Inhibitory protection of low-carbon steel in solutions of hydrochloric, sulfuric, and phosphoric acids¹

Ya.G. Avdeev,¹[®] A.V. Panova,¹ V.V. Al'brandt,² K.L. Anfilov,³ A.G. Berezhnaya⁴[®] and T.A. Vagramyan²[®]

 ¹A.N. Frumkin Institute of Physical Chemistry and Electrochemistry, Russian Academy of Sciences, Leninsky pr. 31, 119071 Moscow, Russian Federation
²Mendeleev University of Chemical Technology, Russia, Moscow, Miusskaya sq., 9, 125047 Moscow, Russian Federation
³Bauman Moscow State Technical University (Kaluga Branch), Bazhenov str. 2, 248000 Kaluga, Russian Federation
⁴South Federal University, Bol'shaya Sadovaya str. 105/42, 344006 Rostov-on-Don, Russian Federation
*E-mail: avdeevavdeev@mail.ru

Abstract

The possibility of inhibitor protection of 08PS steel in 2 M HCl, 2 M H₂SO₄ and 2 M H₃PO₄ in the temperature range $t = 25-95^{\circ}$ C was studied. Commercial forms of industrially manufactured corrosion inhibitors of Invol-2 m. A, Invol-2 m. B, GREENCOR m. V, VNPP-2-V, VNPP-2-MV, and Catamin AB brands were studied as corrosion inhibitors at their content of 10 g/L in the corrosive environment. Significant inhibition of 08PS steel corrosion in 2 M HCl at $t \le 60^{\circ}$ C is provided by the additives Catamin AB, Invol-2 m. B, and VNPP-2-V, while at $t \le 95^{\circ}$ C, additives of GREENCOR m. V, Invol-2 m. A, and VNPP-2-MV inhibitors are efficient. In solutions of H₂SO₄ and H₃PO₄, the presence of these inhibitors alone often fails to provide a significant reduction in the corrosion rate of steel. To improve their efficiency in slowing down steel corrosion in H₂SO₄ and H₃PO₄ solutions, it is recommended to use the inhibitors studied in combination with 2 g/L NaCl or 0.2 g/L NH₄CNS. In H₂SO₄ solution at t $\le 95^{\circ}$ C, the GREENCOR m. V + NaCl, VNPP-2-V + NaCl, or GREENCOR m. V + NH₄CNS combinations should be used to protect steel, while in H₃PO₄ solution, combinations of Catamin AB, Invol-2 m. B, GREENCOR m. V, and VNPP-2-W with NH₄CNS are recommended.

Received: February 6, 2024. Published: March 4, 2024

doi: 10.17675/2305-6894-2024-13-1-25

Keywords: acid corrosion, low carbon steel, hydrochloric acid, sulfuric acid, phosphoric acid, corrosion inhibitors.

¹ This study was carried out as part of R&D (2022–2024): "Chemical resistance of materials, protection of metals and other materials from corrosion and oxidation" (EGISU registration number 122011300078-1, inventory number FFZS-2022-0013).

Introduction

Solutions of mineral acids are common process fluids used in the oil and gas production industry, metallurgy, and public utilities [1-10]. Such process fluids are used to stimulate the production of raw hydrocarbons from oil- and gas-bearing formations and to remove scale, corrosion products, and mineral deposits from steel items and from the internal surfaces of metal equipment. Corrosive acid solutions come into contact with steel items and equipment. These process operations require special measures for metal protection that significantly reduce the corrosive effect of acid solutions on steel. The optimal way to protect steels in acid solutions is to use corrosion inhibitors represented by organic compounds or mixtures on their basis [11-15].

Numerous compounds that can slow down the corrosion of steels in acid solutions have been reported [16]. The reference literature [17–20] published in the second half of the 20th century summarized data on the most important commercial inhibitors that were produced at that time. However, information about the properties of corrosion inhibitors produced on an industrial scale in the recent decades is scant. Table 1 presents data on the study of such products [21–33]. The data presented clearly show that the protective effect of industrially produced corrosion inhibitors has been mainly studied for such widespread structural materials as low-carbon steels. The studies are focused on HCl solutions, while only a few studies have been carried out in H₂SO₄ solutions. To our best knowledge, no information on the protection of steels by commercial inhibitors in phosphoric acid solutions is available. Most often, the protective properties of such corrosion inhibitors are studied at room temperature (*t*), although this does not always coincide with the conditions of their industrial use that can be much more severe. It may be assumed that the lack of results on the effect of commercial inhibitors on the corrosion of steels in H₃PO₄ solutions and in hot acid solutions indicates that such additives have only low protective effects under these conditions.

No.	Inhibitors	Corrosive environments	Protected metals	Research methods	Ref.
1	VNPP-2-V, KI- 1 and IKU	22.3% HCl + 0.06% HF; 26.28% HCl + 5.98% HF; 37.32% H ₂ SiF ₆ + 1.7% SiO ₂ (room temperature). Additionally, 0.01% Fe(III) was added.	St3 steel	Corrosion rates were determined gravimetrically (from weight losses of specimens) or electrochemically (linear polarization method).	[21]

Table 1. Commercial inhibitors of steel corrosion in acid solutions.

No.	Inhibitors	Corrosive environments	Protected metals	Research methods	Ref.
2	VNPP-2-V, Soling m. 3, Napor-KB and V-2	20% HCl (abgasic acid) (20–95°C)	Mild steel	Corrosion rates were determined gravimetrically (from weight losses of specimens)	[22]
3	Katasol 28-3, VNPP-2-V, Iproden K-1 m. B, Optima-061, IKU-1, Dodicor 2275, Azol 5010, Scimol WS-2111, Sonkor 9510K, KI-1MR, Napor KB and Soling m. L	12% HCl (90°C)	St35 steel, gray cast iron, Ni Resist alloy, powder steel ZhGr1D15	_//_	[23]
4	Akvatek-50 standart and Akvatek-50 premium	23% HCl (room temperature).	Mild steel	_//_	[24]
5	AI-600, AI-250, NRUST CM 150, Sinol IKK and Sinol IK- 001	20% HCl (20°C)	Mild steel	_//_	[25]
6	Inhibitors of the "FLEK" series, KhPK-002 (120) B and ScimolWS 2111	0.01-2 M HCl (room <i>t</i>); 0.1 M HCl and 0.1 M HCl + $100 \text{ mg/L H}_2\text{S}$ (20-60°C); 1 M HCl and $1 \text{ M H}_2\text{SO}_4$ (room temperature).	St3 steel	Corrosion rates were determined gravimetrically (from weight losses of specimens), Volt-Ampere measurements, Electrochemical Impedance Spectroscopy	[26–28]
7	Inhibitors of the "SONKOR" series	0.1 and 1 M HCl; 0.1 and 1 M H ₂ SO ₄ (room temperature).	St3 steel	Corrosion rates were determined gravimetrically (from weight losses of specimens), Volt-Ampere measurements	[29]

No.	Inhibitors	Corrosive environments	Protected metals	Research methods	Ref.
8	Inhibitors of the "SOLING" series	1 M HCl and 1 M H ₂ SO ₄ ; 5 and 15% HCl and 5% H ₂ SO ₄ (room temperature).	St3 steel	_//_	[30, 31]
9	VNPP	27–33% HCl; 14% HCl + 5% HF (20-80°C).	Low carbon steel	_//_	[32]
10	Katasol 28-3, SONKOR 9510 (K), NAPON- KB, VNPP-2-V, Invol-2 m. A, Invol-2 m. B, Chemiks-IK, SNPKh-6438, NJ-100, IKU- 118, INKOR-ES	15% HCl, 15% sulfamic acid, 15% sulfamic acid + 0.5 or 3% citric acid (20°C).	St3 steel	Corrosion rates were determined gravimetrically (from weight losses of specimens)	[33]

In this regard, it seems important to systematically explore the protective effect of some commercially available inhibitors on steel corrosion in solutions of hydrochloric, sulfuric, and phosphoric acids in a wide temperature range ($t=25-95^{\circ}$ C). We studied the following industrially produced corrosion inhibitors: Invol-2 m. A, Invol-2 m. B, GREENCOR m. V, VNPP-2-V, and VNPP-2-MV (manufactured by INKORMET LLC). In parallel, the commercial product Catamin AB often used as a component of inhibitor compositions was also studied. Our goal was also to consider whether the protective properties of commercial forms of corrosion inhibitors in the acid solutions could be enhanced by adding other additives.

Experimental

The corrosion rate of 08PS low-carbon steel (composition, in wt.%: C 0.08; Mn 0.5; Si 0.11; P 0.035; S 0.04; Cr 0.1; Ni 0.25; Cu 0.25; As 0.08) in 2 M HCl, 2 M H₂SO₄, and 2 M H₃PO₄ was determined by measuring the weight loss of tape samples measuring 50 mm×20 mm× 0.5 mm (no less than 3 samples per point) using 50 mL of an acid solution per sample. The duration of the experiments was 2 hours. Before each experiment, the samples were cleaned using an abrasive wheel (ISO 9001, grit 60) and degreased with acetone.

The content of commercial corrosion inhibitors in acid solutions was 10 g/L, *i.e.*, the optimal value recommended by the manufacturer.

The efficiency of inhibitors was estimated by the corrosion inhibition coefficient $\gamma = k_0/k_{in}$, where k_0 and k_{in} are the corrosion rates in the background solution and in the solution with the additive under study, respectively.

Results and Discussion

Hydrochloric acid

In 2 M HCl, the corrosion rate of 08PS steel (*k*) increases with increasing temperature, *t*. An increase in *t* from 25 to 95°C accelerates corrosion by a factor of 260 (Table 2). The acid solution heated to 95°C is the most corrosive to steel. The maximum metal corrosion rate under the experimental conditions is $1 \text{ kg/(m^2 \cdot h)}$.

Table 2. Corrosion parameters of 08PS steel in 2 M HCl containing 10 g/L of corrosion inhibitors. The steel corrosion rate *k* is reported in $g/(m^2 \cdot h)$.

Inhibitor	Ŀν		Te	mperatur	re, °C		Free k I/mol
minoitor	κ, γ	25	40	60	80	95	L'act, KJ/IIII
_	k	3.9	9.6	70	460	1000	76
Cotomin AP	k	0.52	0.78	2.8	15	24	54
	γ	7.5	12	25	31	42	54
Invol-2 m. A	k	0.55	0.71	0.91	1.8	1.9	17
	γ	7.1	14	77	260	530	17
Invol 2 m D	k	0.65	0.69	2.6	14	36	55
Шуог-2 Ш. Б	γ	6.0	14	27	33	28	55
CDEENCOD m V	k	0.35	0.48	0.63	1.1	1.6	10
GREENCOR III. V	γ	11	20	110	420	630	19
VNDD 2 V	k	0.52	0.61	1.6	5.2	34	
VINPP-2-V	γ	7.5	16	44	88	29	—
VNDD 2 MV	k	0.43	0.45	1.1	2.7	3.7	21
V INFF-2-IVI V	γ	9.1	11	64	170	270	51

All the additives studied slow down steel corrosion at $t \le 60^{\circ}$ C significantly. The least efficient corrosion inhibitor under the experimental conditions, Catamin AB, provides $k=0.52-2.8 \text{ g/(m^2 \cdot h)}$. In the background environment, the value of k is 3.9–70 g/(m² \cdot h). The best result is provided by the GREENCOR m. V inhibitor; in its presence, $k=0.35-0.63 \text{ g/(m^2 \cdot h)}$ for steel.

A further increase in *t* leads to a significant loss of the protective effect of the additives Catamin AB, Invol-2 m. B, and VNPP-2-V on steel corrosion. The GREENCOR m. V, Invol-2 m. A, and VNPP-2-MV inhibitors provide efficient protection of steel in the range of $t=25-95^{\circ}$ C. For these inhibitors, the maximum observed values are k=1.6, 1.9, and 3.7 g/(m²·h), respectively, which is an interesting result. Steel corrosion slows down by a factor of 630, 530, and 270.

For all the additives studied, the steel corrosion inhibition coefficients (γ) systematically increase with increasing *t*. The maximum values of γ , at least up to 95°C, are not reached, which formally allows them to be classified as high-temperature inhibitors [34]. Moreover, in the presence of Catamin AB, Invol-2 m. B, and VNPP-2-V at *t*=95°C, the corrosion rates of steel are high, which does not provide grounds to expect efficient metal protection at higher temperatures. In contrast, in the case of the GREENCOR m. V, Invol-2 m. A, and VNPP-2-MV inhibitors, the corrosion rates of steel in HCl solution at *t*=95°C are low, indicating that they can be considered high temperature inhibitors.

The corrosion of 08PS steel in 2 M HCl, both in the background environment and in the presence of the additives under study, exhibits a linear dependence of lg k on T^{-1} (Figure 1), which makes it possible to determine the effective activation energy (E_{act}) of these processes. The plot is not linear in the case of the VNPP-2-V additive only, which indirectly implies that the corrosion mechanism changes significantly in the studied temperature range.



Figure 1. Dependence of $\lg k$ on T^{-1} for corrosion of 08PS steel in 2 M HCl containing 10 g/L of corrosion inhibitors.

In the background acid solution, steel corrosion is characterized by a high value of $E_{act}=76$ kJ/mol. All the additives studied reduce the E_{act} value, which, in our opinion, results from an increase in the fraction of the diffusion component in the process due to corrosion inhibitors. It is important to note that the GREENCOR m. V and Invol-2 m A inhibitors affect the corrosion process so strongly that the effective activation energy is below 20 kJ/mol. This E_{act} value is typical of corrosion processes with diffusion control. Most

likely, these corrosion inhibitors form a protective layer on the steel surface, which creates diffusion limitations for the supply of protons to the metal surface and/or removal of corrosion products.

All the corrosion inhibitors we have studied effectively protect steel in the HCl solution at $t \le 60^{\circ}$ C. Inhibitors of the GREENCOR m. V, Invol-2 m. A, and VNPP-2-MV brands provide protection to steel at $t \le 95^{\circ}$ C. Under the most severe experimental conditions $(t=95^{\circ}$ C), their protective effects increase in the following series: VNPP-2-MV < Invol-2 m. A < GREENCOR m. V. It should be noted that in the case of Catamin AB, Invol-m. B, and, especially, VNPP-2-V, temporary overheating of the HCl solution to $t=80^{\circ}$ C would not lead to significant corrosion losses of the metal.

Sulfuric acid

At 2 M H₂SO₄, the corrosion rate of 08PS steel increases 100 times upon *t* increase from 25 to 95°C (Table 3). The acid heated to 95°C, where *k* is $1.2 \text{ kg/(m^2 \cdot h)}$, is the most corrosive towards steel.

Inhibitor	kw	Temperature, °C						
minortor	κ, γ	25	40	60	80	95		
_	k	12	18	72	320	1200		
Cotomin AP	k	0.70	1.5	1.6	4.9	20		
Cataniin AB	γ	17	12	45	65	60		
	k	1.6	2.7	23	_	_		
Invol-2 m. A	γ	7.5	6.7	3.1	_	_		
Invol 2 m D	k	0.65	0.78	1.7	5.5	22		
Шуог-2 Ш. Б	γ	18	23	41	58	55		
CDEENCOD m V	k	0.64	0.92	27	_	_		
GREENCOR III. V	γ	19	20	2.7	_	_		
	k	0.61	1.1	13	_	_		
VINPP-2-V	γ	20	16	5.5	_	_		
	k	0.79	8.4	11	_	_		
VNPP-2-MV	γ	15	2.1	6.5	_	_		

Table 3. Corrosion parameters of 08PS steel in 2 M H₂SO₄ containing 10 g/L of corrosion inhibitors. The steel corrosion rate, *k*, is given in $g/(m^2 \cdot h)$.

It should be noted that all the studied corrosion inhibitors in individual form are generally less efficient in protecting 08PS steel in H_2SO_4 solutions than in the hydrochloric

acid environment. The products studied, with the exception of VNPP-2-MV, are efficient in inhibiting steel corrosion in 2 M H₂SO₄ at $t \le 40^{\circ}$ C. Addition of Catamin AB and Invol-2 m. B to the acid solution will provide satisfactory protection of steel at $t \le 80^{\circ}$ C.

The results obtained show that none of the studied industrial products in individual form can provide effective protection of 08PS steel in an H_2SO_4 solution in the selected temperature range. A simple and inexpensive way to enhance the protective effect of corrosion inhibitors is to create mixed formulations on their basis that slow down metal corrosion more efficiently than the original components [15]. It is therefore reasonable to investigate the possibility of modifying the corrosion inhibitors in question with some readily available compounds for expanding their efficient temperature range in the H_2SO_4 solution. We used NaCl and ammonium thiocyanate as such compounds. NaCl is well known as an additive that enhances the protection of steels from corrosion by organic inhibitors in H_2SO_4 solutions [13, 35–43]. The rhodanide anion is often studied as a component of mixtures with organic compounds for steels protection in H_2SO_4 solutions [42–45]. It enhances the effect of corrosion inhibitors not only in H_2SO_4 but also in H_3PO_4 solutions [46, 47].

Addition of 2 g/L NaCl to inhibited H₂SO₄ solutions improves the protection of 08PS steel (Table 4). The most interesting results in 2 M H₂SO₄ were observed for the GREENCOR m. V+NaCl and VNPP-2-V+NaCl formulations. At the highest temperature, they slow down corrosion by a factor of 220 and 210, respectively. In the temperature range studied, the values of *k* are \leq 5.5 and 5.8 g/(m²·h). The other formulations, except for Invol-2 m. A + NaCl, are efficient at *t* \leq 80°C. For all mixtures containing NaCl, the steel corrosion inhibition coefficient increases with increasing *t*. Formally, they can be classified as high-temperature inhibitors, but only the GREENCOR m. V + NaCl and VNPP-2-V + NaCl formulations can actually be considered as such.

Inhibitor	24		Tem	peratur	E _{oct} kI/mol		
	r	25	40	60	80	95	L'act, NJ/III
Cotomin A.B.	k	0.50	0.80	1.8	4.0	12	40
Cataliin AD	γ	24	23	40	80	100	40
Invial 2 m A	k	0.29	0.72	2.8	9.2	12	51
Invol-2 m. A	γ	41	25	26	35	100	51
Invial 2 m D	k	0.40	0.72	1.5	4.7	11	42
шуог-2 ш. Б	γ	30	25	48	68	110	43
GREENCOR	k	0.41	0.46	1.2	3.7	5.5	27
m. V	γ	29	39	65	86	220	57

Table 4. Corrosion parameters of 08PS steel in 2 M H₂SO₄ + 2 g/L NaCl containing 10 g/L of corrosion inhibitors. The steel corrosion rate, k, is given in g/(m²·h).

Inhibitor	~		Tem	peratur	East k I/mol		
minortor	Ŷ	25	40	60	80	95	L'act, KJ/III01
VNIDD 2 V	k	0.45	0.48	2.2	3.7	5.8	27
VINPP-2-V	γ	27	38	33	86	210	37
	k	0.33	0.44	1.9	3.6	11	λ¢
VINTY-2-IVIV	γ	36	41	38	89	110	40

The data on the corrosion of 08PS steel in 2 M H₂SO₄ in the presence of the studied agents combined with NaCl are satisfactorily represented by a straight line in the lg $k-T^{-1}$ coordinates (Figure 2, Table 4). In the background acid solution, steel corrosion is characterized by a high value of $E_{act} = 61$ kJ/mol. The presence of all studied inhibitor formulations reduces the E_{act} value, which, in our opinion, results from an increase in the fraction of the diffusion component in the process due to the action of the mixed corrosion inhibitor.



Figure 2. Dependence of $\lg k$ on T^{-1} for corrosion of 08PS steel in 2 M H₂SO₄ containing 10 g/L corrosion inhibitors + 2 g/L NaCl.

Similarly to NaCl, the addition of 0.2 g/L NH₄CNS to inhibited H₂SO₄ solutions enhances the protection of 08PS steel (Table 5). A significant result in 2 M H₂SO₄ is exhibited by the formulation GREENCOR m. V + NH₄CNS, which even at $t=95^{\circ}$ C slows down the corrosion 340-fold. Mixtures of Catamin AB, Invol-2 m. A, Invol-2 m. B, and VNPP-2-MV with NH₄CNS are efficient at $t \le 80^{\circ}$ C. The VNPP-2-V + NH₄CNS mixture protects steel satisfactorily in solution with temperatures up to 60°C.

Inhibitor	kv		Ter	nperatu	East kI/mol		
ministron	к, ү	25	40	60	80	95	
Cotomin AD	k	0.53	0.62	0.77	4.1	7.9	26
Cataliiii Ab	γ	23	29	94	78	150	30
Invol 2 m A	k	0.40	0.49	0.57	2.3	13	
IIIvoi-2 III. A	γ	30	37	130	140	92	—
Invol 2 m P	k	0.33	0.60	0.70	2.7	6.5	27
111v01-2 111. B	γ	36	30	100	120	180	57
CREENCOR m V	k	0.40	0.44	0.59	0.7	3.5	28
OKEENCOK III. V	γ	30	41	120	190	340	28
VNDD 2 V	k	0.27	0.30	1.7	22	170	
VINFF-2-V	γ	44	60	42	15	7.1	—
WNDD 2 MV	k	0.30	0.36	0.50	2.5	19	
V INFF-2-IVI V	γ	40	50	140	130	63	—

Table 5. Corrosion parameters of 08PS steel in 2 M H₂SO₄ + 0.2 g/L NH₄CNS containing 10 g/L of corrosion inhibitors. The steel corrosion rate, k, is given in g/(m²·h).

The calculated values of E_{act} for corrosion of 08PS steel in 2 M H₂SO₄ containing mixtures of Catamin AB, Invol-2 m. A, Invol-2 m. B, and GREENCOR m. V with NH₄CNS show that these mixed inhibitors, like the formulations with NaCl, reduce this parameter in comparison with the background medium (Figure 3, Table 5).



Figure 3. Dependence of $\lg k$ on T^{-1} for corrosion of 08PS steel in 2 M H₂SO₄ containing 10 g/L corrosion inhibitors + 0.2 g/L NH₄CNS.

In conclusion, it should be noted that in the selected temperature range, in individual form, all the corrosion inhibitors studied are not sufficiently efficient in slowing down the corrosion of steel in H_2SO_4 solutions. The protection of steel against corrosion in this environment can be enhanced if they are used as mixtures with NaCl or NH₄CNS. The formulations promising for the protection of low-carbon steel include GREENCOR m. V + NaCl, VNPP-2-V + NaCl, and especially GREENCOR m. V + NH₄CNS.

Phosphoric acid

In 2 M H₃PO₄, the corrosion rate of 08PS steel increases by a factor of 39 with an increase in *t* from 25 to 95°C (Table 6). The maximum *k* value of steel in the solution with t = 95°C is 340 g/(m²·h), which is significantly smaller than in 2 M H₂SO₄ and 2 M HCl. In individual form, all the inhibitor additives that we tested protect steel poorly. It is not expedient to use these additives in individual form in H₃PO₄ solutions. Their protective effect is somewhat enhanced when combined with the addition of 2 g/L NaCl, but only the Invol-2 m. B + NaCl combination provides satisfactory protection of steel at $t \le 80$ °C (Table 7).

Inhibitor	k.v	Temperature, °C						
	<i>n</i> , ₁ -	25	40	60	80	95		
_	k	8.7	14	57	280	340		
Cotomin A P	k	1.6	3.2	18	_	_		
Cataliin AB	γ	5.4	4.4	3.2	_	_		
Invel 2 m A	k	2.4	6.0	39	_	_		
Invoi-2 m. A	γ	3.6	2.3	1.5	_	_		
Invel 2 m D	k	1.2	1.8	14	_	_		
Invoi-2 m. B	γ	7.3	7.8	4.1	_	_		
CDEENCOD V	k	7.1	24	67	_	_		
GREENCOR III. V	γ	1.2	0.58	0.85	_	_		
VNDD 2 V	k	1.6	8.5	58	_	_		
VINPP-2-V	γ	5.4	1.6	0.98	_	_		
VNIDD 2 MM	k	1.3	3.7	17	_	_		
VINPP-2-IVIV	γ	6.7	3.8	3.4	_	_		

Table 6. Corrosion parameters of 08PS steel in 2 M H₃PO₄ containing 10 g/L of corrosion inhibitors. The steel corrosion rate, *k*, is given in $g/(m^2 \cdot h)$.

Inhibitor	kv	Temperature, °C						
minoitor	κ, γ -	25	40	60	80	95		
Cotomin AD	k	1.4	2.0	7.7	_	_		
Catamin AD	γ	6.2	7.0	7.4	—	_		
Invol 2 m A	k	1.7	2.3	15	_	_		
Invol-2 m. A	γ	5.1	6.1	3.8	—	_		
Invol 2 m D	k	0.8	1.5	4.2	4.9	11		
111v01-2 111. D	γ	11	9.3	14	57	31		
CDEENCOD m V	k	2.8	4.6	32	—	—		
GREENCOR III. V	γ	3.1	3.0	1.8	—	—		
WNDD 2 V	k	1.6	3.0	26	_	—		
VINFF-2-V	γ	5.4	4.7	2.2	—	—		
WNIDD 2 MM	k	1.3	2.0	9.0	_	—		
V INF F-2-IVI V	γ	6.7	7.0	6.3	_	_		

Table 7. Corrosion parameters of 08PS steel in 2 M H₃PO₄ + 2 g/L NaCl containing 10 g/L of corrosion inhibitor. The steel corrosion rate, k, is given in g/(m²·h).

Mixtures of the studied inhibitors with NH₄CNS exhibit a significantly different result in the protection of 08PS steel in 2 M H₃PO₄. All the inhibitors studied, except for VNPP-2-V and Invol-2 m. A, provide efficient metal protection at $t \le 95^{\circ}$ C (Table 8). Inhibitors of the VNPP-2-V and Invol-2 m. A brands provide satisfactory protection at $t \le 80^{\circ}$ C. The most efficient additives, Catamin AB and VNPP-2-MV, slow down corrosion at $t = 95^{\circ}$ C by a factor of 310 and 340, while the corrosion rate of steel is 1.1 and 1.0 g/(m²·h), which is an important result.

Table 8. Corro	sion parameters	of 08PS stee	l in 2 M	$H_3PO_4 + 0.2 \text{ g/L}$	NH ₄ CNS	containing	10 g/L of
corrosion inhib	itors. The steel c	orrosion rate, <i>k</i>	, is given	in g/(m ² ·h).			

Inhibitor	k, y		Те	East k.I/mol			
		25	40	60	80	95	
Catomin AD	k	0.30	0.60	0.70	0.79	1.1	14
Catamin AB	γ	26	23	81	350	310	14
Invel 2 m A	k	1.4	2.1	2.3	2.7	10	20
IIIvoi-2 III. A	γ	6.2	6.7	25	100	34	20
Invol-2 m. B	k	0.39	0.68	0.73	0.98	1.3	14

Inhibitor	k, y	Temperature, °C					Frat k I/mol
		25	40	60	80	95	
	γ	22	21	78	290	260	
GREENCOR m. V	k	0.60	0.88	0.91	1.3	3.4	10
	γ	15	16	63	220	100	19
VNPP-2-V	k	1.1	2.0	0.64	4.3	82	
	γ	7.1	7.0	89	65	4.1	_
VNPP-2-MV	k	0.55	0.62	0.65	0.78	1.0	7
	γ	16	23	88	360	340	/

In a background H_3PO_4 solution, steel corrosion is characterized by the value $E_{act} = 53 \text{ kJ/mol}$. All the additives studied, except for VNPP-2-V and NH₄CNS, significantly reduce E_{act} (Figure 4, Table 8). In the presence of these mixed corrosion inhibitors, the effective activation energy is below 20 kJ/mol, indicating diffusion-controlled corrosion. It may be assumed that such mixtures of corrosion inhibitors form a protective layer on the steel surface, thus creating diffusion limitations for the supply of protons to the metal surface and/or removal of corrosion products.



Figure 4. Dependence of lg k on T^{-1} for corrosion of 08PS steel in 2 M H₃PO₄ containing 10 g/L corrosion inhibitor + 0.2 g/L NH₄CNS.

If the corrosion inhibitors studied in this work are used to protect low-carbon steel in H₃PO₄ solutions, they should be used in mixtures with NH₄CNS. The mixtures of Catamin AB, Invol-2 m. B, GREENCOR m. V, and VNPP-2-MV with NH₄CNS significantly inhibit metal corrosion at $t \le 95^{\circ}$ C.

Conclusions

- 1. Efficient protection of 08PS steel in 2 M HCl at $t \le 60^{\circ}$ C is provided by addition of 10 g/L of Catamin AB, Invol-2 m. B, or VNPP-2-V. If it is possible that 2 M HCl can be heated to $t = 95^{\circ}$ C, then 10 g/L of GREENCOR m. V, Invol-2 m. A, or VNPP-2-MV inhibitors should be used to protect steel significantly. In the presence of the most efficient corrosion inhibitor under these experimental conditions, GREENCOR m. V, the corrosion rate of steel is $0.35-1.6 \text{ g/(m^2 \cdot h)}$, which means that steel corrosion is hindered by a factor of 11-630.
- 2. To significantly reduce the corrosion rate of 08PS steel in 2 M H₂SO₄ or 2 M H₃PO₄, it is recommended to use not individual corrosion inhibitors but their combinations with NaCl or NH₄CNS, which allows the metal to be protected at $t \le 95^{\circ}$ C. In the H₂SO₄ solution, these requirements are met by the GREENCOR m. V + NaCl, VNPP-2-V + NaCl, and especially GREENCOR m. V + NH₄CNS mixtures. For the latter mixture, in the selected *t* range $k_{\text{max}} = 3.5 \text{ g/(m^2 \cdot h)}$. In 2 M H₃PO₄, low-carbon steel can be protected by mixtures of Catamin AB, Invol-2 m. B, GREENCOR m. V, or VNPP-2-MV with NH₄CNS. The best mixtures, *i.e.*, Catamin AB + NH₄CNS and VNPP-2-MV + NH₄CNS, provide $k_{\text{max}} =$ 1.1 g/(m²·h).

References

- C. Verma, M.A. Quraishi and E.E. Ebenso, Corrosive electrolytes, *Int. J. Corros. Scale Inhib.*, 2020, 9, no. 4, 1261–1276. doi: <u>10.17675/2305-6894-2020-9-4-5</u>
- P. Rae and G. Di Lullo, Matrix Acid Stimulation A Review of the State-Of-The-Art, in: *Society of Petroleum Engineers*, SPE European Formation Damage Conference, 13– 14 May, 2003, The Hague, Netherlands, SPE-82260-MS. doi: <u>10.2118/82260-MS</u>
- L.V. Hong and H.B. Mahmud, A Comparative Study of Different Acids used for Sandstone Acid Stimulation: A Literature Review, *In IOP Conf. Series: Mater. Sci. and Eng.*, 2017, 217, 012018. doi: 10.1088/1757-899X/217/1/012018
- 4. B. Guo, X. Liu and X. Tan, Chapter 13. Acidizing, *In Pet. Prod. Eng.*, Gulf Professional Publishing, 2nd Edition, 2017, 367–387. doi: <u>10.1016/B978-0-12-809374-0.00013-1</u>
- 5. A. Agrawal and K.K. Sahu, An overview of the recovery of acid from spent acidic solutions from steel and electroplating industries, *J. Hazar. Mater.*, 2009, **171**, 61–75. doi: 10.1016/j.jhazmat.2009.06.099
- F. Rögener, Yu.A. Lednova, M.Yu. Andrianova and A.V. Lednov, Sustainable stainless steel A review on acid regeneration systems for application in continuous pickling lines, *Vestnik Magnitogorskogo gosudarstvennogo tekhnicheskogo universiteta im. G.I. Nosova (Vestnik of Nosov Magnitogorsk State Technical University)*, 2019, **17**, no. 2, 38–48 (in Russian). doi: 10.18503/1995-2732-2019-17-2-38-48
- 7. B.J. Goode, R.D. Jones and J.N.H. Howells, Ultrasonic pickling of steel strip, *Ultrasonics*, 1998, **36**, no. 1–5, 79–88. doi: <u>10.1016/S0041-624X(97)00078-4</u>

- J. Ding, B. Tang, M. Li, X. Feng, F. Fu, L. Bin, S. Huang, W. Su, D. Li and L. Zheng, Difference in the characteristics of the rust layers on carbon steel and their corrosion behavior in an acidic medium: Limiting factors for cleaner pickling, *J. Clean. Prod.*, 2017, 142, no. 4, 2166–2176. doi: <u>10.1016/j.jclepro.2016.11.066</u>
- Ya.G. Avdeev and Yu.I. Kuznetsov, Organic Inhibitors of Metal Corrosion in Acid Solutions. I. Mechanism of Protective Action. *Russ. J. Phys. Chem. A*, 2023, 97, 413– 427. doi: 10.1134/S0036024423030056
- Ya.G. Avdeev and Yu.I. Kuznetsov, Iron oxide and oxyhydroxide phases formed on steel surfaces and their dissolution in acidic media. Review, *Int. J. Corros. Scale Inhib.*, 2023, **12**, no. 2, 366–409. doi: <u>10.17675/2305-6894-2023-12-2-1</u>
- 11. G. Schmitt, Application of Inhibitors for Acid Media, *Br. Corros. J.*, 1984, **19**, no. 4, 165–176. doi: <u>10.1179/000705984798273100</u>
- 12. M. Finšgar and J. Jackson, Application of corrosion inhibitors for steels in acidic media for the oil and gas industry: A review, *Corros. Sci.*, 2014, **86**, 17–41. doi: 10.1016/j.corsci.2014.04.044
- S.A. Umoren and M.M. Solomon, Effect of halide ions on the corrosion inhibition efficiency of different organic species A review, *J. Ind. Eng. Chem.*, 2015, 21, 81–100. doi: <u>10.1016/j.jiec.2014.09.033</u>
- M. Goyal, S. Kumar, I. Bahadur, C. Verma and E.E. Ebenso, Organic corrosion inhibitors for industrial cleaning of ferrous and non-ferrous metals in acidic solutions: A review, J. Mol. Liq., 2018, 256, 565–573. doi: <u>10.1016/j.molliq.2018.02.045</u>
- Ya.G. Avdeev and Yu.I. Kuznetsov, Organic Inhibitors of Metal Corrosion in Acid Solutions. II. Ways of Increasing the Protective Action and Main Groups of Compounds, *Russ. J. Phys. Chem. A*, 2023, 97, 541–549. doi: <u>10.1134/S0036024423040052</u>
- 16. Ya.G. Avdeev and Yu.I. Kuznetsov, Acid corrosion of metals and its inhibition. A critical review of the current problem state, *Int. J. Corros. Scale Inhib.*, 2022, **11**, no. 1, 111–141. doi: 10.17675/2305-6894-2022-11-1-6
- 17. A.I. Altsibeeva and S.Z. Levin, *Ingibitory korrozii metallov. Spravochnik (Metal Corrosion Inhibitors. Handbook)*, Khimiya, Leningrad, 1968, 264 pp. (in Russian).
- 18. L.I. Antropov, E.M. Makushin and V.F. Panasenko, *Metal corrosion inhibitors*, Kiev, Technika, 1981, 57–81 (in Russian).
- 19. S.M. Reshetnikov, *Ingibitory kislotnoi korrozii metallov (Metal Corrosion Inhibitors in Acids)*, Khimiya, Leningrad, 1986, 144 pp. (in Russian).
- 20. E.S. Ivanov, *Metal Corrosion Inhibitors in Acidic media*, Metallurgiya, Moscow, 1986, 175 pp. (in Russian).
- 21. A.B. Shein and A.V. Denisova, Choice of effective corrosion inhibitors for acid treatment of wells, *Prot. Met.*, 2006, **42**, 34–37. doi: <u>10.1134/S0033173206010061</u>
- 22. A. Shipilov, Acid stimulation: measure seven times..., *Zhurnal «Neftegazovaya vertikal'» (Journal "Oil and Gas Vertical")*, 2008, no. 12, 50–51 (in Russian).

- 23. V.N. Glushchenko, A.V. Denisova and S.B. Yakimov, Determination of the corrosion rate of metal materials in acidic compositions and the effectiveness of the protective action of acid corrosion inhibitors, *Inzhenernaya praktika (Engineering practice)*, 2011, Special issue no. 1, 91–93 (in Russian).
- 24. S.V. Baranov, Inhibitor protection of oilfield equipment, *Inzhenernaya praktika* (*Engineering practice*), 2011, Special issue no. 1, 79–81 (in Russian).
- 25. S.V. Malayko and S.V. Chapurkin, Modern methods of combating metal corrosion when carrying out hydrochloric-acid and clay-acid treatments, *Korroziya «Territoriya «NEFTEGAZ»» (Corrosion "Territory "NEFTEGAZ"")*, 2013, September, 22–26 (in Russian).
- 26. M.D. Plotnikova, Kh.Kh. Borzaev, D.S. Kopitsyn, A.S. Viktorov and A.B. Shein, Study of a number of industrial compositions as inhibitors of acid and hydrogen sulfide corrosion, *Bashkirskiy khimicheskiy zhurnal (Bashkir Chemical Journal)*, 2012, **19**, no. 4, 182–187 (in Russian).
- 27. M.D. Plotnikova and A.B. Shein, Corrosion inhibition of low-carbon steel in acidic and neutral environments, *Izvestiya Vysshikh Uchebnykh Zavedenii. Khimiya i Khimicheskaya Tekhnologiya*, 2013, **56**, no. 3, 35–40 (in Russian).
- 28. M.D. Plotnikova and A.B. Shein, Protection of steel from hydrogen sulfide corrosion with «FLEK» inhibitors at elevated temperatures, *Izvestiya Vysshikh Uchebnykh Zavedenii. Khimiya i Khimicheskaya Tekhnologiya*, 2014, **57**, no. 1, 91–96 (in Russian).
- 29. M.I. Zyryanova, A.V. Melnikova, A.P. Figilyantov and A.B. Shein, Study of the effectiveness of industrial compositions SONCOR as corrosion inhibitors of low-carbon steel in acidic hydrogen sulfide-containing environments, *Bulletin of Perm University*. *Chemistry*, 2014, **15** no. 3, 37–48 (in Russian).
- I.A. Menshikov and A.B. Shein, Protection against corrosion of low carbon steel in acid environments with SOLING series inhibitors, *Izvestiya Vysshikh Uchebnykh Zavedenii*. *Khimiya i Khimicheskaya Tekhnologiya*, 2016, **59**, no. 2, 70–73 (in Russian). doi: <u>10.6060/tcct.20165902.5265</u>
- A.S. Kalinina, I.S. Polkovnikov and A.B. Shein, Investigation of some compositions of the "SOLING" series as corrosion inhibitors for low-carbon steel in acidic media, *Bulletin of Perm University. Chemistry*, 2021, **11**, no. 4, 254–262 (in Russian). doi: 10.17072/2223-1838-2021-4-254-262
- A.G. Berezhnaya, V.V. Chernyavina and O.E. Kryuchkova, On modification problem of industrial inhibitor VNPP for protection of low-carbon steel in concentrated hydrochloric acid media, *Korroz.: Mater., Zashch. (Corrosion: Materials, Protection)*, 2019, no. 3, 23–27 (in Russian). doi: <u>10.31044/1813-7016-2019-0-3-23-27</u>
- 33. M.A. Silin, L.A. Magadova, L.F. Davletshina, M.D. Pakhomov, Yu.M. Timerbulatova and E.A. Samsonenko, Research of Current Corrosion Inhibitors Action in Acid Systems, *Theory and Practice of Corrosion Protection*, 2016, **82**, no. 4, 22–30 (in Russian).

- 34. Ya.G. Avdeev and Yu.I. Kuznetsov, Inhibitory protection of steels from high temperature corrosion in acid solutions. A review. Part 2., *Int. J. Corros. Scale Inhib.*, 2020, **9**, no. 3, 867–902. doi: 10.17675/2305-6894-2020-9-3-5
- E.E Oguzie, C. Unaegbu, C.N Ogukwe, B.N Okolue and A.I Onuchukwu, Inhibition of mild steel corrosion in sulphuric acid using indigo dye and synergistic halide additives, *Mater. Chem. Phys.*, 2004, 84, no. 2–3, 363–368. doi: 10.1016/j.matchemphys.2003.11.027
- 36. L. Tang, X. Li, G. Mu, L. Li and G. Liu, Synergistic effect between 4-(2-pyridylazo) resorcin and chloride ion on the corrosion of cold rolled steel in 0.5 M sulfuric acid, *Appl. Surf. Sci.*, 2006, 252, no. 18, 6394–6401. doi: <u>10.1016/j.apsusc.2006.05.008</u>
- 37. L. Tang, X. Li, L. Li, G. Mu and G. Liu, The effect of 1-(2-pyridylazo)-2-naphthol on the corrosion of cold rolled steel in acid media. Part 2: Inhibitive action in 0.5 M sulfuric acid, *Mater. Chem. Phys.*, 2006, **97**, no. 2–3, 301–307. doi: <u>10.1016/j.matchemphys.2005.08.014</u>
- X. Li, L. Tang, L. Li, G. Mu and G. Liu, Synergistic inhibition between ophenanthroline and chloride ion for steel corrosion in sulphuric acid, *Corros. Sci.*, 2006, 48, no. 2, 308–321. doi: <u>10.1016/j.corsci.2004.11.029</u>
- L.G. Qiu, Y. Wu, Y.M. Wang and X. Jiang, Synergistic effect between cationic gemini surfactant and chloride ion for the corrosion inhibition of steel in sulphuric acid, *Corros. Sci.*, 2008, **50**, no. 2, 576–582. doi: <u>10.1016/j.corsci.2007.07.010</u>
- 40. A. Khamis, M.M. Saleh and M.I. Awad, Synergistic inhibitor effect of cetylpyridinium chloride and other halides on the corrosion of mild steel in 0.5 M H₂SO₄, *Corros. Sci.*, 2013, **66**, 343–349. doi: <u>10.1016/j.corsci.2012.09.040</u>
- 41. A.El Guerraf, A. Titi, K. Cherrak, N. Mechbal, M.El Azzouzi, R. Touzani, B. Hammouti and H. Lgaz, The Synergistic Effect of Chloride Ion and 1,5-Diaminonaphthalene on the Corrosion Inhibition of Mild Steel in 0.5 M Sulfuric Acid: Experimental and Theoretical Insights., *Surf. Interfaces*, 2018, **13**, 168–177. doi: <u>10.1016/j.surfin.2018.09.004</u>
- 42. V.P. Grigor'ev and V.V. Boginskaya, Acid corrosion of iron in the presence of mixtures of anionic additives and compounds of the reaction series of *o*-hydroxyazomethine derivatives with nucleophilic substituents, *Prot. Met.*, 2006, **42**, 583–587. doi: 10.1134/S0033173206060105
- 43. V.P. Grigor'ev and V.V. Boginskaya, Effect of some compounds on the sensitivity of the inhibitive properties of *o*-hydroxyazomethine derivatives to variation in the polarity of their electrophilic substituents, *Prot. Met.*, **42**, 2006, 479–484. doi: <u>10.1134/S0033173206050067</u>
- 44. Ya.G. Avdeev, E.N. Yurasova, K.L. Anfilov and T.A. Vagramyan, Protection of lowcarbon steel in solutions of mineral acids by nitrogen-containing pharmaceutical agents of triphenylmethane series, *Int. J. Corros. Scale Inhib.*, 2018, **7**, no. 1, 87–101. doi: <u>10.17675/2305-6894-2018-7-1-8</u>

- 45. Ya.G. Avdeev, D.S. Kuznetsov, M.V. Tyurina and M.A. Chekulaev, Protection of nickel-chromium steel in sulfuric acid solution by a substituted triazole, *Int. J. Corros. Scale Inhib.*, 2015, **4**, no. 2, 146–161. doi: <u>10.17675/2305-6894-2015-4-1-146-161</u>
- 46. Ya.G. Avdeev, M.V. Tyurina and Yu.I. Kuznetsov, Protection of low-carbon steel in phosphoric acid solutions by mixtures of a substituted triazole with sulfur-containing compounds, *Int. J. Corros. Scale Inhib.*, 2014, **3**, no. 4, 246–253. doi: <u>10.17675/2305-6894-2014-3-4-246-253</u>
- 47. Ya.G. Avdeev, O.A. Kireeva, Yu.I. Kuznetsov and I.G. Gorichev, Effect of the anionic composition of acidic solutions containing Fe(III) on the protection of low-carbon steel by a triazole inhibitor, *Int. J. Corros. Scale Inhib.*, 2016, 5, no. 4, 333–346. doi: 10.17675/2305-6894-2016-5-4-4

*** * ***