounds of the imidazoline-type exhibited excellent solubility property in hydrocarbons and provided appreciable corrosion protection in sour environments. This report was followed by the report of Caldwell and Lytle [65] in 1956, whereby high molecular weight imidazolines were deployed for the inhibition of the internal casing corrosion in sour oil wells. The imidazoline is one of the reigning chemistries today in the area of sour corrosion inhibitor development. A quick search of the keyword "imidazolines as H_2S corrosion inhibitors" on Google Scholar search engine produced approximately 1100 results, excluding patent information. Similar search on various patent databases produced about 749 results.

Based on corrosion literature, polymers were actually deployed in oil field operations to reduce water production in high water-cut oil producing wells. For instance, in 1973, White et al. [66] reported the successful use of polymers to reduce water–oil ratios in nearly 200 field treatments in the Mid-Continent area. It does appear that the anticorrosion property of polymers were not fully explore in the 1900s. Aside from the patented work on carboxymethyl cellulose and cellulose sulphate granted to Savoy [67] in April 15, 1952, information on polymers as sour corrosion inhibitors was scarce in the 1900s.

Another class of organic compound utilized as sour corrosion inhibitors is the surfactant, more specifically, Gemini surfactants
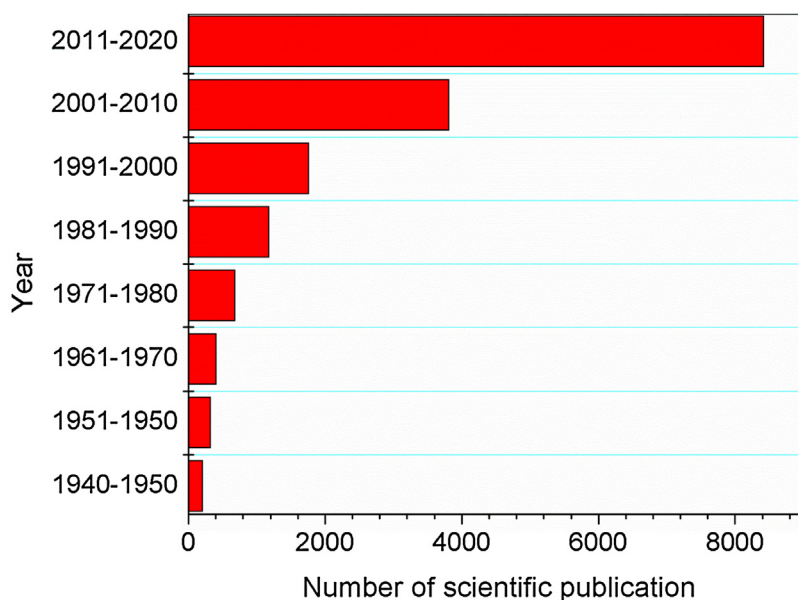

Fig. 4. A bar chart showing the distribution of scientific literature on sour corrosion inhibitor per decade.

[68]. In fact, Gemini surfactant chemistry is the present-day sour corrosion inhibitor chemistry. It appears that this chemistry was first introduced in the late 1900s, specifically in 1996 [69], and the report by Hongbing and Zhongal [69] seems to be the first. The chronological order of sour corrosion development is presented in Fig. 5. Based on this analysis, there are four main groups of sour corrosion inhibitors: amines, imidazolines, Gemini surfactants, and water-based polymers. A plot of the percentage distribution of
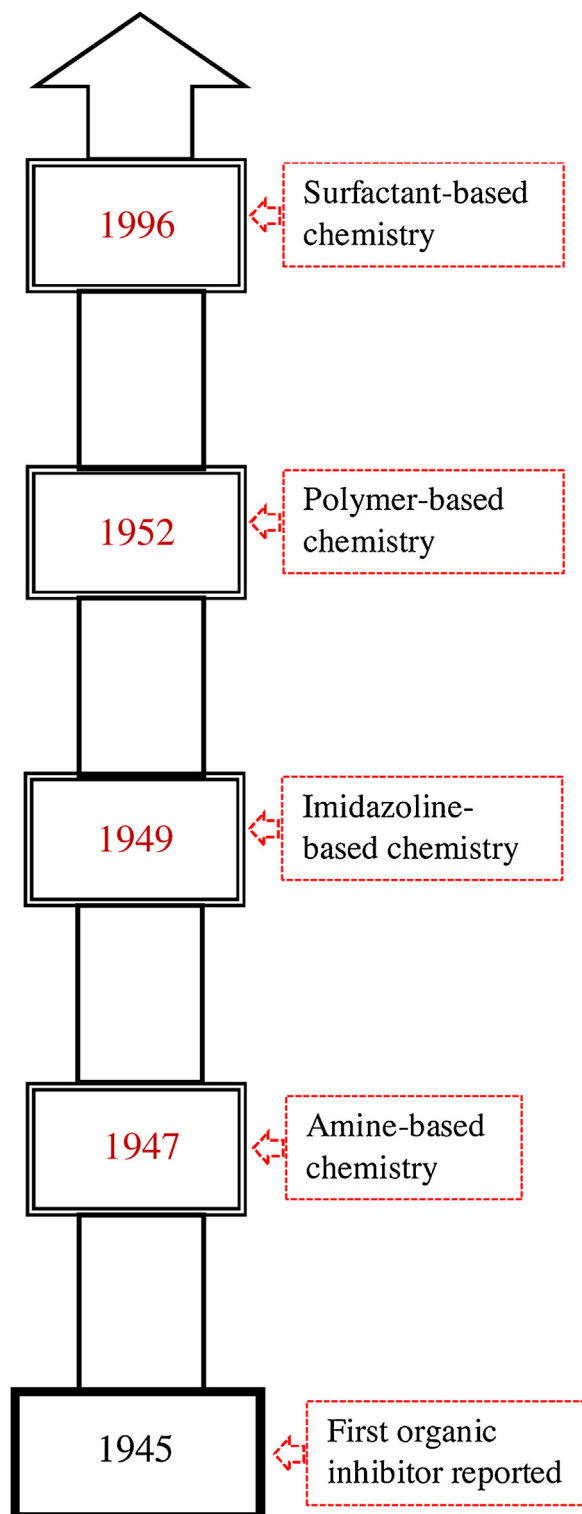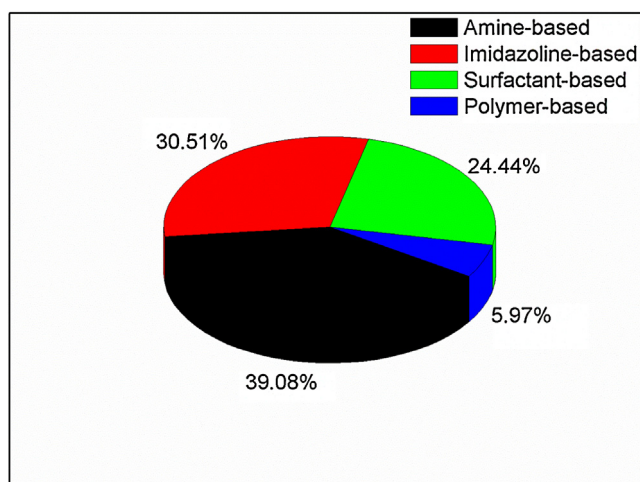

Fig. 6. A pie chart showing the percentage of scientific information on sour corrosion inhibitors.

these four classes of sour inhibitors (Fig. 6) reveals that, 46.28% of scientific information on sour corrosion inhibitor is based on amine chemistry. The imidazoline chemistry received 30.82% attention while the surfactant chemistry is the third most popular with 18.9%. The least is the polymer chemistry. The selected structures of the different chemistries reported as sour corrosion inhibitor are given in Fig. 7.

Amine-based inhibitors

Amines are organic compounds containing basic nitrogen atoms with characteristic electron pairs. They are derived from ammonia and are grouped into primary, secondary, and tertiary amines based on their nature and the number of substituents on the nitrogen atom. Methylamine, dimethylamine, and trimethylamine are examples of primary, secondary, and tertiary amines, respectively. When the substituent is a cyclic group, the amine is said to be a cyclic amine. The electronic properties of the substituent and the degree of solvation have a profound effect on the basicity of amines. Amines have gained numerous industrial applications as commodities for the manufacture of rubber, dyes, pharmaceuticals, synthetic resins, fibres, *etc.* [70–73]. They are good metal corrosion inhibitors in diverse kinds of corrosive environments [11,45].

The effectiveness of oil-soluble amine-type inhibitors in retarding carbon steel corrosion in sour environments has been established [62,74,75]. For instance, an oil-soluble filming amine corrosion inhibitor was developed for sweet and sour corrosion by Papir et al. [62]. The evaluation of the product was carried out both in the laboratory using the wheel test method and in the field. The developed amine-based inhibitor was compared with a Chevron sour commercial inhibitor. It was found that the developed inhibitor performed better than the commercial inhibitor at lower concentrations (500–2000 ppm), longer times (72 h), and higher temperatures (86–150 °F). The average corrosion rate of the developed amine-based inhibitor was 1.6 mpy, whereas that of the commercial inhibitor was 2.5 mpy.

Stewart et al. [75] subjected several amine-based corrosion inhibitors (Inhibitor A–E) to the following test conditions: pressure — 830 kPa, temperature — 60 °C (140 °F), duration — 72 h, pH_2S — 620 kPa, pCO_2 — 210 kPa, brine — synthetic, brine volume — 270 mL, hydrocarbon volume — 30 mL, and stir rate — 120 rpm. Inhibitors A and E were routinely used by the oil and gas industry; inhibitors B, C, and D were new candidate products; C and D contained amines and quaternary amines; and B contained a unique

Fig. 5. The chronological developmental order of sour corrosion inhibitors.

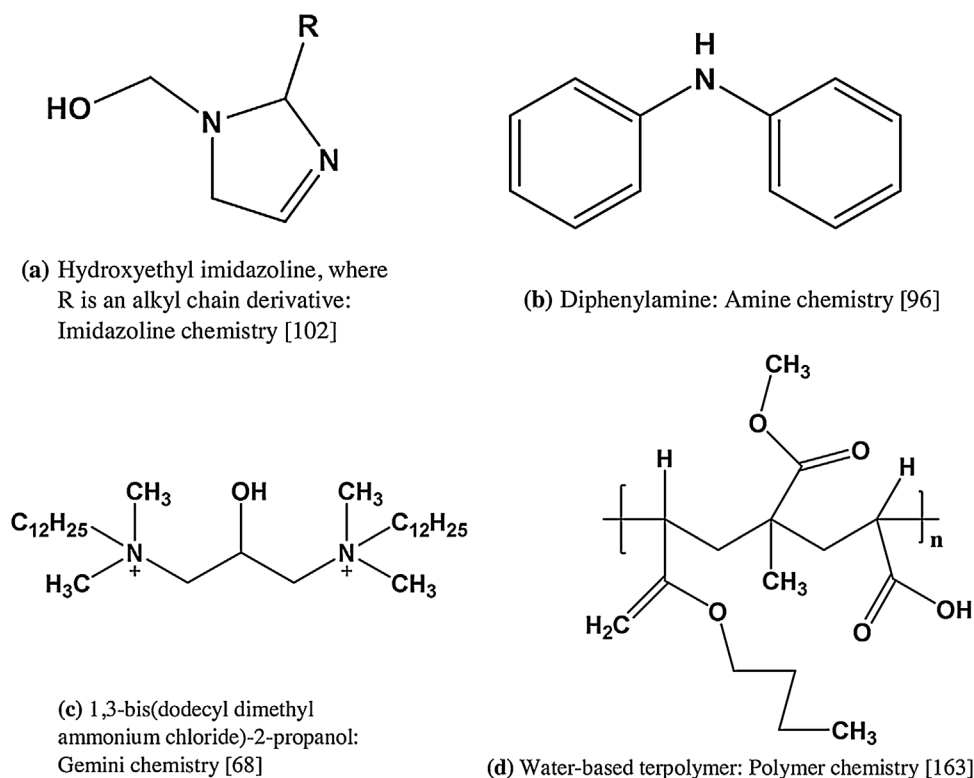**(a)** Hydroxyethyl imidazoline, where R is an alkyl chain derivative: Imidazoline chemistry [102]

(b) Diphenylamine: Amine chemistry [96]

(c) 1,3-bis(dodecyl dimethyl ammonium chloride)-2-propanol: Gemini chemistry [68]

(d) Water-based terpolymer: Polymer chemistry [163]

Fig. 7. Selected structures of the different chemistries reported as sour corrosion inhibitor.

amine-based chemistry. The new candidate inhibitors were found to be chemically and thermally stable than the commercial inhibitors and demonstrated superior inhibitive strength against pitting corrosion of carbon steel. Mok et al. [74] have also claimed that amine-based inhibitors are capable of providing up to 99% protection to carbon steel in sour conditions. Kashkovskiy et al. [76] presented tributylamine as an effective volatile inhibitor for sour corrosion of steels.

There are also a handful of amine-based disclosures, mainly on the reaction products of amines with α, β-ethylenically unsaturated aldehydes, ketones, fatty acids, organic halides, epoxides, and transition metals [77–88]. Specifically, the amine components in most disclosures are ethylenediamine, triethylenetetraamine, phenylenediamine, trimethylenediamine, N-aminoethylethanol-amine, propylenediamine, methyliminobispropylamine, cyclohex-ylamine, 2-methylcyclohexylamine, tetraethylenepentamine, pentaethylenehexamine, polyoxypropyleneamine, diglycolamine, dodecylamine, cocoamine, hexadecylamine, octadecylamine, and nonethylenedecaamine [77–88]. The mechanism of reaction in most cases is the well-known condensation reaction of amine and carbonyl functional groups. In addition, there are commercially available amine-based sour corrosion inhibitors. Some of them include, CORTRON AR-505 [89], CONQOR 303A [90], and Fentacare 1227 [91]. CORTRON AR-505 is manufactured by the Champion Technologies. Al-Baker et al. [90] reported that 0.097 mg CORTRON AR-505 rapidly decreased the corrosion rate of 1018 carbon steel from 7 mm/year to 1 mm/year. CONQOR 303A and Fentacare 1227 are produced by Schlumberger and Solvay, respectively and are specifically designed for the protection of oilfield tubular goods [90,91].

The amines mostly inhibit corrosion by film-forming mecha-nism [45]. In sour environment, HS^- ions is preferentially adsorbed on carbon steel surface and negatively charged the surface [18]. The lone pair electrons of N atom in amine compounds tend to bind the hydrogen ions produced from the cathodic reactions (Eqs. (10)

and (11)) to form amide cations in the solution [92]. This cationic component is bind to the HS^- layer adsorbed on the metal surface through electrostatic interaction [92], the so-called physisorption process. On the surface, the lone pair electron on the N atom can be donated to the empty d-orbitals in Fe atoms to form coordinate covalent bonds between the inhibitors and the metal surface (chemisorption process). The oily layer formed by amine com-pounds on carbon steel surface prevents the contact of acid gases with the surface. Zhang and Zhao [92] had demonstrated the film formation mechanism of amines on carbon steel surface in H_2S and CO_2 brine solution using the X-ray photoelectron spectroscopy technique.

The amine-based corrosion inhibitors can protect metals surfaces against corrosion in both the shallow, upper part of wells, and in the deeper hotter area. With appropriate dosage, they can provide protection at the bottom hole temperatures up to 177 °C [93]. They can as well protect both tubular goods and completion tools exposed to workover or clear completion brines. In addition, amine-based corrosion inhibitors are compatible with most oilfield chemicals. These merits may have been the reason that the amine-based chemistry dominated the sour inhibitors scientific world particularly between 1991 and 2000 (Fig. 8). However, inspection of Fig. 8 reveals that there is a shift away from the amine-based chemistry pertaining to application in environ-ments containing H_2S/CO_2 gases. This may have to do with the criticism on alkanolamine (common amine component in most disclosures) upon reaction with acid gases. Butwell et al. [94] had reported that monoethanolamine irreversibly degraded upon reaction with CO_2 gas to produce N-(2-hydroxyethyl) ethylene diamine, which is corrosive at concentrations above 0.4% by weight. Diglycolamine, which had been disclosed as an amine component by Martinez et al. [82], was reported to degrade in the presence of CO_2 gas to produce N,N'-bis(hydroxyethoxyethyl) urea that was similar to N-(2-hydroxyethyl) ethylene diamine in terms of corrosivity [81]. In addition, the willingness of scientists to
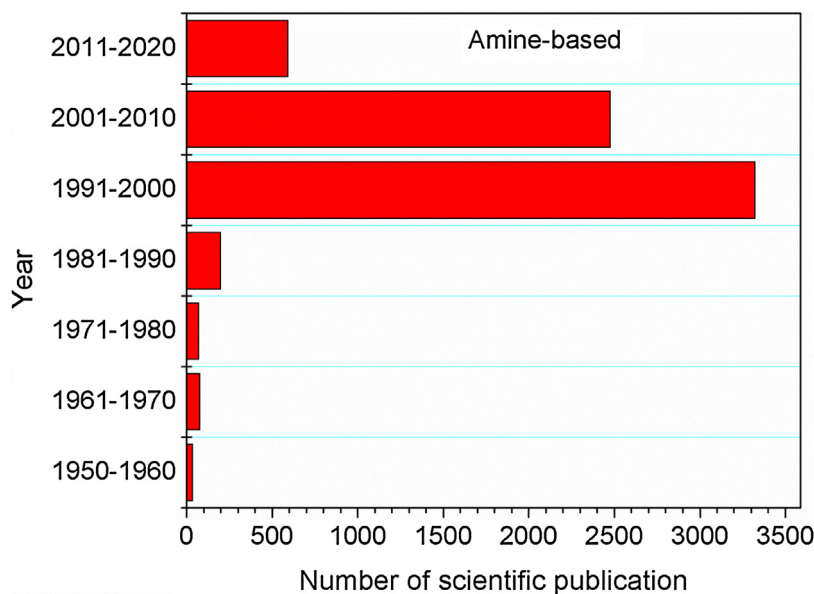
Fig. 8. A representative bar chart showing the number of scientific information on amine-based sour corrosion inhibitors deposited per decade.

embrace green chemistry may have also limited the utilization of aromatic amines which are effective corrosion inhibitors [62,95] but possess high toxicity. The summary of scientific information on amine-based chemistry is given in Table 1.

Imidazoline-based inhibitors

Imidazolines are nitrogen-containing heterocycles derived from imidazoles. The imidazoline structure can be dissected into three parts: the pendant group (hydrophilic head), the imidazoline ring (five-membered heterocyclic ring), and the substituent (hydrophobic tail). Imidazolines exist in three isomeric forms, namely, 2-imidazoline, 3-imidazoline, and 4-imidazoline. Of these three isomeric forms, 2-imidazoline is the most commonly found, as its ring occurs in some natural products and pharmaceuticals [98,99]. This isomeric form has gained application as an antihyperglycaemic, anti-inflammatory, antihypertensive, antihypercholesterolemic, and antidepressant reagents [98,99].

Imidazolines and their derivatives are potent corrosion inhibitors [100–103,104–106], and most of the commercial inhibitors such as the Marcor 310, 550, 900, and Ps9 designed specifically for oilfield applications by Solvay are based on imidazoline chemistries [91]. The mechanism of inhibition by imidazoline in a corrosive environment is one of the contentious issues among corrosion scientists. Edwards et al. [103] proposed that corrosion inhibition by imidazoline is primarily due to the bonding of the imidazoline ring in a planar orientation to the metal surface. According to the authors, the hydrophobic portion plays a vital role on the inhibition performance whereas the pendant group contributes less to the corrosion inhibition performance by imidazoline molecules as such variation in the chemistry of the group is unimportant. Gusmano et al. [107] seems to agree with Edwards et al. on the strong interaction between the imidazoline ring and substrate surface, although the orientation was not considered but differed on the role of the pendant group. Gusmano et al. held that the pendant group could improve the inhibition performance by enhancing molecular adsorption. This was demonstrated in the work of Zhao et al. [108], where an imidazoline inhibitor containing three phenyl groups was designed and analysed. Excellent inhibition efficiency of 94% was achieved for carbon steel in H_2S/CO_2 environment with 50 mg/L of this inhibitor.

It is also argued that the mechanism of corrosion inhibition by imidazoline is a combined effect of blocking, activation, and energy-related factors [71]. To provide more insight into the corrosion inhibition mechanism by imidazolines in an H_2S-containing environment, Szyprowski [68] synthesized seven homogeneous imidazoline inhibitors and examined their performance on St3S carbon steel and 1H18N9T austenitic stainless steel corrosion in 2 wt% NaCl containing hydrocarbon phase and saturated with H_2S gas. It was found that inhibitors with the shortest hydrophobic portion exhibited the lowest corrosion inhibition efficiency and that the corrosion inhibition performance was a function of the length of the hydrocarbon chain. Ramachandran et al. [109] used atomistic simulations (quantum mechanics and molecular dynamics) to explain the corrosion inhibition mechanism by imidazoline and concluded that a self-assembled monolayer is formed on the native oxide surface of the metal. This layer performs the function of corrosion inhibition by forming a hydrophobic barrier against the ingression of small ions. The hydrocarbon tail must be sufficiently long, with approximately 12 or more carbon atoms and the hydrophobic tail, and the hydrophilic head must lead to an octanol/water partition coefficient (log P) below a critical value for monolayer assembly to be formed [109]. This proposition seems to confirm the description of the most effective imidazoline compounds by Blair et al. [63]. Blair et al. in US Patent 2,466,517 had described the most effective imidazoline inhibitors to be those with long hydrocarbon chain bonded to one of the nitrogen atoms of the imidazoline ring or on a relatively small organic radical attached to one of the nitrogen atoms of the ring.

Fig. 9 shows the distribution of scientific information per decade based on imidazoline chemistry. Unlike the amine-based chemistry, it is observed from the figure that less attention was given to the imidazoline chemistry in the 1900s. This may be due to the fact that, imidazoline type inhibitors are prone to hydrolysis, reverting to the precursor amidoamine or an isomer, which was believed to have little or no anticorrosive property [45,110]. This belief may have hampered the development of imidazoline-based inhibitors in the past. It is obvious in Fig. 9 that greater attention has been given to the development of imidazoline based sour inhibitors in the 2000s. The spate of interest on imidazoline based corrosion inhibitors may have arisen due to the realization that the

Table 1
Summary of the scientific literature on amine-based inhibitors for low carbon steel in a sour environment.

Inhibitor	Experimental conditions	Inhibitive performance	Ref.
Dibutylamine	Total sulfur by D5453 = 1.261%; Dissolved H_2S content = 311 ppm; Dissolved CO_2 content = <40 ppm; Naphtha content = 2.6%; pH = 5.9; Tempt. = 75 °C;	Optimum conc. = 4 ml/L CR = 1.83 mm/year IE = 92.28%	[96]
Cyclohexylamine		Optimum conc. = 10 ml/L CR = 2.18 mm/year IE = 90.78%	
Diphenylamine		Optimum conc. = 0.01 M CR = 3.36 mm/year; IE = 85.81% @ 75 °C	
Phenylenediamine		Optimum conc. = 0.001 M; CR = 2.26 mm/year; IE = 90.45% @ 75 °C	
Tributylamine	Tempt. = @ 20 °C and 80 °C; Optimum conc. = 2.0 g/L	CR (20 °C) = 1.19, (80 °C)1.53 g m^{-2} h^{-1}; IE (20 °C) = 96.6%, (80 °C) 97.4%	[76]
Reaction products of diamines or tetraamines with hydrocarbon-substituted homologs	Medium = H_2S-saturated oil well; Tempt. = 180 °F; Inhibitor conc. = 50 ppm	IE = 80%	[78]
Inhibitor selected from the group consisting of diethylenetriamine-*N-N'*-dibutyronitrile, decyltridecylaminobutyronitrile, diethylaminoacetonitrile, monoethanolaminopropionitrile, *N,N'*-dipropionitrile, and dibutylaminoacetonitrile	Total pressure = 50 at.; pH_2S = 3.0 at.; pCO_2 = 2.0 at.; Tempt. = 30 °C; Inhibitor conc. = 0.005 to 1 g/L	IE = 85–95%	[80]
Reaction mixture of formaldehyde component, acetophenone component, cyclohexylamine component or aliphatic carboxylic acid component.	Tempt: 150–250 °F; Inhibitor conc. = 0.2 vol.%	CR = 0.01–0.52 lb/ft^2/day	[81]
Reaction products of α,β-ethylenically unsaturated aldehydes with organic polyamines and monofunctional amines.	Tempt. = 350 °F; 2000 psi pressure with 10% H_2S, 10% CO_2, 80% CH_4. Inhibitor conc. = 100 ppm	IE = 80%; CR = 27.0 mpy	[82]
Reaction products of α,β-ethylenically unsaturated aldehydes with organic amines which is further reacted with organic halide or expoxide.	Tempt. = 350 °F; 90% brine; 8% heptane; 2% kerosene; 2000 psi pressure (25 °C); 10% H_2S, 10% CO_2. Rotation speed 26 rpm; Immersion duration 24 h; Inhibitor conc. = 100 ppm	IE = 82–91%	[83]
Same as above	Tempt. = 175 °F; Brine solution (89.89% deionized H_2O, 9.62% NaCl, 0.305% $CaCl_2$, 0.186% hydrated $MgCl_2$); pH 3.8; 300 ppm H_2S; Rotation speed 26 rpm for 24 h; Inhibitor conc. = 200 ppm	CR = 10.8–71.0 mpy; IE = 74.6–86.1%	[84]
Reaction products of alkylenepolyamines and formaldeyde.	Tempt. = 65 °C; Isopar M (Exxon) as hydrocarbon phase; 0.1 M Na_2SO_4; 0.65 g NH_4Cl; 25 mg H_2S; Rotation speed 400 rpm; Inhibitor conc. = 200 ppm	CR = 1.5–12 mpy	[77]
Reaction products of aqueous alkanolamine with acid gas.	Tempt. = 240 °C; H_2S loading 0.5 mol/mol; Test duration 10 days	CR = 3.6–12.4%	[84]
Reaction products of polyamine with sulfonic acid salts	Synthetic and field brine; Tempt. = 60 °C; Rotation speed 150 rpm; Test duration 18 h	CR = 0.02–0.04 mmpy; IE = 98.2–98.5%	[88]
Oil soluble to water-dispersible corrosion inhibiting solution containing 3–200 ppm ethoxylated, propyxylated dialkyphenol amine.	Oil brine and 100% brine; Tempt. = 49 °C; Rotation speed 30 rpm; Test duration 72 h; Inhibitor conc. = 7.5 ppm	CR = 0.9 mpy in oil brine; 2.6 mpy in 100% brine.	[95]
Products formed from a direct or an indirect reaction of an aldehyde with a thiol and/or an amine functionalized ring structure.	Static conditions; Pressurized with 100 psi H_2S. Tempt. = 300–325 °F; Immersion duration 3 h; Inhibitor conc. = 3 vol. %	Corrosion loss = 0.012–0.087 lb/ft^2	[97]

CR = corrosion rate; IE = inhibition efficiency.

corrosion inhibition efficacy of imidazolines can be enhanced by its reaction with suitable organics like organic acids capable of increasing its partitioning in aqueous medium. Meyer [111] has patented a typical example of such reaction and Martins et al. [112] and Benitez Aguilar et al. [113] have patented imidazoline-based inhibitors with outstanding performance.

The greenness of chemicals is one of the cardinal goals of this century. A green chemical is expected to meet the following requirements by the Registration, Evaluation, Authorization and Restriction of Chemicals (REACH) and the Oslo Paris Commission (OSPAR) [114,115]: (i) non-bioaccumulative, (ii) biodegradable, and (iii) have zero or very low marine toxicity. Toxicity is defined in terms of the LC_{50} and EC_{50} value. EC_{50} is the effective dosage of a chemical required to adversely affect 50% of a population. LC_{50}, on the other hand, is the dosage of a chemical that would kill 50% of the population [114,115]. A green corrosion inhibitor should have a LC_{50}/EC_{50} value greater than 10 mg/L [114]. The OSPAR requirement for biodegradation acceptance is that 60% of a chemical should degrade in a biological system within 28 days [115]. Bioaccumulation test examines the level of product build-up in the

body and it is measured by partition coefficient (*i.e.,* a measure of the distribution of a product between an octanol and water mixture); it is usually expressed as log (Po/w) [99]. A green corrosion inhibitor is expected to have log (Po/w) of less than 3 [114].

The tendency of the imidazoline compounds to bio accumulate would have been a limiting factor to their utilization. However, there have been substantial research efforts to modify imidazoline with compounds of natural origin to make the inhibitors green. For instance, Rivera-Grau et al. [102] modified imidazoline with coconut oil to derive aminoethyl-amine imidazoline and subjected the so-called green corrosion inhibitor to the investigation as an inhibitor for 1018 carbon steel in an H_2S environment. Aminoethyl-amine imidazoline demonstrated excellent corrosion retardation performance with 25 ppm of the inhibitor lowering the current density from 0.0 11 mA/cm^2 in free 3% NaCl + H_2S solution to 0.0011 mA/cm^2 in the inhibited solution. Diaz et al. [104] examined the anticorrosion property of carboxyethyl-imidazoline for high strength carbon steel pipeline (API X120) in 3 wt% NaCl solution containing H_2S with and without diesel. The investigations were
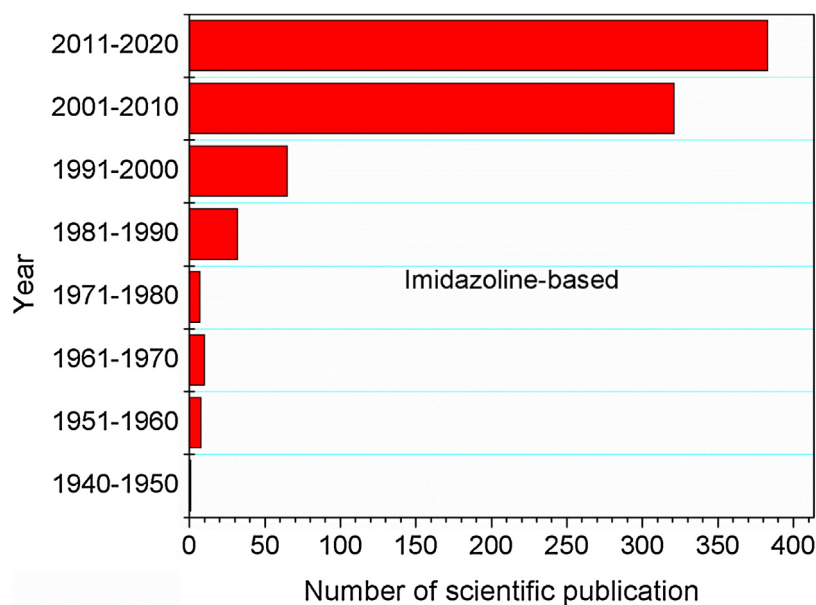
Fig. 9. A representative bar chart showing the number of scientific publications on imidazoline-based sour corrosion inhibitors deposited per decade.

performed at a temperature of 50 °C with diverse concentrations of the carboxyethyl-imidazoline. To generate H₂S, Diaz et al. reacted sodium sulphide (Na₂S) with acetic acid. The dilution of the inhibitor was achieved using pure 2-propanol. An inhibitor concentration of 50 ppm was found to afford a corrosion inhibition efficiency of 98%. In a similar investigation by Lucio-Garcia et al. [116], 5 and 10 ppm hydroxyethyl imidazoline were found to protect API X120 steel by almost 95% at 50 °C. Although these authors claimed the modified imidazoline compounds were green, it would have been justifiable if experimental results for toxicity, biodegradation, and bioaccumulation tests were provided. In Table 2 is summarized the imidazoline-based inhibitors reported for sour corrosion inhibition of carbon steel.

Gemini surfactant-based inhibitors

The term "surfactant" is used to describe surface-active organic compounds having the tendency to lower the interfacial tension (surface tension) between two interfaces that could be liquid–liquid, gas–liquid, or liquid–solid [110]. Surfactants are amphiphilic, that is, they have both hydrophilic and hydrophobic portions. The hydrophilic part is usually the head, while the tail is the hydrophobic portion. This dual characteristic often referred to as hydrophilic and lipophilic tendencies make surfactants compatible with oily materials and water. Surfactants have a wide range of applications as detergents, wetting agents, emulsifiers, dispersants, foaming, and stabilizing agents, *etc.* [110,123].

Based on the type of polar head group, surfactants are classified as anionic, cationic, zwitterionic (amphoteric), and non-ionic. Anionic surfactants are those having a negatively charged hydrophilic head. They are subdivided into four sub-classes: carboxylates $(R - CO_2^-)$, *e.g.,* sodium stearate, sodium lauroyl sacosinate, and perfluorono-nanoate; sulphonates $(R - SO_3^-)$, *e.g.,* perfluorooctanesulphonate and perfluorobutanesulphonate; sulphates $(R - O - SO_3^-)$, *e.g.,* ammonium lauryl sulphate and sodium dodecyl sulphate; and phosphates (PO_4^{3-}), *e.g.,* alkyl ether phosphates.

Cationic surfactants are those with a positively charged hydrophilic head, and examples include laurylamine hydrochloride and trimethyl dodecylammonium chloride.

The hydrophilic head of zwitterionic surfactants carries both negative and positive charges. pH variation influences the behaviour of this class of surfactants. For instance, in an alkaline medium, zwitterionic surfactants behave as anionic surfactants. In an acidic environment, they behave as cationic surfactants, and they behave as amphoteric compounds in neutral medium [110,123]. Examples of zwitterionic surfactants are lauryl betaine and lauramidopropyl betaine.

As the name implies, nonionic surfactants have no formal charge on the polar head. They can be subdivided into five groups: ethoxylates; fatty acid esters of polyhydroxy compounds; amine oxides, *e.g.,* lauryldimethyl oxide also called dodecyldimethylamine oxide; sulphoxides, *e.g.,* dimethyl sulphoxide; and phosphine oxides, *e.g.,* phosphine oxide. The classification of surfactant is summarized in Fig. 10.

Surfactants present interesting adsorption chemistry because of their dual tendencies. Ionic surfactants, similar to other organic molecules, can adsorb on the metal surface via physical or chemical adsorption mechanism. The physisorption mechanism is driven by the hydrophobic, lateral, and electrostatic interactions [124]. Ionic surfactants adsorption through the mechanism of physisorption can be categorized into adsorption on hydrophobic solids and adsorption on hydrophilic solids.

In the case of adsorption of ionic surfactants on a hydrophobic surface, the driving force is the hydrophobic interaction between the hydrophobic solid surface and the hydrophobic surfactant tail. For the adsorption of ionic surfactants on hydrophilic solids, the driving force is the electrostatic force between the polar metal surface and the polar surfactant head.

Chemisorption of ionic surfactants occurs only when the surfactants interact with hydrophilic solids electron sharing or transfer; that is, new bonds are formed. Ionic surfactants adsorption through chemisorption mechanism is characterized by low adsorption rate and monolayer coverage [124]. A typical example of chemisorption of ionic surfactant is the adsorption of xanthates on sulphide minerals in froth flotation [125]. Leppinen et al. [125] reported that ethyl xanthate adsorbed on sulphide mineral surfaces by covalent binding. Jong et al. [126] also demonstrated that in the flotation of salt minerals, fatty acid salts chemically bind on mineral surfaces.

Table 2
A summary of the scientific literature on sour corrosion inhibitors based on imidazoline chemistry.

Inhibitor	Experimental conditions	Inhibitive performance	Ref.
Imidazoline (derivatives of cyclopentylic and cyclohexylonaphthenic acids)	pH = 5.5; Tempt. = 20, 40, & 60 °C; Optimum conc. = 25 ppm;	IE = 77–99% @ 20 °C, 78–99% @ 40 °C, and 85–99% @ 60 °C	[105]
2-Phenylbenzimidazole	pH = 2.6; Tempt. = 25 °C; Optimum conc. = 0.001 M	CR = 0.079 mg cm^{-2} h^{-1}; IE = 87%	[100]
Hydroxyetyl-imidazoline	Tempt. = 50 °C; Optimum conc. = 25 ppm	IE = 84.6%	[102]
Aminoehtyl-amine imidazoline	Tempt. = 50 °C; Optimum conc. = 25 ppm	IE = 84.6%	[102]
Carboxyethyl imidazoline	3 wt% NaCl + H$_2$S without and with 10% diesel; Tempt. = 50 °C; Optimum conc. = 50 ppm	IE = 98%	[104]
Hydroxyethyl imidazoline	3 wt% NaCl + H$_2$S; Tempt. = 50 °C; Optimum conc. = 5 and 10 ppm	IE = 95%	[116]
Reaction products of longer fatty acids with polyamines then with aromatic acids.	pH$_2$S = 1.5 MPa; pCO$_2$ = 1 MPa; Total pressure = 4 MPa; Rotation speed = 800 rpm; Tempt. = 60 °C; Test duration = 168 h; Inhibitor conc. = 200 ppm	CR = 0.0562–0.0731 mm/year	[117]
Naphthylethyl thioacylmorpholine generated from methyl-alpha-naphthyl ketone, morpholine, and sulfur using Willgerodt–Kindler method.	300, 400 mg/L H$_2$S; 800, 1000 mg/L HCl; Inhibitor conc. = 100 mg/L	CR = 0.036 mm/year, IE = 97.20%	[118]
Water-soluble corrosion inhibitor of composition: 20%–30% of heptadecyl ethoxyl imidazoline, 10%–20% of sodium benzoate, 5%–10% of zinc vitriol, 5%–10% of sodium molybdate and 30%–60% of water.	Dynamic indoor weight loss method; H$_2$S conc. = 200 mg/L; Tempt. = 80 °C; Test duration = 72 h; Inhibitor conc. = 100 mg/L	CR = 0.042–0.055 mm/year; IE = 86.1–89.3%	[119]
Water-soluble corrosion inhibitor composed of 1, 2-substituted imidazoline. The 1-substituent has from 1 to 30 ethoxy units and the 2-substituent is an unsaturated or polyunsaturated fatty chain of from 6 to 30 carbons.	3% NaCl solution sparged with CO$_2$ and Na$_2$S.H$_2$O. H$_2$S conc. = 50 ppm; pH = 5.5; Test duration = 24 h; Inhibitor conc. = 250 ppm	CR = 0.046–0.061 mm/year	[112]
Reaction products of polymeric acid with 1-aminoalkyl-2-alkyl-2-imidazoline	10% light gas oil; 90% brine saturated with H$_2$S; Inibitor conc. = 25 ppm	CR = 5.7% mpy	[120]
Normal and acid salts of substituted imidazolines and saturated aliphatic mono- and dicarboxylic acids (3 to 5 carbon atoms)	Brine saturated with H$_2$S; Inibitor conc. = 25 ppm	CR = 0.6–7.6 mpy	[121]
Reaction products of imidazolines.	3% NaCl saturated with CO$_2$ and H$_2$S; Rotation speed =40 rpm; Tempt. = 80 °C; Test duration = 16 h; Inhibitor conc. = 250 ppm	Amount eroded = 30.0–81.2 mg	[122]
Imidazoline inhibitors derived from vegetable oil from sunflower, canola, soybean, safflower, corn, and mixtures thereof reacted with polyalkylated polyamines.	90% brine; 10% kerosene; 500-600 mg/L H$_2$S; Tempt. = 60 °C; Inhibitor conc. = 5–50 mg/L	IE = 89.64–95.33%	[113]

CR = corrosion rate; IE = inhibition efficiency.

Generally, the adsorption of non-ionic surfactants is physisorption and the driving forces are the hydrophobic attraction, lateral interaction, and hydrogen bonding [124]. Detailed information on the adsorption behaviour of surfactants on metals surfaces can be found in Chang et al. [124].

The performance of surfactants as corrosion inhibitors is influenced by the electrolyte and chemical structure of the surfactant.

The influence of electrolyte is obvious when an ionic surfactant is involved. Electrolyte screens the electrostatic forces involved in the adsorption process of ionic surfactants. Depending on the ionic strength of the electrolyte, it can increase or decrease the adsorption rate [124]. In physical adsorption and at low ionic strength of electrolyte, the electrostatic repulsion between adsorbed monomers and incoming monomers is remarkably screened, and this increases
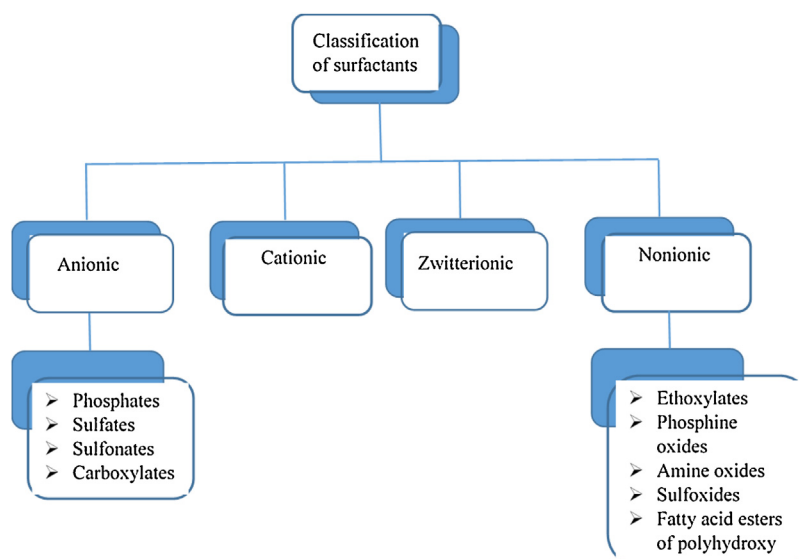
Fig. 10. Classification of surfactants.

the adsorption rate of surfactant molecules [126]. High ionic strength electrolyte would produce more co-ions that would compete with ionic surfactant molecules. The effect would be a decrease in the adsorption rate [124,126]. The discussed effect has equally been reported in the case of chemical adsorption [124].

The chemical structure encompasses the nature of the head group (charged or not charged), the length of the tail, and the charge density. Despite the fact that all surfactants contain polar and the non-polar sections, the relative dominance of each group differs. The hydrophile–lipophile balance (HLB) of surfactants is determined by the chemical nature of the polar and non-polar moieties within the surfactant molecule [123]. The HLB determines the solubility property of a surfactant in water [123] and this helps to predict the behaviour of surfactant in different media. Surfactants with a low HLB (between 4 and 6) are more lipids loving and suited to be used as a water in oil emulsifier while those with a high HLB (between 8 and 18) are more hydrophilic and can be used as an oil in water emulsifier [123].

To investigate the influence of the head group of surfactants in oil/water interface conditions, Xu et al. [127] selected four surfactants, namely, sodium dodecyl sulphonate (SDSn), sodium dodecyl sulphate (SDS), sodium dodecyl benzene sulphonate (SDBS), and sodium dodecyl-di(oxyethylene) ether (AES). These surfactants have the same alkyl tail but a different head functional group. Xu et al. found that the interfacial tension of the studied interface was decreased by the surfactants in the following order: AES > SDBS > SDS > SDSn. The implication is that as the polarity of the head functional group was increased by the addition of oxygen atom, benzene ring, or oxyethyl group, the interaction strength of the surfactant with water molecules was enhanced.

Jiao et al. [128] studied the effect of alkyl chain length on the interfacial property of modified lignosulphonate and found that by increasing the alkyl chain length or the number of lipophilic groups, the interfacial property of the surfactant improved and the optimum surfactant concentration required to reach ultra-low interfacial tension decreased. This is because the increase of alkyl chain length enhances the lipophilicity of the surfactant.

Charge density affects medium viscosity, particularly a medium containing ionic surfactants. As noted by authors [123,129,130], the increase in the charge density of surfactants resulted in a decrease of medium viscosity because of increased electrostatic repulsion between ionic functional heads.

Gemini surfactants have received considerable attention in recent years as low carbon steel corrosion inhibitors. As seen in Fig. 6, surfactant received approximately 24.44% research attention relative to other organic-based chemistries. In oilfield application, the Gemini surfactant as quarternized salts are the most considered. Gemini surfactant is a name given to a class of synthetic amphiphiles possessing two hydrophobic chains and two polar head groups covalently attached through a spacer group. Compared to the conventional surfactant, they exhibit lower critical micelle concentrations, better wetting properties, lower limiting surface tensions, and unusual aggregation morphologies [131]. Quaternization of nitrogen containing compounds during corrosion inhibitors formulation was adopted to refrain from producing reaction products that contain either imino or amido moieties [132]. As mentioned earlier, these moieties are considered to have little to no corrosion inhibition activity [132–134]. Quaternary nitrogen compounds form protective films on the metal substrate surface and the films are stable over a wide range of pH and temperature [135].

The Gemini surfactants tested as low carbon steel inhibitor in a sour environment include cocodimethyl ammonium chloride [136], alkyl pyridinum ammonium chloride [136] and 1,3-bis (dodecyl dimethyl ammonium chloride)-2-propanol [60]. Others are 1,3-bis(myristyl dimethyl ammonium chloride)-2-propanol [137], 1,3-bis(hexadecyl dimethyl ammonium chloride)-2-propanol [137], and 1,3-bis(octadecyl dimethyl ammonium chloride)-2-propanol [138] (Table 3). There have also been numerous claims on this class of inhibitors for sour corrosion inhibitions and some of the claims are also summarized in Table 3. The most effective with corrosion inhibition efficiency exceeding 95% (see Table 3) were 1,3-bis(dodecyl dimethyl ammonium chloride)-2-propanol, 1,3-bis (myristyl dimethyl ammonium chloride)-2-propanol, and 1,3-bis (hexadecyl dimethyl ammonium chloride)-2-propanol.

Synergism has been a focus of corrosion inhibition in recent years. Motivated by the fact that quinolone derivatives are excellent corrosion inhibitors in HCl [139,140] and NaCl [141,142] media and Gemini surfactants are effective corrosion inhibitors in HCl [143,144], sweet [145], and sour [129,136,137] environments, Zhao et al. [68] opted to study the effect of the

Table 3
Summary of the surfactant-based inhibitors for low carbon steel in a sour environment.

Inhibitor	Experimental conditions	Inhibitive performance	Ref.
Cocodimethyl ammonium chloride	Water cut = 100%; pCO_2 = saturated; Aqueous phase = ASTM method D-1141-52; Tempt. = 25 °C; Sulfur = 1.0 g/L and 10 g/L; Duration = 6 h;	CR = 0.1 mpy (0.0025 mmpy)	[136]
Alkyl pyridinum ammonium chloride	Optimum conc. = 1000 ppm	CR = 2.8 mmpy	
Ammonium chloride)-2-propanol derivatives	Optimum conc. = 35 mg/L; Tempt. 60 °C; pH 4.5; Measurement time 72 h	CR = 0.0296–0.0480 mg cm^{-2} h^{-1}; IE = 69.46–97.28%	[137]
1-benzyl-quinolinium chloride (QB)	Optimum conc. = 100 mg/L; Tempt. 60 °C; pH 4.5; Measurement time 72 h	IE = 95.2	[68]
1,3-bis(dodecyldimethylammonium chloride)-2-propanol (12-3OH-12)	Optimum conc. = 50 mg/L; Tempt. 60 °C; pH 4.5; Measurement time 72 h	IE = 91.7%	[68]
A combination of quaternary pyridinium salt and a lower alkylene polyamine or corresponding polyalkylene polyamine	30% ethanolamine saturated with CO_2 and containing the equivalent of 100 ppm, 300 ppm, and 500 ppm H_2S as $(NH_4)_2S$; Total pressure =40 psi; Tempt. = 125 °C; Test duration = 16-18 h; Inhibitor conc. = 100, 500 ppm	IE = 76.5–95.2%	[153]
Corrosion inhibitor composed of a polymeric quaternary ammonium salt prepared by a reaction of a polyepihalohydrin with tertiary amine	NACE brine and LVT 200 (90:10) solution made sour by bubbling H_2S through the solution. Inhibitor conc. 15, 25 ppm.	IE = 86.0–90.0%	[154]
Inhibitor consisted of 20–30% Mannich base quaternary ammonium propargyl alcohol, 15–20% quaternary ammonium salt 8-hydroxyquinoline, 10–17% fatty alcohol polyoxyethylene ether phosphate potassium salt, 5–12% 2-ethyamino ethanol, 1–2% emulsifier, and 30–35% solvent.	Tempt. = 60 °C; Test duration = 168 h; H_2S content of 2000 mg/L; pCO_2 = 0.5 MPa; Total pressure = 10 MPa; Inhibitor conc. = 200 mg/L	IE = 98.5%.	[155]

CR = corrosion rate; IE = inhibition efficiency.

combination of these two class of compounds on corrosion inhibition properties. A quinolinium quaternary ammonium salt (QB) and a Gemini surfactant, 1,3-bis(dodecyldimethylammonium chloride)-2-propanol (12-3OH-12), were selected, and their corrosion inhibition effect on mild steel in H_2S and CO_2 saturated solution upon combination was examined using polarization, impedance, and X-ray photoelectron spectroscopy methods. Interestingly, a synergistic effect was observed with a dosage of Gemini surfactant less than 50 mg/L in combination with 100 mg/L quinolinium quaternary ammonium salt. The synergistic effect disappeared upon a combination of a dosage of Gemini surfactant higher than 50 mg/L with 100 mg/L quinolinium quaternary ammonium salt. The plausible explanation to the findings by Zhao et al. [68] was the existence of cooperative and competitive adsorptions in the former and later scenarios, respectively. It is possible that quaternary ammonium ions adsorbed on HS^- recharged metal surface through electrostatic attraction. The phase angle plots measured by Zhao et al. in a solution containing 100 mg/L 12-3OH-12 alone revealed that the adsorbed film was defective. When a small amount of Gemini surfactant was added, the surfactant molecules cooperatively adsorbed on spare active sites of the metal, which led to a more compact adsorption film and better protection. When a large amount of the surfactant was added, the two compounds competed for adsorption, and this led to a decrease in inhibition efficiency. These two kinds of adsorption, *i.e.*, cooperative and competitive can be differentiated by calculating the synergism parameter (S_θ). Most often, S_θ is calculated using the following equation [146,147]:

$$S_\theta = \frac{1 - (\theta_1 + \theta_2 - \theta_1\theta_2)}{1 - \theta_{1+2}^1} \tag{1}$$

where θ_1 is the degree of surface coverage by inhibitor A, θ_2 is the degree of surface coverage by inhibitor B and θ_{1+2}^1 is the degree of surface coverage of inhibitors A + B combination. In a scenario where a synergistic (cooperative adsorption) effect is in place, S_θ is greater than unity, whereas S_θ less than unity signifies antagonistic (competitive adsorption) effect [147,148]. The claim of synergistic and antagonistic effects between QB and 12-3OH-12 at lower and higher concentrations of 12-3OH-12, respectively, laid by Zhao et al. [68] would have been justified if the synergism parameter was calculated. By looking at the results (Table 4) presented by Zhao et al., the decrease in inhibition efficiency with increasing 12-3OH-12 concentration is insignificant. The decrease could as well be caused by solution saturation. In this case, the adsorbed inhibitor species began to interact with un-adsorbed species, thereby leading to film desorption and subsequently a decline in corrosion protection [149,150].

One of the main concerns with the utilization of Gemini surfactants as corrosion inhibitors is their resistance to biodegradation and high toxicity. Tehrani-Bagha et al. [151] reported that two Gemini surfactants, namely, dodecyl betainate Gemini and dodecyl

esterquat Gemini were not readily biodegradable. It took 35–40 days for 60% of these surfactants to degrade. As previously mentioned, OSPAR and the Organisation for Economic Co-operation and Development (OECD) guidelines require that 60% of a chemical to degrade within 28 days under aerobic conditions [114]. Tehrani-Bagha et al. [152] observed that Gemini surfactants were toxic to aquatic organisms, with an EC_{50} value of 0.27 mg/L. Natural-based surfactants such as lignosulphonate should be an alternative but have been found to exhibit a limited corrosion inhibition ability [123]. Modification to enhance inhibition efficiency is difficult because of the complex and unreactive nature of Lignin [123].

Polymers-based inhibitors

Polymers are macromolecules characterized by repeating unit (s) called monomers, which are in a sufficient amount to give a set of characteristics. Based on origin, polymers are classified into natural, synthetic, and semi-synthetic. The natural polymers are from natural sources, typically plant and animal sources. Examples include shellac, silk, cellulose and wool. Much emphasis is on this class of polymers recently due to their abundance in the environment and ecological friendliness [156,157]. The synthetic polymers are manufactured polymers, and examples include polyvinyl chloride, polyethylene, and polystyrene. The semi-synthetic as the name implies are from natural sources but modified to derive the final product. Rayon and Terylene are common examples.

Based on the molecular forces, polymers can also be classified as thermoplastics, thermosets, elastomers, or fibres. Thermoplastics are polymers with the ability to soften upon heat treatment and solidify upon cooling. Polystyrene, polyethylene, and polyvinyl chloride belong to this category. Thermoplastics have gained wide industrial applications as insulators in automobiles and food packaging industries [156]. Thermosets, unlike thermoplastics, can deform structurally upon thermal treatment. Examples are melamine and fibreglass. Thermosets are used in making toys, varnishes, boat hulls, glues, *etc.* [156]. Elastomers, such as vulcanized rubber, have weak intermolecular forces between their chains and are elastic and can be stretched. Finally, fibres, such as silk have strong intermolecular forces (hydrogen bonding or dipole-dipole interactions) between their chains, hence possessing high tensile strength and boiling point but less elasticity.

Generally, unmodified polymers moderately inhibit metals corrosion when used as an inhibitor [158,159] due to their insolubility in aqueous medium occasioned by their hydrophobic nature conferred on them mostly by the presence of methylene groups. Again, most polymers considered for corrosion inhibition cannot withstand high temperatures [156], probably, the reasons for the less scientific information as seen in Fig. 6. Significant research efforts have been made particularly in the present century to overcome the aforementioned shortcomings and enhance the corrosion inhibition of polymers. Some of the approaches that have been adopted are copolymerization [158], combination with substances that exert synergistic influence [160], cross-linking [161], and compositing [162].

In sour environments, acrylic terpolymers (polymers derived from three discrete monomers) have been advocated for use as corrosion inhibitors because they satisfy the green corrosion inhibitor requirements (environmentally friendly, non-bioaccumulative, biodegradable, very low marine toxicity level) [163]. As mentioned earlier, the challenge with the use of polymers generally as metal corrosion inhibitors are their poor solubility in aqueous medium and their decomposition at elevated temperatures [156]. For instance, in the study undertaken by Vakili Azghandi et al. [163] under a stagnant condition, 0.8 mmol/L acrylic terpolymer of methyl methacrylate/butyl acrylate/acrylic acid could only afford 62.8% corrosion inhibition to SAE 1018

Table 4

Corrosion inhibition performance of quinolinium quaternary ammonium salt (QB) and 1,3-bis(dodecyldimethylammonium chloride)-2-propanol (12-3OH-12) on mild steel in H_2S and CO_2 saturated solution [68].

Inhibitor concentration (mg/L)		Inhibition efficiency (%)	
QB	12-3OH-12	Impedance	Polarization
0	50	87.6	91.7
100	0	94.1	95.2
100	10	94.8	97.1
100	30	96.1	98.7
100	50	93.6	96.8
100	70	92.0	94.7

carbon steel. The terpolymer was, however, effective under hydrodynamic conditions. With a rotation speed of 500 rpm and a Reynolds number of 1433, 0.8 mmol/L of the terpolymer afforded inhibition efficiency of 85.1%. When the rotation speed was increased to 1000, 1500, and 2000 rpm and the Reynolds number was 2865, 4298, and 5731, respectively, the inhibition efficiency increased to 85.3%, 88.7%, and 93.3%, respectively. The solubility of the terpolymer under hydrodynamic corrosion was probably better enhanced compared to the stagnant condition, improving mass transport of inhibitor molecules to the metal surface.

The oil and gas industry is desirous of having a multifunctional chemical because of the problems of chemical incompatibility usually encountered in the field [164]. Although the development of multifunctional chemicals is truly challenging, scientists have recently started to design their studies with this goal. For instance, Kudryavtsev et al. [165] modified polyethyleneimine to obtain an alkylated polyethyleneimine (APEI) that can function as a corrosion inhibitor for steel in H_2S and CO_2 media and as a biocide against sulphate-reducing bacteria. It was reported that APEI showed promise as an inhibitor and biocide. Strong bactericidal activity against sulphate-reducing bacteria was observed at APEI concentration of 100 mg/L. Between 10–25 mg/L APEI, inhibition efficiency of 90–99% was noted against H_2S corrosion, and 70–73% corrosion protection against CO_2 corrosion was observed at 25–50 mg/L APEI dosage.

Beside the amine-, imidazoline-, surfactant-, and polymer-based sour corrosion inhibitors, few other organic compounds have been considered as actives in sour corrosion inhibitor compositions. These organic compounds include hydrazines [166], thiol esters [167], pyrazines [168], azoles [169], imines [170], and azines [171]. The claims on them are summarized in Table 5 and the selected structures of the different chemistries disclosed as sour corrosion inhibitor in disclosures/inventions are shown in Fig. 11.

Existing knowledge gap on sour corrosion inhibitors

Green sour corrosion inhibitor

The corrosion inhibitor world is evolving. Generally, there has been a paradigm shift from the use of toxic inhibitor compounds, such as chromates, dichromates, aromatic amines and their salts, to greener chemicals [172]. It appears that the total compliance with the use of green chemicals is not yet realizable with respect to sour corrosion inhibitors. Compounds with a known toxic effect such as aromatic amines are still part of some recent formulations [173]. In fact, tetrakis hydroxymethyl phosphonium sulphate ($C_8H_{24}O_{12}P_2S$), which is known for the generation of toxic fumes of phosphorus oxides and

sulphur oxides [174] upon heating is part of some commercially available sour corrosion inhibitors (FUSE™ and WCW3444 are typical examples). There is a dearth of information on green sour corrosion inhibitors.

Inadequate information on mechanism

There is a missing link on the mechanism of metal corrosion and corrosion inhibition in sour medium by organic inhibitors. The general mechanism described under Section "Degradation mechanism of carbon steel in sour environment" in this article is a simplified mechanism. The mechanism assumes an ideal sour environment containing hydrogen sulphide gas that can dissolve in produced water to produce HS^- ions, which get adsorbed on the metal surface [24–26]. Charged inhibitor molecules are believed to adsorb thereafter. In a real situation, produced fluid is a mixture of numerous anions and cations, and their contributions to corrosion and corrosion inhibition cannot be undermined. The mechanism of corrosion and corrosion inhibition is therefore more complex and not fully understood at present.

Disparity between laboratory and field data

There is a wide gap between laboratory data and field experience. Most times, the laboratory data do not agree with the field data. One of the reasons for this is the non-adherence to standard protocols during experimental design, testing, and results analysis. The gap could be closed if research scientists strictly follow standards.

Limited information on flow characteristics

It is surprising that most studies [92,102,104,163] have not considered the contributions of flow rate to sour corrosion inhibition. Obviously, most corrosion inhibitors reported as effective for sour corrosion inhibition may not retain their effectiveness under a hydrodynamic condition, which is the actual condition encountered in the field. It is imperative that attention is given to this area of research.

Limited information on localized and pitting corrosion

The localized and pitting corrosion of carbon steel in sour medium have not received the full attention they deserve. There is very limited information on the corrosion inhibition of these two forms of corrosion in a sour environment at present. In fact, Alanazi et al. [16] claimed that there is no corrosion inhibitor for these types of sour corrosion.

Table 5
Summary of some patents based on other organic compounds.

Disclosed inhibitor	Experimental conditions	Formulation performance	Ref.
A combination of sufficient amount of hydrazine to maintain a residual hydrazine concentration of 0.01 to 1.0 ppm with 2–200 ppm of imidazolines	Gas lift wells of average temperature of 130 °F; 18 month inspection. 0.9 ppm hydrazine/3 ppm imidazoline injected.	CR = 0.4 mpy	[166]
Water dispersible thiol with the nucleus of a dimerized fatty acid.	Oil-brine consisted of Texaco EDM fluid, 10% synthetic brine, 1 mL dilute acetic acid, gassed with H_2S for 5 to 10 min. Rotation speed = 30 rpm; Tempt. = 49 °C; Inhibitor conc. = 25, 30, 100, & 500 ppm	CR = 3.2, 2.1, 4.8, & 5.2 mpy	[167]
Corrosion inhibitor prepared from amino substituted pyrazine compounds such as aminopyrazine and epoxy compounds such as glycidyl ether.	Brine solution; pH = 3.8; H_2S content = 300 ppm; Tempt. = 175 °F; Rotation speed = 26 rpm; Test duration = 24 h; Inhibitor conc. = 720 ml	CR = 6.2–6.6 mpy; IE = 81–87%	[168]
Zwitterionic water-soluble imine.	90% by vol. seawater brine; 10% by vol. paraffinic hydrocarbon; sparged with H_2S; Tempt. = 80 °C; Test duration = 14 h; Inhibitor conc. 10, 25, or 50 ppm.	IE = 84–91%	[170]

(a) Macrocyclic tetramine disclosed in U.S. 3977981: Amine chemistry [78]

(b) Imidazoline-based chemistry disclosed in U.S. 3623979 [120]. R^1 = hydrocarbonaceous moiety of a polymeric acid; A = bivalent radical.

(c) Quaternary salt chemistry disclosed in US2006/0062753A1 [154]. where R_1 and R_2 are organic moieties or H of the polyalcohol $R_1(CHOH)_nR_2$, n=1 to 10, y=3 to 150, A is the tertiary amine and X is a halide.

(d) Pyrazine-based chemistry disclosed in U.S. 4, 895, 702 [168].

(e) Zwitterionic water-soluble imine-based chemistry disclosed in U.S. 6171521B1 [170], wherein R_1 is heterocyclyl, heteroaryl, aryl, arylalkyl, cycloalkyl or lower alkyl; R_2 is alkyl, alkenyl, aminoalkyl, diaminoalkyl, hydroxyalkyl, alkoxyalkyl, thioalkyl, alkylthioalkyl or arylalkyl; R_3 is hydrogen and lower alkyl.
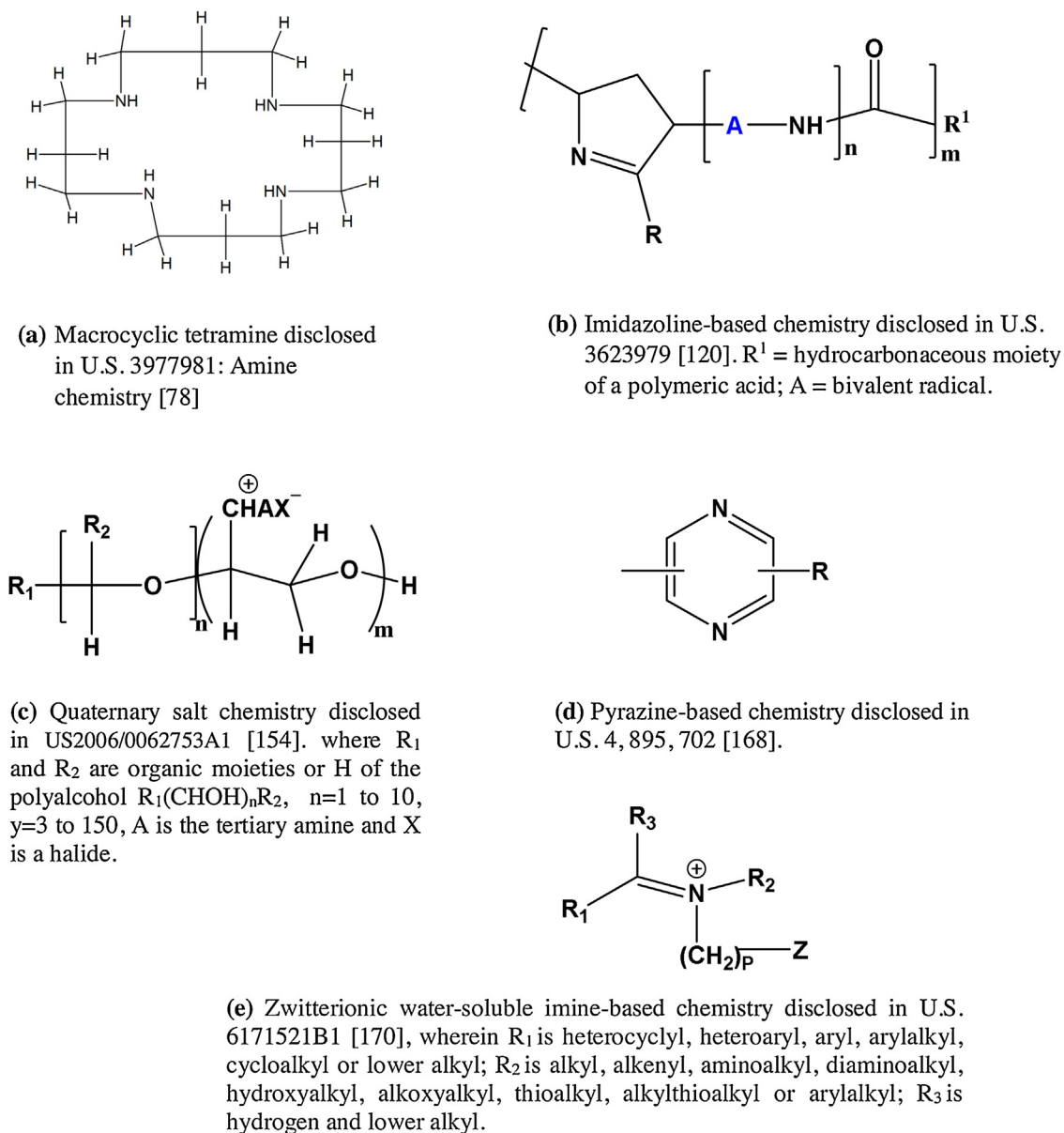
Fig. 11. Selected structures of the different chemistries disclosed as sour corrosion inhibitor in disclosures/inventions.

Molecular modeling approach

The use of molecular modeling in predicting, modeling, and selecting organic molecules with potential corrosion inhibition property has been widely advocated recently [175,176]. This approach does not seem to be patronized in the search for new sour corrosion inhibitors.

Future research directions

Search for green sour corrosion inhibitors

As previously mentioned, most of the current sour inhibitors or their formulations no longer meet the REACH and OSPAR requirements because their primary active ingredients may be harmful if discharged into the environment. The current research goal is to develop alternative corrosion inhibitors. Notable classes of compounds that meet the REACH and OSPAR requirements that are under exploration or have not yet been explored as sour

corrosion inhibitors include amino acids, polymers, and natural polymers, plant extracts, and ionic liquids, in particular.

Amino acids, apart from being non-toxic, biodegradable, and non-bioaccumulative, are soluble in aqueous medium and relatively cheap [177]. In the investigation of Schmitt and Saleh [178], polyaspartic acid, lactobonic acid, polysuccinimide, and their derivatives were found to exhibit excellent corrosion inhibition. The corrosion rate of carbon steel in a sour environment at 90–130 °C was reduced to approximately 0.10 mm/year. Gowri et al. [179] noted that amino acids have the ability to control the corrosion of various metals, including carbon steel, zinc, tin, and copper, in diverse kinds of corrosive media.

Natural polymers are abundant in nature, cost-effective, eco-friendly, inherently stable in the environment of usage, and possess multiple adsorption centres. Although the corrosion effectiveness of this class of compounds is always hampered by their insolubility in aqueous medium and instability at elevated temperatures, researchers [161,180] have reported that these shortcomings can be overcome using modification techniques such as

copolymerization, functionalization, combination with intensifiers, cross-linking, blending, and compositing.

Plants are easily accessible, economically viable, and environmentally compatible. The bioactive compounds in plant extracts have been found to be as effective as synthetic inhibitors [181,182]. Despite the fact that the 21st century has witnessed tremendous research activity on plant extracts as metal corrosion inhibitors, scanty information is available in the sour environment. Fattahalhosseini and Mahdis Noori [183] demonstrated that in the presence of 2.7 g/L lemon verbena extract, carbon steel can be protected against corrosion in a H_2S-containing environment up to 95.61%.

Ionic liquids (ILs) are a unique class of compounds composed entirely of organic cations and inorganic anions [184]. They are nontoxic, have a low melting point and exist as a liquid at room temperature [184,185]. ILs are highly stable, conduct electricity, and possess low vapor pressure, characteristics that have endeared them for various kinds of applications [185]. In fact, Siedlecka and Stepnowski [186] described them as "one of the leading chemicals for the tomorrow." Future studies in the area of corrosion inhibitor development for the sour environment should therefore target full exploration of these classes of compounds.

Deployment of theoretical approaches

Theoretical modelling and calculation techniques, as mentioned earlier, have proven very useful in the prediction of the important properties of organic molecules [175,176]. With this approach, the active sites and the interactive strength of an organic molecule can be ascertained. In addition, with the help of certain software, parameters such as solubility and toxicity can be predicted. It would be ideal to deploy these approaches in the design and development of new corrosion inhibitors.

Greater insight into inhibition mechanism

Future studies should also focus on providing more insight into the corrosion inhibition mechanism of sour corrosion by various classes of organic inhibitors; information on which seems to be scarce at present.

Multifunctional inhibitors

Development of a single multifunctional compound (a compound that can serve as antiscalant, anticorrosive, *etc.*) should also be explored.

Under-deposit corrosion inhibitors due to iron sulphide scaling

As mentioned earlier, presently, one of the largest challenges is to develop environmentally friendly corrosion inhibitors for under deposit corrosion due to iron sulphide scaling. This task should be a high-priority research focus.

Summary and conclusions

Corrosion of metallic structures due to the presence of acid gases is one of the serious challenges facing the oil and gas industry. Most oil and gas-producing companies drill, transport, and process wet sour crude, and this poses serious corrosion risks to their metallic structures. Factors such as H_2S concentration, temperature, immersion time, steel chemistry, surface deposits, and fluid chemistry affect sour corrosion. One of the methods used for controlling sour corrosion is the use of corrosion inhibitors. These are substances that, when present in a corrosive medium at ppm levels, decrease the rate of corrosion. A review of scientific literature reveals that the current sour corrosion inhibitors are amine-based, imidazoline-based Gemini surfactants and polymers. The pros and cons of each class of sour corrosion inhibitors have been discussed. The existing knowledge gap and the future research direction in the area of sour corrosion inhibitor development have been identified. The authors recommend that research emphases should be placed on green chemistry and on unravelling the mechanism of sour corrosion inhibition by organic inhibitors.

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