

Acid corrosion of metals and its inhibition. A critical review of the current problem state*

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Abstract

A critical analysis of the current state of studies on the acid corrosion of metals and its inhibition based on data presented in more than 100 review articles, mainly those published over the past 10 years, is presented. The industrial application of acid solutions at enterprises of the oil-and-gas and metallurgical industries and at housing and communal services objects, the specifics of metal corrosion in acid environments, the assortment of corrosion inhibitors (CIs) of metals in these environments, and the specifics of the mechanism of their protective action are considered. Theoretical studies in the field of inhibitory protection of metals in acid solutions should be aimed at determining the true rather than effective values of the thermodynamic parameters of CI adsorption. To identify the features of the mechanism of CI action, a wider range of electrochemical methods (voltammetry and EIS) has to be involved. A thorough theoretical study of the issues of creating mixed CIs is also required, taking into account their prospects for industrial use. Despite the existence of numerous reviews dealing with environmentally friendly (“green”) CIs, the practical implementation of this approach is currently very difficult. In fact, no clear criteria based on which environmentally friendly CI for acid media could be searched for have been formulated. Moreover, no detailed studies exist that would make it possible to estimate the compliance of environmentally friendly CIs with the full set of requirements for products recommended for application in industrial environments. As an alternative, a technology should be developed for application of inhibited acid solutions that meet the production and environmental requirements of modern industry. The bibliography includes 127 sources.

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Introduction

Solutions of mineral and organic acids are widely used at enterprises of the metallurgical industry, oil-and-gas complex, and housing and communal services. They are used for the treatment of oil- and gas-bearing layers in order to increase the yield of hydrocarbons [1–6], remove thermal scale from the surface of steel products, and wash the inner and outer surfaces of metal items and equipment from mineral deposits and corrosion products [7–11]. During operation, these corrosive solutions come into contact with metal surfaces of process structures and with metal items. If no special protective measures are used, this can cause considerable corrosion damage. The use of corrosion inhibitors (CIs) is a simple and widely used method for the protection of metals in such process environments.

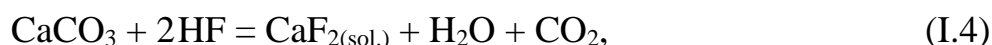
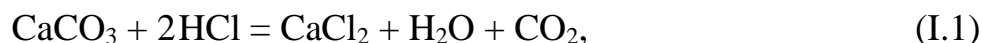
Nearly 40 years ago, G. Schmitt published the first review [12] summarizing the information on the inhibitory protection of metals in acid media accumulated by that time. It covered the CIs that were promising at the time for the protection of metals, primarily iron and steels, in solutions of mineral (HCl, HF, HNO₃, H₂SO₄, H₃PO₄, NH₂SO₂OH) and organic (formic, acetic, hydroxyacetic, citric) acids. The possibility of using these CI for the acid etching of steels, removal of deposits, acid cleaning, and acid stimulation of oil-and-gas wells was noted. Reference information on the inhibiting capability of the following groups of compounds was provided: N-containing compounds (amines, Mannich bases, alkynoxymethylamines, ammonium compounds, heteroaromatics, oximes, nitriles, nitro compounds), acetylenic alcohols, S-containing compounds (mercaptans, thioethers, sulphonium compounds, sulfoxides, thioureas, thariocyanates, heteroaromatics, *etc.*) and complexones. However, no detailed analysis of the mechanism of their effect on the corrosion process was given.

The intensity of studies in the field of inhibitory protection of metals and alloys in acid solutions increased significantly in the past decade. This is reflected in the growth in the number of reviews published in this field of science, considering that more than ten reviews appear annually. It seems important to summarize and analyze the information on the inhibitory protection of metals in acid media given in reviews. This would make it possible to identify important areas of studies, discuss the most significant results obtained to date, and understand the promising problems that still have to be solved. A detailed understanding of the problems of inhibitory protection of metals in acid media and the mechanism of this phenomenon is impossible without studying the corrosion process itself. In view of this, let us consider the fields of practical application of acids and their solutions and summarize the overview information on the study of metal corrosion in these media.

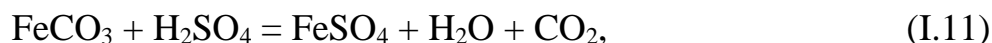
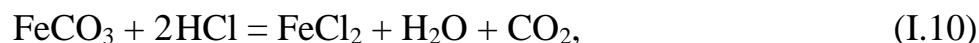
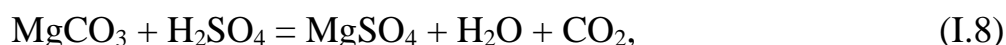
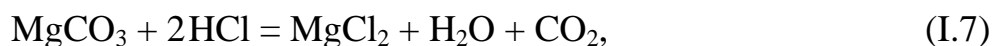
I. Specific features of the industrial application of acid solutions

Carbonate oil-and-gas rocks are composed of calcite CaCO₃ (more than 50%), dolomite CaMg(CO₃)₂ and magnesite MgCO₃. The total mass fraction of calcite and dolomite is above 50%. Moreover, they comprise inclusions of siderite FeCO₃, marl – carbonates + clay particles, gypsum CaSO₄·2H₂O, anhydrite CaSO₄, *etc.* [13]. A number of mineral (HCl, HF,

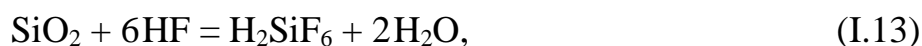
H₂SO₄, H₃PO₄, NH₂SO₂OH) and organic acids (formic, acetic, monochloroacetic, citric, *etc.*) or mixtures based on these are employed for the acid stimulation of oil- and gas-bearing formations in order to boost the output of raw hydrocarbons [1–6, 13]. Dissolution of calcite in the presence of the most common acidic solutions gives, in addition to H₂O and CO₂, end products that differ in solubility:



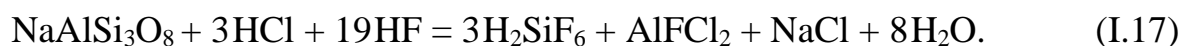
The use of H₂SO₄ is considered promising for dissolving magnesite and siderite because soluble MgSO₄ and FeSO₄ are formed:



The main method for stimulating oil production from reservoirs formed by quartz sand and various aluminosilicates involves their treatment with a HCl + HF mixture. Hydrofluoric acid dissolves silicon (IV) oxide or silicates according to the equations:



If a combination of HCl and HF is used, more complex processes occur, for example, for the Na-feldspar mineral (NaAlSi₃O₈):



The most difficult targets for acid stimulation include oil- and gas-bearing formations with elevated temperatures (*t*) at the bottomhole that can exceed 100°C considerably.

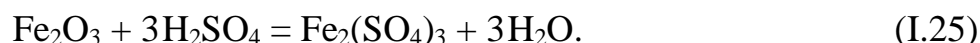
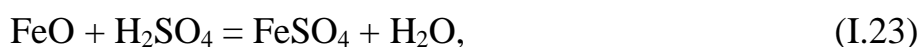
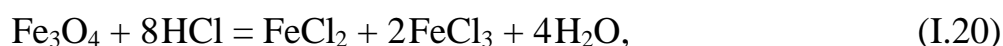
In the course of acid stimulation of such formations, acid solutions are heated to *t* > 100°C, which significantly increases their corrosivity not only toward the rocks

composing the hydrocarbon field but also the oilfield equipment materials. This procedure becomes technically infeasible without efficient inhibitory protection of its metallic parts [14].

At the oil-and-gas industry plants, mineral deposits can form in the ground and underground production equipment. It causes various problems, such as formation damage, a decrease in its productivity and pressure therein, and premature failure of the downhole equipment. These mineral deposits predominantly comprise calcium and magnesium carbonates [15], iron and zinc sulfides, calcium, strontium and barium sulfates [16]. In the cases where oil field equipment is damaged due to hydrogen sulfide corrosion, its surface is covered with deposits of corrosion products, including iron sulfides [17], or iron (II) carbonate in the case of carbon dioxide corrosion [18]. HCl solutions are used most commonly to remove these deposits.

Solutions of organic acids (formic, acetic, citric, maleic, succinic), chelating agents (ethylene diamine tetraacetic acid, hydroxyethyl ethylene diamine tetraacetic acid, diethylene triamine pentaacetic acid, hydroxyethyl iminodiacetic acid, *L*-glutamic acid, *N,N*-diacetic acid, methylglycinediacetic acid, nitrilotriacetic acid, tetrakis hydroxymethyl phosphonium sulfate), as well as organic acid – chelating agent mixtures are suggested as ecologically safe alternatives to such media [8].

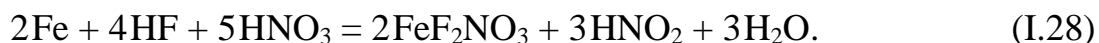
Enterprises of the metallurgical complex employ HCl and H₂SO₄ solutions in order to remove thermal scale layers from steel [9]. The scale formed on low-carbon steels has inhomogeneous structure and, in simplified terms, consists of the wustite phase (FeO) that is immediately adjacent to the metal and that passes to magnetite (Fe₃O₄). The outer part of scale consists of the hematite phase (Fe₂O₃). In these solutions, the following processes occur when scale is etched away from steels:



Due to accumulation of scale dissolution products, *i.e.*, FeCl₃ and Fe₂(SO₄)₃, in the corrosive environment, a reaction of the metal with these solution components additionally occurs:



which enhances the corrosion damage of steels. The etching process is more complicated in the case of stainless steels. In this case, cations of alloying elements are accumulated in an acid solution along with iron salts. Mixtures of HNO₃ (90–160 g/L) and HF (10–40 g/L) are often used for etching these steels. It is believed that the main process occurring in this case is as follows:



Heat exchange equipment that contacts water containing hardness salts is covered with scale that mainly consists of calcium carbonate and magnesium compounds [10]. This scale is quickly removed with an HCl solution by reaction (I.1) and



Moreover, due to the action of corrosive environment components on metals, their surface is often covered with corrosion products that are strongly bound to the surface. The most typical example of such a process is the formation of rust on steel in contact with a humid air atmosphere [19]. Acid solutions are also used to clean metal items from corrosion products [20].

In the course of thermal scale etching and acid cleaning of metals, the properties of acid solutions change significantly due to accumulation of dissolution products formed from scale, surface contaminants on metals, and metal materials themselves in the acid. An increase in the corrosivity of acid solutions toward the metals in contact with them is facilitated by the accumulation of oxidizing cations, among which Fe(III) cations are most dangerous [20]. It is important to take this fact into account in the industrial use of acid solutions, since a change in their composition, and hence, in their properties during operation can significantly affect the quality of inhibitory protection of metals in these media. In addition, to intensify the technological procedures for etching and cleaning of metals, acid solutions used for this purpose can be heated to temperatures close to 100°C, which also increases their corrosivity toward metals.

At present, a wide range of mineral and organic acids with significantly different properties are used in industrial applications. Modern operating conditions of acid solutions in production imply the possibility of their artificial or natural heating up to $t=100^\circ\text{C}$ or higher at the oil-and-gas industry enterprises. Acid solutions accumulate the products of dissolution of mineral impurities and metals themselves during long-term operation, which changes their properties. Consequently, modern production conditions require CIs for solutions of mineral and organic acids with various properties in a wide range of temperatures, including high-temperature solutions, which retain protection at $t > 100^\circ\text{C}$. The CIs should not be sensitive to the accumulation of various contaminants in acid solutions.

II. Acid corrosion of metals

Unfortunately, the acid corrosion of metals and, above all, the mechanisms of these processes are not considered sufficiently in scientific literature. Fan *et al.* [21] presented reference

information on metallic materials that are resistant to the action of HCl solutions. More detailed information on the corrosion of various steels, Ni, Cu, Ti, Zr, Ta, and alloys based on them in solutions of HCl, HF, HBr, and HI was given in review [22]. It was noted that hydrochloric acid manufactured industrially has a mass fraction of $\omega \leq 38\%$ (w/w), above which it fumes that creates problems during storage and transportation. Various grades of hydrochloric acid with $\omega \leq 30\text{--}35\%$ (w/w) are manufactured in large amounts. The produced amount of hydrofluoric acid ($\omega = 49$ and 70% (w/w)) is smaller. The production of hydrobromic and hydroiodic acids is insignificant. HBr (47–49%) and HI (47 or 55%) are produced commercially. It is noted in these works that the corrosivity of HCl solutions toward metals increases significantly if they are contaminated with oxidants such as dissolved molecular oxygen or chlorine, Fe(III) and Cu(II) cations. Oxidizing agents that increase the electrode potential of metals and alloys nearly always have a detrimental effect on the corrosion resistance in hydrohalic acids where metals and alloys are almost unable to form protective passive films.

We failed to find any generalizing studies on the corrosion of metals in other acids. Work [23] where the specific features of corrosion of carbon steels in concentrated H_2SO_4 are considered is an exception. The issues of general corrosion of carbon steels are discussed, as well as the possibility of specific damage, such as hydrogen grooving, blistering and preferential weld attack. It should be noted that the authors of that article set forward debatable ideas on the chemistry of concentrated H_2SO_4 reduction in reactions with steels.

Reference information on the corrosion resistance of Al and its alloys in solutions of mineral and organic acids is given in [24, 25]. Materials of this kind are often characterized by extremely low corrosion resistance in acid solutions.

High-temperature acid corrosion is the least developed but an extremely practically important area of corrosion science [14]. Data on the corrosion resistance of low-carbon and chromium–nickel steels in hot solutions of mineral and organic acids, in some cases at temperatures up to 250°C , are summarized. The data presented unambiguously indicate that these materials have low resistance in such environments. The methodological specifics of experimental studies of high-temperature acid corrosion of steels are considered. Moreover, the difficulties that arise in these studies and in the interpretation of the results obtained are analyzed.

Analysis of the effect of Fe(III) cations on the corrosion of steels in solutions of mineral acids showed its ambiguity [20]. Depending on the nature of the acidic environment, the chemical composition of the steel, and the hydrodynamic conditions of the process, Fe(III) can accelerate corrosion or slow it down. If this additive accelerates corrosion, the increment in steel weight loss due to the presence of Fe(III) salts in a corrosive environment can be comparable to the mass loss caused by the reaction with the acid itself. The accelerating effect of Fe(III) results from their additional participation in the cathodic reaction of the metal as a depolarizer along with protons. Corrosion can slow down if the presence of Fe(III) cations in a corrosive environment accelerates the cathodic reaction to such an extent that the corrosion potential of steel increases to values in the region of its passive state. The

review [20] also discusses the modern concepts of the corrosion mechanism of low-carbon steels in solutions of mineral acids containing Fe(III) salts. The corrosion of low-carbon steel in this environment occurs through three independent partial reactions, *i.e.*, anodic ionization of iron, reduction of protons and Fe(III) cations. The first two reactions are characterized by kinetic control, while the third occurs in diffusion mode.

The contact of steels with acid solutions causes not only general corrosion that manifests itself as a mass loss of the metal, but also their hydrogenation that occurs due to the penetration of the released hydrogen into the metal structure [26]. It is an extremely undesirable process: hydrogen penetrating into the metal structure can significantly change its properties. This is especially dangerous for high-strength steels whose hydrogenation results in the loss of their plastic properties. The theoretical aspects of the hydrogenation of metals, including that in acid media, are discussed in detail in [27–31]. Issues that are important for understanding the nature of hydrogenation of metals in acid solutions are discussed, namely, the mechanisms of cathodic hydrogen evolution, the calculation of the degree of iron surface coverage with hydrogen, and the concentration of hydrogen atoms in the metal phase. The effect of adsorbed and absorbed hydrogen on the rate of iron dissolution depending on the electrode potential and the electrolyte composition is considered. Experimental techniques for studying the hydrogen absorption by metals (thermal desorption spectrometry, hydrogen microprint (silver decoration) technique, Devanathan–Stachurski method, electrochemical impedance spectroscopy, electrochemical noise) and their application are summarized.

The general experimental approaches to the study of metal corrosion in liquid-phase media used at oil-and-gas enterprises are discussed in [32]. Many of these methods are also widely used to study the acid corrosion of metals.

It should be stated that at present there are significantly fewer studies dealing with the problems of corrosion of metals in acids than studies mainly focused on their protection with inhibitors. At the same time, the issues of the detailed corrosion mechanism are left behind, although they are important in considering the problems of inhibitory protection of metals and the mechanism of CI action. Without understanding the details of the corrosion process mechanism, analysis of the mechanism of the protective action of CIs becomes formal to a considerable extent.

III. The range of acid corrosion inhibitors

Analysis of review literature dealing with the inhibitory protection of metals in acid media published in the past 20 years allows us to distinguish 16 main groups of CIs (Table 1). It should be emphasized that our classification of CIs into groups is rather arbitrary since it is based on several attributes, namely, the chemical nature of compounds that are CIs; the chemical composition of the acid environment in which the metal is to be protected; the nature of the metal to be protected; fields of industrial CI applications; and the prospects for their application as environmentally friendly products. In the CI classification, we primarily focused on the approaches used by the authors of review studies.

Table 1. Assortment of inhibitors of acid corrosion of metals.

Number	Corrosion inhibitors groups	Considered compounds	Reference
1	Unsaturated organic compounds	Acetylene compounds	[33]
		Acetylene compounds, unsaturated aldehydes and azomethines	[34]
		Unsaturated aldehydes, ketones and azomethines	[35]
		Acetylene compounds, unsaturated aldehydes, ketones and azomethines	[36]
2	Azomethines	Schiff bases	[37, 38]
3	S-containing organic compounds	Thiourea and thiadiazole derivatives	[39]
4	N-containing heterocyclic organic compounds	Quinoxaline derivatives	[40]
		Quinoline derivatives	[41]
		Pyridine based N-heterocyclic compounds	[42]
		Pyrimidine derivatives	[43]
		Triazines	[44]
		Quinoline, pyridine and pyridine derivatives, imidazole based corrosion inhibitors	[45]
		Nitrogen-containing six-membered heterocyclic compounds	[46]
		Imidazole based corrosion inhibitors	[47]
		Imidazoles, pyrazoles, oxazoles, pyridines, triazines, tetrazines, pyrazines, pyridazines, pyrimidines, triazoles, tetrazoles, thiazole, thiadiazoles, macrocyclic compounds	[48]
		Imidazoles, azoles, pyridines, diazines, quinolines, quinolones, quinoxalines, quinazolines, triazines, tetrazines, macrocyclic compounds	[49]
		1,2,4-Triazole derivatives	[50]
		Imidazo[1,2- <i>a</i>]pyridines	[51]
		Pyrazole derivatives	[52]
		Phthalocyanine, naphthalocyanine and their derivatives	[53]
Nitrogen-containing heterocyclic compounds	[54]		
Nitrogen-containing heterocyclic high-temperature corrosion inhibitors	[55]		

Number	Corrosion inhibitors groups	Considered compounds	Reference
		Nitrogen-containing five-membered heterocyclic compounds	[34, 56]
		Neutral, acidic, basic, functionalized and supported ionic liquids	[63]
		Protic, polymer protic, aprotic and polymer aprotic ionic liquids	[64]
5	Ionic liquids	Ionic liquids	[65]
		Ionic liquids based on imidazolium, triazolium, thiazolium, indolium, pyrrolidinium, pyridinium, picolinium, piperidinium, thiazinium, pyridazinium, ammonium, amino acid, phosphonium, chitosan, acrylamide, and sulfonium.	[66]
6	Amino acids	Amino acids derivatives	[68]
		Glutamic acid derivatives	[69]
7	Polymeric organic compounds	Natural and synthetic polymers	[70–72]
		Poly(phenylenediamine)	[73]
8	Drugs	Different groups of drugs	[74, 75]
		Expired Drugs	[76]
9	Corrosion inhibitors of steel in phosphoric acid solutions	Individual organic compounds, triazole derivatives – based mixed corrosion inhibitors	[77]
		Individual organic compounds	[78]
10	Corrosion inhibitors of steels in acid solutions containing Fe(III) salts	Mixed corrosion inhibitors based on triazole derivatives	[20]
		Individual organic compounds, plant extracts, mixed corrosion inhibitors	[79]
11	Corrosion inhibitors for copper	Azole derivatives, amines, amino acids, triphenylmethane derivatives, S-containing organic compounds, alkyl sulfonates, phthalazine derivatives, propargyl alcohol, phthalimide derivatives, isatin.	[80]
		Azole derivatives, amino acids, plant extracts, pharmaceutical compounds	[81]
		1,2,3-Benzotriazole	[82, 83]

Number	Corrosion inhibitors groups	Considered compounds	Reference
12	Corrosion inhibitors for aluminum	Organic compounds	[84]
		Green corrosion inhibitors	[85]
13	Mixes of corrosion inhibitors	Mixes of halide ions with organic dyes, surfactants, drugs, polymers, plant extracts	[87]
		Mixes of metal cations with surfactants, organic compounds, inorganic compounds, polymer–polymer and polymer–cation compositions, organic compounds compositions	[88]
14	Corrosion inhibitors for the oil-and-gas industry	A variety of organic compounds including acetylenic alcohols, aromatic aldehydes, alkenylphenones, amines, amides, nitrogen-containing heterocycles (<i>e.g.</i> imidazoline-based or triazole-based), nitriles, imminium salts, triazoles, pyridine and its derivatives or salts, quinoline derivatives, thiourea derivatives, thiosemicarbazide, thiocyanates, quaternary salts and condensation products of carbonyls and amines. Natural products. Mixed corrosion inhibitors including active substance, surfactant, solvent, intensifier and other additives.	[5]
		Azomethines, aromatic aldehyde derivatives, triazole derivatives, pyrimidine derivatives, pyran derivatives, macrocyclic compounds	[6, 91]
		Imidazoline and triazole derivatives	[92]
		Environmentally benign corrosion inhibitors for organic acid	[93]
		Amines	[94]
		Polymeric corrosion inhibitors	[95]
15	Corrosion inhibitors for acid cleaning of metals	Corrosion inhibitors for acid cleaning (descaling)	[10]
		Eco-friendly corrosion inhibitors	[11]
		Organic compounds having heteroatoms (N, S, O and P)	[97]
16	Eco-friendly (“green”) corrosion inhibitor	Natural products	[98, 99]
		Plant extracts	[100–108]
		Aqueous extract of henna leaves (<i>Lawsonia inermis</i>)	[109]
		Coumarins	[110]
		Alkaloids	[111]

Number	Corrosion inhibitors groups	Considered compounds	Reference
		Plant extracts, essential oils, ionic liquids, drugs, amino acids, eco-friendly polymers, inorganic green inhibitors	[112]
		Plant extracts, natural polymers, bio-mimicking of green inhibitors	[113]
		Solid waste	[114]

Unsaturated organic compounds have been widely studied as CIs of various steels in HCl solutions [33–36]. The interest in this group of compounds is determined by the fact that they can serve as a basis for creating mixed CIs for the protection of steel structures from the action of HCl solutions under high-temperature corrosion conditions. This is very important for preventing the corrosion of field equipment in the oil-and-gas industry where HCl solutions are used to stimulate oil reservoirs with elevated temperatures, *i.e.*, to increase the output of raw hydrocarbons. To date, the most important structures of unsaturated compounds that are promising for efficient protection of steels have been identified among derivatives of acetylene, unsaturated aldehydes, ketones and azomethines. The approaches to the creation of formulations capable of protecting steels in hydrochloric acid under high-temperature corrosive conditions on their basis are considered. The protection of steels at $t > 200^{\circ}\text{C}$ should be considered an outstanding result. The mechanism of action of these CIs under such severe conditions is based on the ability of their molecules, after adsorption on the surface of steels, to undergo chemical reactions resulting in a protective polymer layer. A drawback that limits the use of these compounds is that their molecules undergo destruction and polymerization in the corrosive environment, which reduces the CI content therein.

The widespread use of azomethines as CIs of metals in acid media is largely determined by the simplicity of their chemical synthesis. A huge number of compounds of this group with significantly different chemical structures have been studied [37, 38]. The drawbacks of this CI group in acid media include their tendency to undergo hydrolysis giving an aldehyde and a protonated amine. Sulfur-containing organic compounds have the same drawback [39] as they are very likely to undergo destruction in an acid medium. It is most expedient to use sulfur-containing compounds not in individual form but in composite CIs where the content of these compounds, which often have high toxicity, in a corrosive environment can be reduced considerably.

A promising approach to the protection of metals from corrosion is to study N-containing heterocyclic compounds, including both six-membered [40–46, 48, 49, 55] and five-membered [47–56] structures. From our point of view, derivatives of azoles, in particular triazoles, are the most promising of these compounds [55, 56]. Due to the presence of an azole moiety in their structure, these compounds are capable of being adsorbed on a metal surface to form a chemisorbed monolayer of CI molecules, on top of which a polymer

complex bound to it can be formed from triazole molecules and Fe(II) cations. As a result, a polymolecular protective layer of the CI is formed, in which its molecules are chemically bound to each other and to the surface of the metal being protected. This makes it possible to provide the most efficient protection of metallic materials even in such corrosive environments as high-temperature acid solutions. It should be noted that the ability of azoles to undergo chemisorption on the surface of metals makes them versatile CIs [57] that can significantly slow down the corrosion of metals not only in solutions of mineral acids, but also in aqueous (carbon dioxide containing [58, 59], neutral [60], alkaline [61]) and vapor-phase [62] media. Imidazole derivatives play an important role among ionic liquids [63–66] studied as inhibitors of acid corrosion of metals.

Unfortunately, M. Quraishi's classification of N-containing heterocyclic compounds as environmentally friendly ("green") CIs is not always justified sufficiently. In his review [67], based on data from the European Economic Community, Paris Commission, he identifies green CIs based on the following criteria:

- *Toxicity*. The LD_{50} value of an eco-friendly inhibitor should be more than 500 mg/kg weight of rat.
- *Biodegradation*. The biodegradability of an eco-friendly inhibitor should be 60% in 28 days.
- *Bioaccumulation*. Bioaccumulation is the ability of any chemical to accumulate in living organisms that can be calculated using the partition coefficient value ($\log P_{o/w}$); its value should be smaller than 3.0.

$$P_{o/w} = \frac{\text{Concentration of inhibitor in octanol}}{\text{Concentration of inhibitor in water}} \quad (\text{III.1})$$

However, he does not provide specific data on how the CIs under consideration comply with these requirements.

Amino acids are low-efficiency CIs for acid media [68, 69]. Their protective effects are generally low even in cold solutions of acids. The environmental friendliness of some of the compounds of this group is questionable since, along with naturally occurring compounds, substances obtained synthetically and not characteristic of natural objects are also studied. CIs based on natural polymers [70–72] are more interesting, but they do not always provide good protection of metals, either. Synthetic polymeric compounds are also studied as acid corrosion inhibitors [70–73].

Many organic compounds that are known as pharmaceuticals have been studied as CIs and provide strong inhibition of metal corrosion in acid media [74, 75]. The idea of practical application of these compounds is questionable due to the complexity of their synthesis and high cost. In view of this, it is suggested to use expired pharmaceuticals, which is considered as a way of their disposal [76]. An important conclusion about the environmental friendliness of pharmaceuticals used as CIs was made by G. Gece [74]. He noted that not all of these compounds are readily degraded by microorganisms, and the products of their

transformations can be equally or even more hazardous to the environment. Therefore, additional studies are required before a pharmaceutical product is finally classified as an environmentally friendly CI.

Phosphoric acid solutions represent a specific corrosive medium in many respects [77, 78]. It is difficult to achieve a high degree of protection of steels in a wide temperature range using individual organic CIs in this medium [77]. In contrast, the use of composite CIs (triazole derivative + sulfur-containing organic compound or alkali metal thiocyanate) can significantly slow down the corrosion of low-carbon steels at $t \leq 100^\circ\text{C}$. Rather a unique property of H_3PO_4 solutions is that they the protective effect of some composite CIs based on substituted triazoles in the protection of steels in situations where Fe(III) salts are accumulated in the corrosive medium can be retained [20]. This effect is due to the ability of phosphate anions to bind Fe(III) into complex compounds, which decreases their oxidizing properties and the mobility of these cations in a corrosive environment. The protection of steels with CI formulations based on a substituted triazole in acid solutions containing Fe(III) is possible not only in phosphoric acid based media but also in $\text{H}_2\text{SO}_4 + \text{H}_3\text{PO}_4$ and $\text{HCl} + \text{H}_3\text{PO}_4$ mixtures. This opens prospects for creating inhibited acid solutions for steel etching that are resistant to the accumulation of Fe(III) salts.

Along with the development of CIs for steels in acid solutions, active studies in the field of inhibitory protection in these media are being carried out for copper [79–83], aluminum [84, 85] and their alloys. In the case of protecting copper alloys in acid solutions, a significant reduction in corrosion can be provided by azole compounds, primarily, various triazole derivatives. The protection of Al alloys in environments with a high acid content and at high temperatures encounters serious difficulties. In the case of environmentally friendly CIs, their ability to slow down the corrosion of these alloys is low in most cases [85].

An important way to improve the inhibitory protection of metals is to switch from single-component CIs to multicomponent ones. This approach makes it possible to enhance the protective effect of CIs, which allows one to reduce their total content in a corrosive environment, and hence, the consumption of compounds used for these purposes. In addition, mixed CIs cover a wider temperature and concentration range of corrosive media where they can be used than individual CIs. All this is important for industrial application of CIs.

Insufficient attention is given in scientific literature to the problem of creating mixed CIs, including those for acid media. Various approaches that make it possible to give a mathematical assessment of the presence or absence of a synergistic effect between the components of mixed inhibitors are summarized and analyzed in [86]. The simplest parameter that allows the action of mixture components to be characterized quantitatively is the coefficient of their mutual effect:

$$K_m = \frac{\gamma_{\text{mix}}}{\prod_{i=1}^m \gamma_i}, \quad (\text{III.2})$$

where γ_{mix} is the coefficient of corrosion inhibition by a mixture of inhibitors, $\prod_{i=1}^m \gamma_i$ is the product of the coefficients of corrosion inhibition by the individual mixture components, and m is the number of components in the mixture. If $K_m < 1$, the protective effects of the mixture components are mutually weakened, at $K_m = 1$ the effects are additive, and only at $K_m > 1$ it should be concluded that the components of the inhibitor mixture mutually enhance the effects of each other. Most often, binary formulations containing halide anions and organic compounds of various nature are used to protect metals in acid media [87]. To analyze the mutual effect of the components of such systems, it is recommended to use the synergistic parameter:

$$S_1 = (1 - Z_{1+2}) / (1 - Z_{\text{mix}}), \quad (\text{III.3})$$

where $Z_{1+2} = Z_1 + Z_2$; Z_1 is the degree of metal protection by a halide anion, Z_2 is the degree of metal protection by an organic compound, and Z_{mix} is the degree of metal protection by the mixture of the organic compound and the halide. If $S_1 > 1$, it is concluded that the mixture components manifest a synergism of action. According to the data presented in [87], a synergism of the action of components is most often observed in binary mixtures of organic compounds and halide anions. When considering binary CI groups with a broader spectrum of chemical composition, another form of equation (III.3) is used to characterize them, in which $Z_{1+2} = Z_1 + Z_2 - Z_1 Z_2$ and Z_1 and Z_2 are the degrees of metal protection by the mixture components [88]. In reviews [87, 88], both forms of equation (III.3) are recommended for a quantitative analysis of the mutual effect of the components of mixed CIs without a theoretical justification of the validity of their application and without possible alternative approaches. Previously, the use of both forms of equation (III.3) was theoretically founded in [89, 90] in an analysis of the properties of several binary CIs containing halide anions. Equation (III.3) is often used as an expression where Z_1 , Z_2 and Z_{mix} are replaced by the corresponding parameters of the degree of coverage of the metal surface with the CIs – θ_1 , θ_2 and θ_{mix} . The use of this form of equation (III.3) is significantly limited by the experimental difficulties in the correct determination of the true values of θ for corrosion inhibitors.

Various groups of compounds are recommended and used to protect metal equipment, primarily steel, from corrosion in contact with acid solutions at the enterprises of the oil-and-gas complex [5, 6, 91–95]. Analysis of literature data [5, 36, 55] shows that there is an urgent need to develop CIs capable of protecting steel structures in a wide range of temperatures, including high-temperature environments ($t > 100^\circ\text{C}$), for the oil-and-gas complex. The majority of CIs suggested for steels in acid environments are not studied for application under such conditions and, judging by their protective properties under milder conditions, cannot provide efficient protection of steels in high-temperature acid solutions. Two approaches to the creation of high-temperature CIs for acid solutions may be distinguished. The most traditional one involves the creation of mixed CIs comprising an

active ingredient (an unsaturated organic compound), a surfactant, a solvent, a synergist, and other additives. The range of surfactants used as corrosion inhibitors for metals was summarized and analyzed in [96]. The drawbacks of this approach are largely due to the low chemical stability of unsaturated compounds in a corrosive environment, which causes their destruction and polymerization in this environment. This results in an excessive consumption of the CI caused by its removal from the acid solution and undesirable resinification of the CI. The second approach is mostly devoid of these drawbacks. Relatively thermostable derivatives of triazoles combined with iodides or bromides of alkali metals and urotropine should be used to create high-temperature CIs. Solutions of organic acids are suggested as acid media with low corrosiveness towards steels for the oil-and-gas industry. In many respects, this is an alternative to inhibited mineral acids. Such media may be operated with significant heating, which sharply increases their corrosivity towards steels. However, there are practically no CIs that protect steels under these conditions [93]. In view of this, mixtures of substituted triazoles with sulfur-containing compounds are promising inhibitors. They significantly slow down the corrosion of low-carbon steels at temperatures close to 100°C in solutions of acetic, formic, and citric acids [55]. Numerous environmentally friendly CIs are recommended for the oil-and-gas industry. High protective effects are noted for many of them, but no data on their properties in hot and, moreover, high-temperature acid solutions are reported [97].

CIs for acid media for cleaning metal surfaces from mineral contaminants are discussed in scientific literature [10, 11, 97]. In an interesting work [10], not CIs themselves are considered, but complete inhibited mixtures based on acids designed to remove mineral deposits. It is noted that there are numerous studies dealing with inhibited media for cleaning various steels and that insufficient attention is given to the problem of cleaning copper and titanium alloys that are also used in the manufacture of heat exchange equipment. As a rule, nitrogen-containing organic compounds are used here as CIs for acid media. Among these, amines and azoles are the most promising compounds.

The so-called environmentally friendly or “green” CIs represent the group of inhibitors of acid corrosion of metals that is most difficult to analyze [63, 64, 66, 85, 97–114]. The idea of using compounds and products of technical or natural origin that are harmless to humans and to the environment as corrosion inhibitors deserves serious attention. However, a detailed analysis of the current state of its implementation is required. First, there are no generally accepted criteria for environmentally friendly CIs intended for the protection of metals in acid media that have been discussed in detail by corrosion scientists. M. Quraishi [67] was the only one to make an attempt to classify them as discussed above. Unfortunately, well known toxic compounds are sometimes defined by the fashionable term “ecologically friendly”. For example, propargyl alcohol was referred to as an environmentally friendly CI in [97], though it is a toxic inflammable compound, like many acetylene derivatives. It is not a natural product and is manufactured by chemical synthesis. Though propargyl alcohol is not environmentally friendly, it is used at oil-and-gas enterprises because of its unique ability to protect steels within composite CIs under conditions of high-temperature acid corrosion

and because it is difficult to find alternative compounds. On the other hand, there are no systematic studies comparing the properties of environmentally friendly CIs with those of industrially used products. Only studies of this kind would make it possible to show that environmentally friendly CIs are at least not inferior to the properties of commercial CIs that are often operated under drastic conditions rather than at room temperature at which eco-friendly CIs are often studied. Sometimes a simple technology for producing a CI, even from potentially safe plant materials, can make it toxic. For example, a methanol extract of *A. Pallens* was considered as a CI of mild steel in 4 M HCl [97]. It is not clear which compounds make a larger contribution to the protective effect: the toxic methanol or compounds extracted by it from the plant raw material? In some cases, it is questionable how safe the technology of preparing a plant extract is.

Many aspects of the development of environmentally friendly CIs requires a new approach. We need to stop searching for environmentally friendly CIs but use safe and environmentally friendly technologies for operation of inhibited acid solutions that meet the stringent requirements of modern production. Compounds that efficiently inhibit the corrosion of metals in the entire possible range of industrial operating conditions should primarily be used to create inhibited solutions. At the same time, one should not forget about the hazard of using acids that are the main components of corrosive media mentioned above.

A few works [115–119], mostly reference books where various CI groups are also discussed, were left outside the scope of our discussion.

Analysis of studies on the development of CIs for metals in acid solutions shows that they are somewhat isolated from the requirements of practical use. In the majority of studies, corrosion of metals in acid solutions in the presence of corrosion inhibitors is determined from the mass loss of metal samples in a corrosive environment and is confirmed by electrochemical methods (voltammetry and electrochemical impedance spectroscopy (EIS)). Based on these data, it is concluded that a particular compound is a CI. However, the requirements for products to be used industrially are much broader. In fact, a number of specific requirements are imposed on CIs used in the oil industry [13]:

- high efficiency of action ($Z \geq 94\%$) in a wide temperature range with a minimum consumption in an acid-based formulation, and at the same time, protection of the metal from hydrogen absorption;
- preservation of the protective effect in the acid formulation for at least 30 days at an elevated content of iron salts;
- prevention of sludge precipitation upon complete neutralization of an acid in the bottomhole formation zone;
- compatibility with other reagents used in oil production;
- no effect on the process of oil preparation and oil refining.

In the case of acid cleaning of metal surfaces from scale or mineral contaminants, it is necessary to know not only how much the CI slows down metal corrosion but also how it affects the rate of scale or contaminant removal. It is undesirable to slow down these

processes. It is also important that the CI should prevent the absorption of evolved hydrogen by steels.

IV. Some aspects of the mechanism of the protective action of inhibitors of acid corrosion of metals

The fundamental aspects of inhibitory protection of metals and alloys in acid solutions were summarized in monographs by S.M. Reshetnikov [120] and by V.P. Grigoriev and V.V. Ekilik [121, 122]. The ways in which CIs of different nature affect the electrode reactions on metals in acid solutions were considered and analyzed [120]. It was noted that the inhibition of electrode reactions of metals and the total corrosion process results from:

- a decrease in the fraction of the metal surface that is free for the process (blocking effect);
- changes in the structure of the electric double layer at the metal/acid solution interface, and hence, the potential value at the site where the electrochemical reaction occurs (energy effect);
- changes in the rate constant of the process due to changes in the activation energy upon CI adsorption on the metal (kinetic effect);
- changes in the electrochemical reaction order and the volume concentrations of the components (chemical effect);
- changes in the electrode potential of the metal.

It is also possible that the adsorption energy of the reacting particles on the metal may change under the action of a CI. In turn, the changes in the adsorption energy of reacting particles affect the rate of the corrosion process. The slopes of the cathodic and anodic polarization of the metal (b_c and b_a) and the transfer coefficients of particles participating in electrode reactions can change under the effect of a CI.

The effects listed above are interrelated. They can overlap, some will predominate, while the effects of others will be insignificant.

The relationship between the inhibitory effect of organic compounds and their electronic structure and the electronic structure of metals being protected in acid media was analyzed in sufficient detail in [121]. Information on the effect of the nature of corrosive acid media on the protective effect of CIs was generalized. Solutions of acids in aqueous, aqueous–organic, and organic solutions were considered as such media [122].

A distinctive feature of the mechanism of action of some important CI groups that show high protective effects on metal corrosion under extreme corrosive environment conditions (elevated temperatures, high acid concentrations, the presence of oxidizing metal cations in the medium) is that they form mono- and polymolecular protective layers strongly bound to the metal surface by chemical forces, as briefly discussed in the previous chapter. The formation of protective layers on a metal results from the specific features of adsorption of CI molecules on its surface, which requires a more detailed discussion.

An important thermodynamic parameter characterizing the adsorption of CI molecules on a metal surface is the standard free energy of adsorption ($-\Delta G_{\text{ads}}^0$). It is believed that if

$(-\Delta G_{\text{ads}}^0)$ is smaller than 20 kJ/mol, then physical adsorption takes place. Only if $(-\Delta G_{\text{ads}}^0) \geq 40$ kJ/mol, one can state with high probability that the CI is chemisorbed. The adsorption of CIs on metal surfaces from acid solutions is satisfactorily described by the Langmuir, Freundlich, Temkin, Frumkin, Flory–Huggins, and Bockris–Swinkels isotherms [123]. There are few works on the estimation of the adsorption of CIs on metals from acid solutions performed by direct methods (determination of the capacitance of the double electric layer on a metal using EIS and ellipsometry). However, there is a lot of data on the determination of $(-\Delta G_{\text{ads}}^0)$ obtained in a less correct way, *i.e.*, by treatment of the results on the mass loss of metal samples in inhibited acid solutions or by measuring the corrosion rate of a metal (corrosion current density, polarization resistance) by electrochemical methods (voltammetry, EIS). The experimental values of $(-\Delta G_{\text{ads}}^0)$ obtained by these methods should be more correctly regarded as effective values, but they can be used for a qualitative interpretation of the nature of the metal–inhibitor bond. For example, as a rule, the values of $(-\Delta G_{\text{ads}}^0)$ for unsaturated organic compounds [36] and azoles [55, 56] indicate that chemical adsorption of these compounds on steels occurs, which is in good agreement with their ability to protect metals in acids under high-temperature corrosion conditions. It should be borne in mind that a high value of $(-\Delta G_{\text{ads}}^0)$ is a necessary but insufficient condition for efficient inhibition of a metal by a CI. For a detailed understanding of the mechanism of CI action, the kinetic laws of its adsorption should be understood. A CI should be quickly adsorbed on a metal surface that is rapidly degraded in a corrosive environment. Otherwise, effective protection of the metal is impossible [77].

To a large extent, attempts to determine the type of the adsorption isotherm and $(-\Delta G_{\text{ads}}^0)$ values for inhibitor formulations whose quantitative composition is unknown lack any theoretical and practical value. Plant extracts are a striking example of such CIs [108, 112]. Important additional theoretical information on the ability of organic compounds to be adsorbed on the surface of metals in corrosive media can be obtained by quantum mechanical methods considered in [124, 125].

In the majority of cases, the standard studies on the properties of CIs by voltammetry and EIS are limited to a statement of the fact that they slow down the cathodic and anodic reactions on the metal and increase the polarization resistance of the corroding system, which only confirms the data of corrosion studies based on the weight loss of metal samples but does not contribute to our understanding of the features of their mechanism of action. A detailed study of the effect of a CI on the partial electrode reactions on metals in acid media allows one to obtain important information on the mechanism of their action. For example, the reason of the low efficiency of propargyl alcohol in the corrosion of steels in H_2SO_4 , H_3PO_4 , and HClO_4 solutions was found to be due to reduction of its molecules on a metal in these media [33, 36].

The voltammetry of a rotating disk electrode is an indispensable method in the study of acid corrosion that involves diffusion stages. It makes it possible to study the effect of the hydrodynamic parameter of a corrosive medium on the kinetics of electrode reactions. It has been shown that the possibility of inhibitory protection of steels in acid solutions containing

Fe(III) salts by composite CIs based on triazoles results from efficient inhibition of three partial reactions of the corrosion process by these CIs: reduction of protons and ionization of iron that occur under kinetic control, and reduction of Fe(III) controlled by diffusion [20, 77]. Study [126] deals with the effect of anodic activation of a steel electrode in acid media in the presence of CIs. The reason for the observed effect is rather complex [127]. The anodic activation of iron and steels is characteristic of both background and inhibited acid solutions. In these environments, the hydrogen uptake by metals and especially their surfaces occurs quickly and thus hinders their anodic ionization. Removal of adsorbed hydrogen from the metal surface and pitting should be considered as the reasons for the anodic activation of iron and steels in solutions of mineral acids. If a CI is present in the acid solution, partial or complete desorption of the CI from the metal surface may also be the reason of the effect mentioned above.

To study mono- and polymolecular protective CI layers formed on the surface of metals in acid media, chromato-mass spectroscopy and X-ray photoelectron spectroscopy (XPS), which make it possible to determine their composition and structure, are successfully used. Chromato-mass spectrometry is most convenient for studying the protective layers formed by unsaturated organic compounds, while XPS is best used for layers formed by azoles. An important stage of XPS studies involves prolonged ultrasonic cleaning of the surface of metal samples from the CI in distilled water or in acid solutions. During this procedure, the CI molecules retained on the metal surface by physical forces are removed from the surface of the samples previously exposed to an inhibited acid solution. CI molecules bound to the metal surface by chemical forces are not removed upon ultrasonic surface cleaning. Such metal samples demonstrate a protective CI after-effect in subsequent corrosion tests in background solutions. Ultrasonic cleaning of a metal surface before XPS is an important stage that proves the nature of the chemical bond between the CI molecules and the metal, since this method cannot distinguish between the CI that is present on the surface of samples as a protective layer and that remains on the metal after incomplete removal of the inhibited corrosive medium from it. Detailed information on the formation of protective layers by unsaturated organic compounds and azoles on the surface of steels in acid solutions is discussed in [36, 55, 56].

Conclusions

This review considers the current state of studies in the acid corrosion of metals, as well as the most significant works in the field of inhibitory protection of metals in these environments. Various technological problems at enterprises of the oil-and-gas industry, metallurgy, housing and communal services are solved using solutions of mineral and organic acids that differ in many properties. Without special protective measures, contacts of solutions of these acids, especially at elevated temperatures, with metal parts of the equipment result in serious corrosion damage.

At present, there are too few studies focused on the problems of corrosion of metals in acids, since the details of the mechanism of their corrosion are ignored. They are especially

important when considering the issues of inhibitory protection of metals and understanding the mechanism of CI action. The operating conditions of acid solutions in production imply that they may be heated to $t \geq 100^\circ\text{C}$. Acid solutions accumulate the products of dissolution of mineral impurities and of the metals themselves, which changes their properties in the course of long-term operation. Modern production conditions require CIs for solutions of mineral and organic acids with various properties in a wide range of temperatures, including high-temperature conditions, which retain protection at $t > 100^\circ\text{C}$. Moreover, the CIs should be insensitive to the accumulation of various contaminants in acid solutions.

Analysis of the assortment of CIs for metals in acid media makes it possible to single out the most studied group of organic compounds represented by various azole derivatives. We believe that a promising direction in the studies in this area involves the development of mixed CIs, which would fully meet the requirements of modern production both in technological and environmental respect, based on the already existing extensive set of these compounds. In fact, mixed CIs for steel protection under very severe corrosive conditions, *i.e.*, high-temperature solutions of mineral acids and acid media containing Fe(III) salts, have been created based on triazole derivatives.

Theoretical studies in the field of inhibitory protection of metals in acid solutions should focus more attention on correct approaches to determining the thermodynamic parameters of CI adsorption, which would make it possible to determine not effective but true values of parameters. A wider and more thorough use of the capabilities of electrochemical methods (voltammetry and EIS) should favor a detailed identification of the mechanism of CI action. Considering the prospects of mixed CIs for industrial use, thorough theoretical studies on the issues of creating such CIs are also required.

Environmentally friendly CIs for metals in acid environments should be considered separately. Unfortunately, though numerous publications on this subject, including reviews, are available, it is doubtful that this approach has been efficiently implemented in practice to date. Firstly, clear, correct and generally accepted criteria have not been formulated to classify a product as an environmentally friendly CI. As a result, the fashionable term “green CI” is too often used for products that do not belong to this group. Secondly, no detailed studies exist that would make it possible to estimate the compliance of environmentally friendly CIs with the full set of requirements for products recommended for application in industrial environments. Thirdly, the technology for producing environmentally friendly CIs must be harmless. We believe that the problem of environmentally friendly CIs should be approached in a broader context. One should not look for yet another “green” CI, but develop technologies for the use of inhibited acid solutions that meet the environmental requirements of the modern industry.

To date, a huge amount of data has been accumulated in the field of acid corrosion of metals and its inhibition, which is reflected in over 100 reviews. In our review, an attempt was made to systematize and critically analyze the available data set already summarized in the reviews, which made it possible to highlight some theoretical and practical problems that corrosion scientists face, as well as important promising areas of studies to be performed.

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