

High-temperature inhibitors of stainless steel corrosion in hydrochloric acid solutions

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Abstract

The corrosion of chromium-nickel steel 08Kh18N10T in 2 M HCl has been studied in a broad temperature range, $t = 0\text{--}160^\circ\text{C}$. Under these conditions, the metal corrosion is enhanced with an increase in temperature to reach $5.0\text{ kg}/(\text{m}^2\cdot\text{h})$ at 160°C . It has been shown that the IFKhAN-92 inhibitor (a substituted triazole) and its formulation with urotropine in a molar ratio of 1:4 protect this steel in 2 M HCl at temperatures up to 120°C , inclusive. The three-component mixture of IFKhAN-92, KI and urotropine (1:1:4) is more promising in this respect, as it efficiently inhibits corrosion at temperatures up to 160°C and allows the protective effect to be maintained for at least 8 h. This formulation also reliably protects low-carbon steel 20 in 2 M HCl at temperatures up to 160°C , inclusive.

Key words: *high-temperature acid corrosion, corrosion inhibitors, stainless steel, triazoles.*

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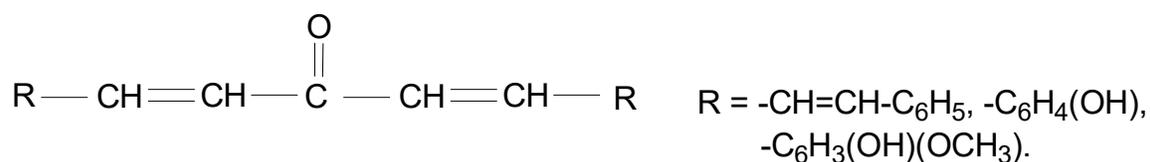
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Acid treatment in the bottom-hole zone of oil-bearing and gas-bearing formations has been used for over 100 years and still remains the main approach for intensifying the production of liquid and gaseous hydrocarbons [1, 2]. Hydrochloric acid treatment of these formations with bottom-hole temperature (t) up to 80°C generally shows no technology-related problems in the inhibitory protection of steel parts of underground equipment of wells and special equipment used in this operation from acid corrosion. At higher temperatures, the vast majority of inhibitors lose efficiency in metal protection from acid corrosion, which makes it impossible to use them in this operation [3]. Development of corrosion inhibitors capable of steel protection in HCl solutions at $t \geq 80^\circ\text{C}$, the so-called high-temperature inhibitors, is performed in two ways: a search for new individual compounds that hinder

metal corrosion under these conditions, as well as the creation of composite inhibitors based on known inhibitors.

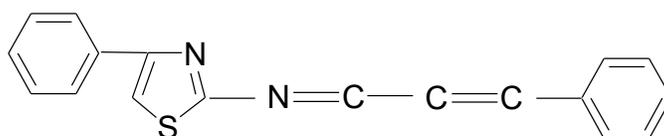
The most popular high-temperature inhibitors of steel corrosion in hydrochloric acid are represented by acetylenic compounds [3, 4]. Of these, propargyl alcohol and hex-1-yn-3-ol are the most prominent ones [5, 6]. The former compound maintains protection up to $t = 110^\circ\text{C}$, while the protective effect of the latter is maintained up to an even higher temperature, *viz.*, 130°C . These compounds undergo resinification in solution at higher temperatures to give insoluble compounds, which impairs the metal protection considerably. Higher protective effects are provided by 6-methylhept-1-yn-3-ol and non-1-yn-3-ol whose protective effects at $t = 95^\circ\text{C}$ are 5 and 15 times higher, respectively, than that of hex-1-yn-3-ol [7].

Quraishi *et al.* [8] used unsaturated ketones for the protection of N80 steel (composition, mass%: C 0.34–0.38; Si 0.20–0.35; Mn 1.45–1.7; P up to 0.02; S up to 0.015; Cr up to 0.15; V 0.11–0.16) in 15% HCl (105°C):



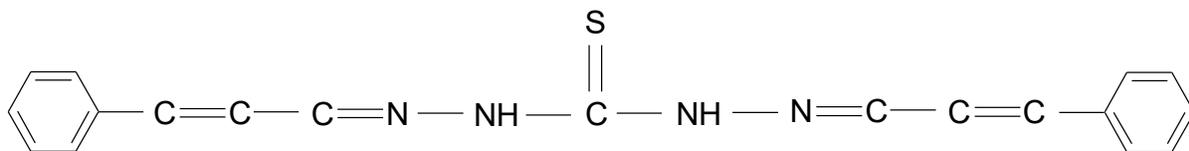
Under these conditions, the highest protective effects are provided by the most strongly unsaturated compound comprising the $-\text{CH} = \text{CH} - \text{C}_6\text{H}_5$ substituent, with $Z = 97.8\%$ at $C_{\text{in}} = 5 \text{ mM}$.

Yet another group of individual inhibitors that hinder steel corrosion in hot hydrochloric acid media consists of azomethines based on cinnamic aldehyde [9]. Using the compound [10]:

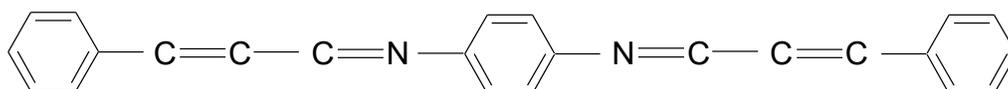


as an example, it has been shown that they can protect mild steel from high-temperature corrosion in HCl. The presence of this inhibitor in 15% HCl (105°C) at $C_{\text{in}} = 1.0\text{--}2.0 \text{ mM}$ ensures that the corrosion rate (k) does not exceed $26 \mu\text{m/h}$, *i.e.*, $Z = 96.8\text{--}98.2\%$. Comparison of the protective effects of these azomethines with an equimolar amount of propargyl alcohol shows that the latter is quite inefficient [$Z(\text{propargyl alcohol}) = 12.2\text{--}23.8\%$], but an increase in its content to as little as 5 mM allows k to be decreased to $4.2 \mu\text{m/h}$ ($Z = 99.7\%$).

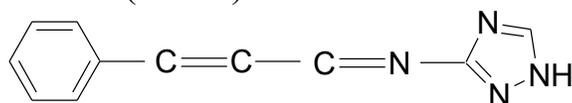
Other conditions being equal, azomethines obtained by condensation of a diamine with two molecules of cinnamic aldehyde are the most efficient corrosion inhibitors. On carbon steel in 15% HCl (110°C), the thiocarbonyl derivative



decreases k to 8.0–16 $\mu\text{m/h}$ at $C_{\text{in}} = 1.5$ mM (depending on the time of contact with the acid solution), *i.e.*, $Z = 99.0\%$. The k of carbon steel decreases with an increase in the duration of the metal contact with inhibited acid from 1 to 6 h [11]. The presence of an azomethine [12]



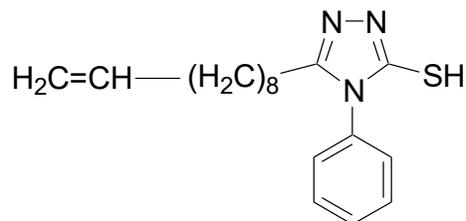
in 15% HCl (105°C) at $C_{\text{in}} = 2.0$ –5.0 mM ensures that the k of N80 steel does not exceed 5.7 $\mu\text{m/h}$, *i.e.*, $Z = 99.67$ –99.75%. The protective effect of this unsaturated azomethine is unstable in time. The k of steel at $C_{\text{in}} = 5$ mM is 3.1 $\mu\text{m/h}$ based on 0.5 h tests, but it is 34 $\mu\text{m/h}$ based on 6 h tests. *N*-Cinnamylidene-1*H*-1,2,4-triazol-3-amine is efficient in the protection of St3 steel in 2 M HCl (100°C).



It slows down the corrosion 278-fold at $C_{\text{in}} = 10$ mM, which corresponds to $k = 3.3$ g/(m²·h) [13].

The CAHMT inhibitor (the composition is not disclosed) [14] deserves attention. It contains an azomethine bond conjugated with a C=C group, as well as a heterocycle incorporating three nitrogen atoms and a sulfide group. The developers of the inhibitor present it as a “green” inhibitor. It decreases the k of N80 steel in 15% HCl (105°C) to 13 $\mu\text{m/h}$ at ($Z = 98.4$ –99.2%) at $C_{\text{in}} \leq 5$ mM, but parallel studies show that addition of an equivalent amount of propargyl alcohol to the solution slows down the corrosion more strongly to achieve the minimum corrosion rate of about 5.1 $\mu\text{m/h}$.

The unsaturated compound 3-(deca-9-ene)-4-phenyl-5-mercapto-1,2,4-triazole [15] should be noted:



It incorporates both a triazole ring, a terminal C=C unsaturated bond, and a thiol group. According to half-hour tests, it provides $Z = 95.5$ –96.2% for mild steel at $C_{\text{in}} = 3.0$ –5.0 mM in 15% HCl (105°C). In these cases, the corrosion rate does not fall below 63 $\mu\text{m/h}$.

Unfortunately, the publications dealing with the above unsaturated ketones, azomethines, and ethylenic inhibitor do not report data on steel protection by these inhibitors in HCl at temperatures considerably higher than 100°C. It is known that a drawback of unsaturated organic corrosion inhibitors, acetylenic compounds in particular, lies in their low thermal and chemical stability, which at certain temperatures results in their resinification in acid solutions and thus in a loss of the protective effect. It may be assumed with high certainty that the compounds considered above will behave in a similar manner. Apart from unsaturated organic compounds, efficient inhibition of steels in HCl solutions at $t \geq 80^\circ\text{C}$ can be provided by thermally stable triazole derivatives. While the mechanism of the inhibitory effect of unsaturated organic compounds is based on the chemisorption of these compounds on steel followed by polymerization resulting in the formation of a protective film than prevents the metal corrosion [3, 4, 9], the effect of triazoles is also based on their chemisorption on a steel surface, but the protective polylayer that is formed above the chemisorbed inhibitor monolayer consists of physically bound inhibitor molecules [16]. Such a protective layer formed by the IFKhAN-92 inhibitor, which is a triazole derivative, considerably hinders the corrosion of low-carbon steel in 2 M HCl at $t \leq 120^\circ\text{C}$ ($C_{\text{in}} = 20 \text{ mM}$) [17, 18]. The temperature maximum of the efficiency of this inhibitor lies at temperatures around 80°C.

In our opinion, attempts to search for individual compounds that would be corrosion inhibitors capable of steel protection in hot HCl solutions show little promise. Though they remain efficient in acid solutions up to a certain temperature (130°C at most), they abruptly lose efficiency and cease to protect the metal. It is more promising to create mixed inhibitors based on these compounds. This makes it possible not only to improve the metal protection, decreasing the corrosion rate, but also expand the temperature range of efficient steel protection.

The protective effect of acetylenic inhibitors can be improved by creating their formulations with nitrogen-containing compounds and inorganic additives of diverse nature. Four-component mixtures of an acetylenic alcohol (hex-1-yn-3-ol or propargyl alcohol), an industrial nitrogen-containing inhibitor (BA-6 or PKU) with SnCl_2 , CrCl_3 and KI make it possible to protect St1 steel in 4 M HCl at temperatures up to 250°C [5, 6]. Keeney and Johnson [19] have patented formulations consisting of an acetylenic alcohol or thioether, a nitrogen-containing compound (amine or pyridine derivative) and CuI, that hinder the corrosion of steels in HCl solutions at $t \leq 230^\circ\text{C}$. Walker [20] described formulations for the protection of N80 steel in HCl solutions at $t \leq 260^\circ\text{C}$ comprising an acetylenic alcohol (5–35%), a quaternary ammonium salt, an aromatic hydrocarbon, and a soluble antimony compound.

Yet another method for improvement of the protective effect of acetylenic compounds is to use them in combination with water-soluble organic compounds (alcohols, aldehydes, ketones). For example, addition of 5 vol.% acetic aldehyde increases 540-fold the protective effect of dodec-1-yn-3-ol on the corrosion of steel in 5 M HCl ($t = 95^\circ\text{C}$) [21].

The authors assume that the effect of these mixtures is based on an increase in the solubility of the acetylenic inhibitor in the corrosive medium by these additives. As a development of this approach, three-component mixtures of acetylenic alcohols, nitrogen-containing inhibitors and aldehydes were created. For example, a mixture of 0.4% dodec-1-yn-3-ol + 0.5% BA-6 inhibitor + 4% acetic aldehyde in 15% HCl ($t = 160^\circ\text{C}$) slows down the corrosion of steel 20 by a factor of 110, so the metal corrosion rate becomes $k = 185 \text{ g}/(\text{m}^2 \cdot \text{h})$. Replacement of saturated acetic aldehyde (4%) by a smaller concentration of unsaturated crotonic aldehyde (1%) nearly does not change the protective effects [7].

A number of composite inhibitors containing cinnamic aldehyde or alkenylphenones as unsaturated organic additives have been created [9]. Cinnamic aldehyde by itself poorly inhibits the corrosion of steels even at $t < 100^\circ\text{C}$ [22], though its protective effect is enhanced by propargyl alcohol [23], *p*-dodecylpyridinium bromide, or an industrial solvent that is a product of the trimethylheptan-1-ol reaction with ethylene oxide [24–26]. The corrosion of J55 steel (composition, mass%: C 0.34–0.39; Si 0.20–0.35; Mn 1.25–1.5; P up to 0.02; S up to 0.015; Cr up to 0.15; Ni up to 0.20; Cu up to 0.20) in 15–28% HCl ($t = 65^\circ\text{C}$) is also poorly hindered by individual alkenylphenones [27] that are considerably inferior in efficiency to oct-1-yn-3-ol. The latter two additives considered above also improve the inhibitory effect of alkenylphenones. Formulations of unsaturated carbonyl compounds with more complex compositions are used at $t > 100^\circ\text{C}$ [28]. A mixture consisting of diverse acetylenic alcohols, phenylvinylketone, KI and HCOOH was recommended for the protection of N80, J55 carbon steels and L80 chromium stainless steel (composition, mass%: C 0.15–0.20; Si up to 1.00; Mn 0.25–1.0; P up to 0.02; S up to 0.010; Cr 12.0–14.0; Ni up to 0.20; Cu up to 0.20) in HCl solutions at $t \leq 150^\circ\text{C}$ [29]. Formulations based on cinnamic aldehyde and a quaternary ammonium salt are used on the same steels at temperatures up to 120°C [26, 29].

Patent [30] presents data on the protection of N80 steel in 15–28% HCl ($t = 150^\circ\text{C}$) containing KI (1–2%) and HCOOH by mixtures of phenylalkenylketones with alkyl- or alkylarylquinolinium salts. Jasinski and Frenier [31] recommend to protect steels containing over 9% Cr in 15% HCl and in its mixture with HF ($t = 120\text{--}250^\circ\text{C}$) by formulations of phenylalkenylketones or substituted cinnamic aldehydes with derivatives of nitrogen-containing heterocycles (alkylpyridinium and alkylquinolinium salts). In order to enhance the protective effect of these mixtures, the effect of compounds soluble in acidic media, namely, Bi(III) and Sb(III) compounds and CuCl, on the above mixtures was studied. Furthermore, the protective effect of mixtures was enhanced by addition of KI or HCOOH.

The mixed inhibitors considered above were created on the basis of unsaturated organic compounds that are liable to polymerization in the acid bulk, which is a considerable drawback of these formulations. More suitable in this respect are mixed inhibitors based on thermally stable compounds. For example, we developed a mixed inhibitor comprising a thermally stable triazole designated as IFKhAN-92 and urotropine,

which protects steel 20 in HCl solutions at $t \leq 160^\circ\text{C}$ [17, 18]. A unique feature of IFKhAN-92 is that it can be used as a basis of formulations capable of hindering the corrosion of various steels in H_2SO_4 solutions at $t \leq 200^\circ\text{C}$ [18, 32–34].

The literature available to us contains almost no information on the high-temperature corrosion of an important group of structural materials, namely, stainless steels, in HCl solutions. Our previous studies on the corrosion behavior of chromium-nickel stainless steels in this medium at $t \leq 100^\circ\text{C}$ [35] allow us to assume that they have low corrosion resistance under these conditions.

In view of the above, it seems expedient to study the corrosion of chromium-nickel stainless steel 08Kh18N10T in HCl solutions in the temperature range from 0 to 160°C and to develop inhibitor formulations for its protection under these conditions. We studied IFKhAN-92 as the basis for the creation of composite inhibitors. Its mixtures with urotropine considerably hinder the corrosion of chromium-nickel steels in HCl solutions at $t \leq 100^\circ\text{C}$ [35] and the corrosion of low-carbon steel in this medium at $t \leq 160^\circ\text{C}$ [17, 18]. It is important to estimate the ability of formulations that we developed for the protection of stainless steels to inhibit the corrosion of low-carbon steels as well.

Experimental procedure

High-temperature corrosion tests ($t = 120\text{--}160^\circ\text{C}$) were carried out in a Huber autoclave (Finland) (the accuracy of temperature control was $\pm 3^\circ\text{C}$). A cylindrical sample (15–50 mm long, depending on the metal corrosion rate, and 18 mm in diameter) of 08Kh18N10T steel (composition, mass%: C 0.08; Cr 17–19; Ni 9–11; Si 0.8; Mn up to 2; S up to 0.02; P up to 0.035; Cu up to 0.3; Ti up to 0.7) was placed into a quartz vessel containing 100 ml of HCl solution. The base duration of the tests was 30, 60, or 120 min. The corrosion tests at $t = 0\text{--}100^\circ\text{C}$ were carried out by a similar technique in temperature-controlled corrosion vessels. The tests at $t = 120\text{--}160^\circ\text{C}$ were carried out in an autoclave using the following technique. A specimen was placed into an acid solution at $t = 100^\circ\text{C}$, heated to a required temperature, kept for 40, 70 or 130 min at that temperature, and cooled to 104°C . In order to take the specimen mass loss during autoclave heating and cooling into account, the tests were duplicated with exposure for 10 min at the corresponding temperatures. The corrosion rates for 30, 60, or 120 min periods were calculated from the difference between the specimen mass loss after 40-, 70-, or 130-minute exposures in the autoclave at the corresponding temperature and the mass loss after a 10-minute exposure.

The same technique was used in the corrosion tests of low-carbon steel 20 (flat specimens, 20 mm \times 20 mm \times 3 mm) in the HCl solution.

The specimens were cleaned on an abrasive disc (ISO 9001, 60 grit) and degreased with acetone prior to each experiment. Due to the low solubility of IFKhAN-92, it was added to HCl solutions as a solution in ethanol. The resulting ethanol concentration in the pickling solution was 0.24 mol/l.

The efficiency of inhibitors was estimated from the inhibition coefficient, $\gamma = k_0/k_{in}$, where k_0 and k_{in} are the corrosion rates in the non-inhibited solution and in the solution with the additive being studied, respectively. In order to estimate the effect of additives on IFKhAN-92 quantitatively, the mutual influence coefficients of the mixture components were calculated [36]:

$$K_m = \frac{\gamma_{mix}}{\prod_{i=1}^m \gamma_i},$$

where γ_{mix} is the corrosion inhibition coefficient for the inhibitor mixture and $\prod_{i=1}^m \gamma_i$ is the product of the corrosion inhibition coefficients for the individual mixture components. At $K_m < 1$, the protective effects of the inhibitor components are mutually reduced; at $K_m = 1$, additive effects are noted; and it is only at $K_m > 1$ that a mutual enhancement of protection by the mixture components is observed.

Experimental results and discussion

08Kh18N10T steel is rather resistant to cold 2 M HCl ($t = 0^\circ\text{C}$): the maximum observed k is $0.68 \text{ g}/(\text{m}^2 \cdot \text{h})$. However, the corrosion of steel systematically accelerates with an increase in t and, according to the data of 0.5 h tests, it reaches $0.10 \text{ kg}/(\text{m}^2 \cdot \text{h})$ at 80°C , $0.32 \text{ kg}/(\text{m}^2 \cdot \text{h})$ at 100°C , and $5.0 \text{ kg}/(\text{m}^2 \cdot \text{h})$ at 160°C (Figure 1).

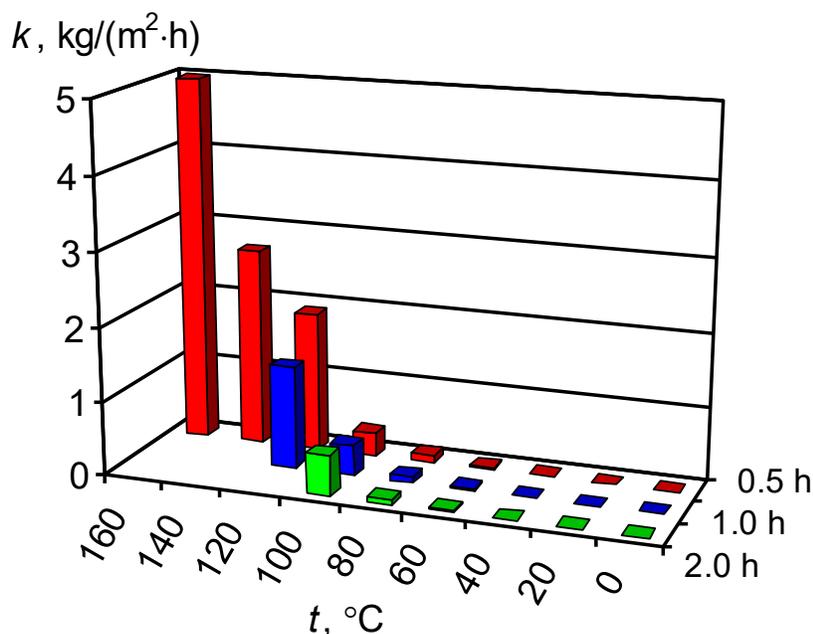


Figure 1. Corrosion rates of 08Kh18N10T steel in 2 M HCl at various temperatures.

The addition of 5 mM IFKhAN-92 considerably hinders the corrosion of stainless steel at $t \leq 120^\circ\text{C}$, where the maximum k value under the conditions of the experiment is $23 \text{ g}/(\text{m}^2 \cdot \text{h})$ (Table 1). At $t \leq 100^\circ\text{C}$, the k value decreases with time in the presence of this additive, but at $t = 120^\circ\text{C}$ the k value increases, which does not allow us to hope that the inhibitor would efficiently hinder corrosion at higher temperatures.

Table 1. Corrosion rates (k , $\text{g}/(\text{m}^2 \cdot \text{h})$) and corrosion inhibition coefficients (γ) of 08Kh18N10T steel in 2 M HCl at various temperatures.

Inhibitor	Test duration					
	0.5 h		1.0 h		2.0 h	
	k	γ	k	γ	k	γ
0–20°C						
5 mM IFKhAN-92	–*	–	–*	–	–*	–
1 mM IFKhAN-92 + 4 mM urotropine	–*	–	–*	–	–*	–
5 mM IFKhAN-92 + 5 mM KI + 20 mM urotropine	–*	–	–*	–	–*	–
40°C						
5 mM IFKhAN-92	0.25	60	0.22	59	0.17	47
1 mM IFKhAN-92 + 4 mM urotropine	–*	–	–*	–	0.027	300
5 mM IFKhAN-92 + 5 mM KI + 20 mM urotropine	–*	–	–*	–	–*	–
60°C						
5 mM IFKhAN-92	1.5	21	1.1	24	0.69	30
1 mM IFKhAN-92 + 4 mM urotropine	0.54	59	0.34	76	0.26	100
5 mM IFKhAN-92 + 5 mM KI + 20 mM urotropine	–*	–	–*	–	–*	–
80°C						
5 mM IFKhAN-92	3.5	29	2.9	30	2.2	33
1 mM IFKhAN-92 + 4 mM urotropine	1.9	53	1.5	58	1.2	60
5 mM IFKhAN-92 + 5 mM KI + 20 mM urotropine	0.14	710	0.16	540	0.13	550

Inhibitor	Test duration					
	0.5 h		1.0 h		2.0 h	
	<i>k</i>	γ	<i>k</i>	γ	<i>k</i>	γ
100°C						
5 mM IFKhAN-92	8.7	37	7.7	53	6.2	89
1 mM IFKhAN-92 + 4 mM urotropine	4.7	68	3.4	120	3.0	180
5 mM IFKhAN-92 + 5 mM KI + 20 mM urotropine	0.90	360	0.77	530	0.60	920
30 mM IFKhAN-92	3.5	91	2.7	150	2.2	250
30 mM KI	2.2	150	2.2	190	2,2	250
30 mM urotropine	53	6.0	60	6.8	61	9.0
5 mM KI + 25 mM urotropine	3.1	100	2.5	160	2.2	250
10 mM IFKhAN-92 + 10 mM KI + 40 mM urotropine	3.2	100	3.1	130	3.1	180
120°C						
5 mM IFKhAN-92	12	160	20	70	23	–
1 mM IFKhAN-92 + 4 mM urotropine	34	56	100	14	97	–
5 mM IFKhAN-92 + 5 mM KI + 20 mM urotropine	6.4	300	4.7	300	4.7	–
10 mM IFKhAN-92 + 10 mM KI + 40 mM urotropine	11	170	12	120	12	–
140°C						
10 mM IFKhAN-92 + 10 mM urotropine	220	12	210	–	160	–
10 mM IFKhAN-92 + 40 mM urotropine	120	23	77	–	63	–
20 mM IFKhAN-92 + 80 mM urotropine	140	19	150	–	110	–
10 mM IFKhAN-92 + 10 mM KI	26	100	55	–	61	–
5 mM IFKhAN-92 + 5 mM KI + 20 mM urotropine	29	93	31	–	33	–
10 mM IFKhAN-92 + 10 mM KI + 40 mM urotropine	23	120	22	–	20	–
160°C						
5 mM IFKhAN-92 + 5 mM KI + 20 mM urotropine	130	38	100	–	84	–
10 mM IFKhAN-92 + 10 mM KI + 40 mM urotropine	93	54	68	–	52	–

* The change in the specimen mass during the corrosion test is below the balance sensitivity (0.1 mg)

The mixture of IFKhAN-92 and urotropine (molar ratio 1:4) that we previously developed [35] for the protection of stainless steels in hydrochloric media efficiently protects the metal at rather low concentrations ($C_{\text{mix}} = 5 \text{ mM}$) in 2 M HCl at $t \leq 100^\circ\text{C}$, where $k \leq 4.7 \text{ g}/(\text{m}^2 \cdot \text{h})$. This mixture is superior to 5 mM of IFKhAN-92 alone. However, a further t increase by 20°C abruptly decreases γ 7.2-fold (in 0.5 h tests). Furthermore, corrosion accelerates with time to reach $100 \text{ g}/(\text{m}^2 \cdot \text{h})$ in the presence of the inhibitor formulation. To improve steel protection in 2 M HCl, we increased the content of this inhibitor mixture (1:4) in the solution to $C = 50 \text{ mM}$. Even at this high C_{in} , steel protection is unsatisfactory at $t = 140^\circ\text{C}$, where, according to 2 h tests, the lowest k value is $63 \text{ g}/(\text{m}^2 \cdot \text{h})$. This fact does not allow us to hope that the mixture would be efficient at higher temperatures. Both a decrease in the urotropine concentration (the formulation containing 10 mM IFKhAN-92 + 10 mM urotropine) and an increase in its content to $C = 100 \text{ mM}$ adversely affect the behavior of the mixture.

Comparison of the protective effect of the 10 mM IFKhAN-92 + 10 mM urotropine formulation with that of a similar formulation containing KI, an additive widely used under high-temperature acid corrosion conditions, instead of urotropine showed that this replacement considerably improved the protection of stainless steel. However, the k of steel increases with time even in the presence of the 10 mM IFKhAN-92 + 10 mM KI mixture. The k value increases 2.3-fold in 2 h tests in comparison with 0.5 h tests.

These studies show that both IFKhAN-92 alone and two-component mixtures on its basis fail to provide efficient steel protection in HCl at $t > 120^\circ\text{C}$. The protection of steel in this medium can be improved by a three-component mixture based on IFKhAN-92. Previously [34], we recommended such a formulation containing IFKhAN-92, KI and urotropine (in 1:1:4 molar ratio) for the protection of stainless steels in H_2SO_4 solutions ($t \leq 200^\circ\text{C}$). Subsequently, we studied this mixture in the HCl solution.

The formulation of 5 mM IFKhAN-92 + 5 mM KI + 20 mM urotropine protects 08Kh18N10T steel in 2 M HCl in a broad temperature range, $0\text{--}160^\circ\text{C}$, while the maximum k value is $130 \text{ g}/(\text{m}^2 \cdot \text{h})$. Stronger steel inhibition can be achieved at $t \geq 140^\circ\text{C}$ by using the 10 mM IFKhAN-92 + 10 mM KI + 40 mM urotropine mixture, while the k value at $t = 160^\circ\text{C}$ is $52 \text{ g}/(\text{m}^2 \cdot \text{h})$ in 2 h tests. Corrosion at $t = 140^\circ\text{C}$ somewhat slows down with time in the presence of this formulation for at least 8 h. The k value is $19 \text{ g}/(\text{m}^2 \cdot \text{h})$ in 4 h corrosion tests and $18 \text{ g}/(\text{m}^2 \cdot \text{h})$ in 8 h tests.

An important feature of the ternary inhibitor mixture is that it can maintain protection in a broad range of C_{HCl} . An increase in C_{HCl} considerably accelerates steel corrosion. According to 0.5 h corrosion tests at $t = 140^\circ\text{C}$, $k = 2.7 \text{ kg}/(\text{m}^2 \cdot \text{h})$ in 2 M HCl, $7.9 \text{ kg}/(\text{m}^2 \cdot \text{h})$ in 4 M HCl, and $10 \text{ kg}/(\text{m}^2 \cdot \text{h})$ in 6 M HCl. The 10 mM IFKhAN-92 + 10 mM KI + 40 mM urotropine mixture gives $k = 36, 39$ and $38 \text{ g}/(\text{m}^2 \cdot \text{h})$ in 4 M HCl and $k = 58, 61$ and $56 \text{ g}/(\text{m}^2 \cdot \text{h})$ in 6 M HCl upon exposure of the samples in the corrosive media for 0.5, 1 and 2 h, respectively. According to 0.5 h tests, the corrosion inhibition factor is 120 in 2 M HCl, 220 in 4 M HCl, and 170 in 6 M HCl.

The formulation in question manifests an antagonism in the action of its components. At $t = 100^\circ\text{C}$, the K_m values are extremely low, 0.0016–0.0044, for the mixture with $C_{\text{in}} = 30$ mM. To a large extent, the observed effect is due to the high efficiency of IFKhAN-92 and especially KI alone in the hindrance of chromium-nickel steel corrosion in HCl solution under these conditions. In contrast, urotropine has poor corrosion inhibition efficiency. An important role of IFKhAN-92 in the protective effect of the ternary mixture is evident from comparison of the efficiency of the formulations containing 5 mM IFKhAN-92 + 5 mM KI + 20 mM urotropine and 5 mM KI + 25 mM urotropine. The absence of IFKhAN-92 in the mixture accelerates corrosion 3.2–3.4 fold.

The ternary mixture of inhibitors (10 mM IFKhAN-92 + 10 mM KI + 40 mM urotropine) is not only efficient in hindering the corrosion of chromium-nickel steel but is also able to protect low-carbon steel 20, which is even less stable in 2 M HCl (Figure 2), at $t \leq 160^\circ\text{C}$, providing $k \leq 160$ g/(m²·h) (Table 2). The corrosion rate of steel does not increase with time for at least 2 h in the presence of the ternary mixture. According to 4 h and 8 h tests, $k = 16$ g/(m²·h). The mixture protects steel 20 in more concentrated HCl solutions, too. Even an increase in C_{HCl} from 2 M to 4 M ($t = 140^\circ\text{C}$) accelerates steel corrosion from 8.1 to 12 kg/(m²·h). At higher $C_{\text{HCl}} = 6$ M, we failed to determine the k of steel 20 in the background solution. Addition of 10 mM IFKhAN-92 + 10 mM KI + 40 mM urotropine hinders the corrosion of steel 20; $k = 42, 82$ and 97 g/(m²·h) in 4 M HCl and $k = 79, 110$ and 120 g/(m²·h) in 6 M HCl upon exposure of the samples in the acid solutions for 0.5, 1 and 2 h, respectively.

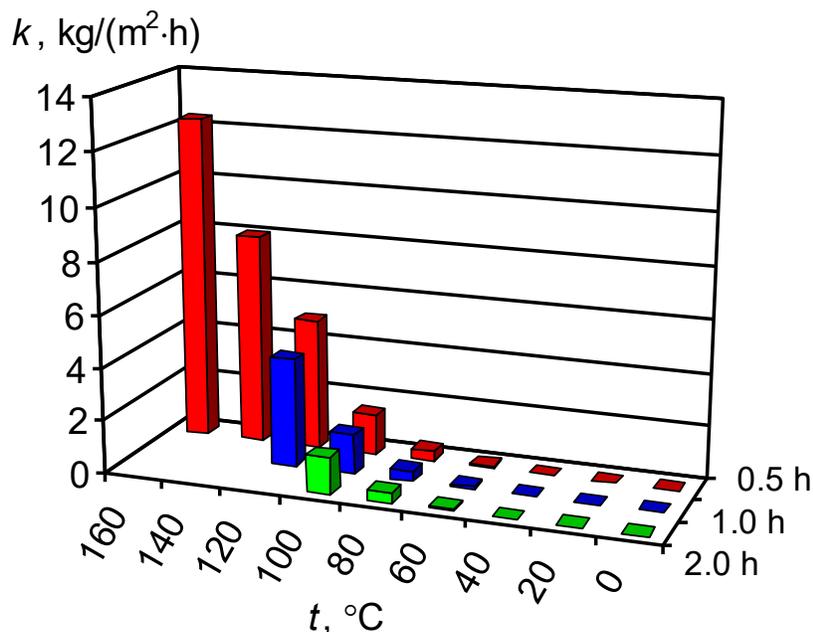


Figure 2. Corrosion rates of steel 20 in 2 M HCl at various temperatures.

Table 2. Corrosion rates (k , g/(m²·h)) and corrosion inhibition coefficients (γ) of steel 20 in 2 M HCl + 10 mM IFKhAN-92 + 10 mM KI + 40 mM urotropine at various temperatures.

Temperature, °C	Test duration					
	0.5 h		1.0 h		2.0 h	
	k	γ	k	γ	k	γ
0	–*	–	–*	–	–*	–
20	–*	–	0.079	110	0.075	75
40	0.26	150	0.22	150	0.21	130
60	1.5	61	1.2	71	0.95	87
80	3.1	130	2.4	170	2.1	180
100	6.3	250	5.6	270	4.8	290
120	7.8	640	7.5	550	7.9	–
140	16	500	16	–	16	–
160	160	78	150	–	140	–

* The change in the specimen mass during the corrosion test is below the balance sensitivity (0.1 mg)

Thus, it has been confirmed that formulations based on IFKhAN-92 can be used for the protection of chromium-nickel steel in HCl solutions under high-temperature corrosion conditions. The three-component formulation of IFKhAN-92, KI and urotropine (1:1:4) that we created reliably protects this steel at $t \leq 160^\circ\text{C}$ in 2–6 M HCl; in some cases, efficiency is maintained for at least 8 h. It is important to note the versatility of this inhibitor mixture, since it allows the corrosion of 08Kh18N10T steel and steel 20 to be hindered considerably even in H₂SO₄ solutions at $t \leq 180^\circ\text{C}$ [34].

The high protective effect of the three-component inhibitor formulation that we developed, both in HCl and H₂SO₄ solutions, is to a large extent determined by the uniqueness of the action mechanism of IFKhAN-92 [37], which is critically important in metal protection under high-temperature corrosion conditions. IFKhAN-92 is strongly adsorbed on the corroding metal surface to form a polymolecular protective layer thereon, which favors high protection. An important role belongs to the thermal stability of the inhibitor that prevents its resinification in the acid bulk. However, this appears to be insufficient for the protection of chromium-nickel steels, whose surfaces are non-uniform in composition and structure, under drastic conditions of high-temperature acid corrosion where the triazole alone does not provide satisfactory metal protection at $t > 120^\circ\text{C}$. Under these conditions, a mixed inhibitor additionally containing KI and urotropine has to be used to achieve high protection of stainless steel. Most likely, addition of iodide ion accelerates the slow chemical adsorption of IFKhAN-92 on steel surface. This is extremely important under conditions of high-temperature acid corrosion where the corroding metal bulk is dissolved with a considerable rate, preventing the formation of a continuous

protective inhibitor layer. We observed a similar effect for rhodanide anion that accelerated the adsorption of IFKhAN-92 on low carbon steel in H_3PO_4 solutions [38].

On the contrary, we assume a somewhat different mechanism of enhancing the protective effect of the inhibitive mixture by urotropine. It is known that this inhibitor undergoes hydrolysis in solutions of mineral acids, including hydrochloric acid, to generate formaldehyde into the corrosive medium [39–41]:



The hydrolysis will occur rather quickly in hot acid solutions. The formaldehyde accumulating in solution is quite reactive and prone to polymerization. The polymerization processes are accelerated by protons present in the solution [42]. It can be assumed that formaldehyde present in an acid solution is adsorbed on the metal above the previously formed adsorbed layers of IFKhAN-92 to form a polymeric protective layer. This combined protection allows the metal surface to be reliably blocked from the acid, thus preventing corrosion. The formation of polymeric protective layers on steel surfaces by various aldehydes was noted previously in the corrosion in HCl solutions [22, 43, 44] and in hydrogen sulfide containing media in the case of formaldehyde [45].

A significant advantage of the three-component formulation based on IFKhAN-92 that we developed, in comparison with the inhibitor mixtures considered above, is the fact that it contains no compounds of metals nobler than iron (Sn, Sb, Bi, Cu). Such components might form phases of the nobler metal on the surface due to contact exchange with iron. This would result in galvanic couples that can locally accelerate steel corrosion both in the acid solution and during further operation of the equipment.

Conclusions

1. Chromium-nickel steel has low corrosion resistance in HCl solutions, especially under high-temperature corrosion conditions ($t \geq 80^\circ\text{C}$). The IFKhAN-92 inhibitor and its formulation with urotropine (1:4) allows this steel to be protected in 2 M HCl at temperatures up to 120°C , inclusive.
2. The three-component mixture of IFKhAN-92, KI and urotropine (1:1:4) is more efficient in this respect. It hinders the corrosion of chromium-nickel steel at temperatures up to 160°C , inclusive, and at HCl concentrations from 2 M to 6 M. This mixture can maintain its protective effect in the acid solution for at least 8 h.
3. The formulation of IFKhAN-92, KI and urotropine (1:1:4) also reliably protects low-carbon steel in HCl solutions in a broad range of concentrations (2–6 M) at temperatures up to 160°C , inclusive.

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