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Despite intensive investigations of hydrogen sulfide corrosion made both in our country and abroad, until now there has not been a common point of view relative to the stimulating influence of hydrogen sulfide on corrosion and hydrogen embrittlement. In the opinion of many scientists, in acid corrosion of metal it is caused by the catalysis of electrode processes. They assume, for example, that in acid media containing hydrogen sulfide there are adsorbed on the surface of the corroding metal hydrosulfide ions occurring in the dissociation of hydrogen sulfide molecules [1] or undissociated hydrogen sulfide molecules [2] which form with the metal the complex compounds  $(\text{FeHS}^-)_{\text{ads}}$  or  $(\text{FeH}_2\text{S})_{\text{ads}}$ , catalyzing anodic solution similarly to hydroxyl ions. In ionization of these intermediate complexes there is regeneration of hydrogen sulfide in the solution favoring the corrosion process. Acceleration of the cathodic reaction is explained by the negative jump in potential in the dense portion of the double layer, the decrease in hydrogen overvoltage, and easing of its discharge on the electrode surface. In addition, hydrogen sulfide, being a catalytic poison, retards molization of the discharged hydrogen ions, which leads to an increase in their concentration on the surface of the metal and promotes its hydrogen absorption. However, in [3, 4] the mechanism of the stimulating influence of hydrogen sulfide in hydrogen absorption is perceived to be in the fact that adsorption of  $\text{HS}^-$  weakens the bonds between the surface atoms of the metal and eases penetration of hydrogen into the metal.

It should be noted that not one of the proposed approaches is able to explain all of the experimentally accumulated material. Additional investigations are necessary for this. The influence of hydrogen sulfide on sulfide embrittlement of steel was judged from the quantity of hydrogen ( $\text{cm}^3/100 \text{ g}$ ) absorbed by the steel determined by the vacuum extraction method and from the change in the original ductility of the steel revealed in bending. In addition, corrosion and electrochemical investigations were made. The tests were made on U8A and St.3 steels. The media were a 0.5% NaCl solution acidified with acetic acid to a pH of 3.6 and a 3% NaCl solution. The solutions were saturated with hydrogen sulfide to a concentration of 1500 mg/liter. All of the experiments under laboratory conditions were made at 20°C.

The investigation of the kinetics of electrode processes showed that hydrogen sulfide is a catalyst of both electrochemical reactions: anodic solution of metal and cathodic reduction of hydrogen (Fig. 1). Hydrogen sulfide accelerates both the cathodic and the anodic reactions, shifting the steady potential of the system about 80 mV in the negative direction. This is an indication of the greater change in the kinetics of the anodic process than in the cathodic. The self-solution current of the steel increases by more than an order of magnitude in the presence of hydrogen sulfide, which is graphically confirmed by the results of corrosion tests (Table 1).

The relationship of the ductility of U8A steel to the quantity of absorbed hydrogen does not have a straight-line character. Even a small concentration of hydrogen causes a strong change in the ductile properties of steel (Fig. 2).

As is known, one of the factors influencing hydrogen absorption is the acidity of the medium. We have investigated hydrogen absorption of steel in buffered solutions containing 0.5% NaCl with a constant hydrogen sulfide concentration. It was established that with an increase in solution alkalinity the volume of hydrogen absorbed by steel drops and correspondingly the ductility of the metal increases (Fig. 3). In acid media the steel completely loses its ductile properties; with a change to weakly acid or neutral media the ductility is gradually restored to 60-80%, and only in strongly alkaline media (pH = 12) is the ductility maintained at the original level.

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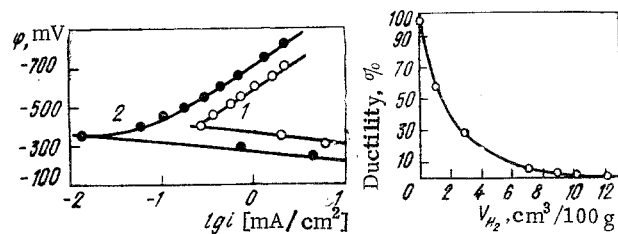


Fig. 1

Fig. 2

Fig. 1 Cathodic and anodic potentiostatic curves recorded on a rotating disk electrode (St.3) in 0.5% NaCl + CH<sub>3</sub>COOH (250 mg/liter) deaerated with argon (curve 1) and in the same solution saturated with hydrogen sulfide to 1500 mg/liter (curve 2).

Fig. 2. The relationship of the ductility of U8A steel to the quantity of hydrogen absorbed in 0.5% NaCl + CH<sub>3</sub>COOH (250 mg/liter) + H<sub>2</sub>S (1500 mg/liter).

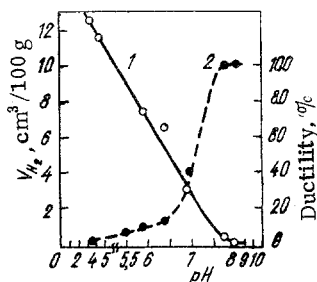


Fig. 3. The influence of solution pH on hydrogen absorption (curve 1) and ductility (curve 2) of U8A steel in a solution of 5% NaCl + H<sub>2</sub>S (1500 mg/liter).

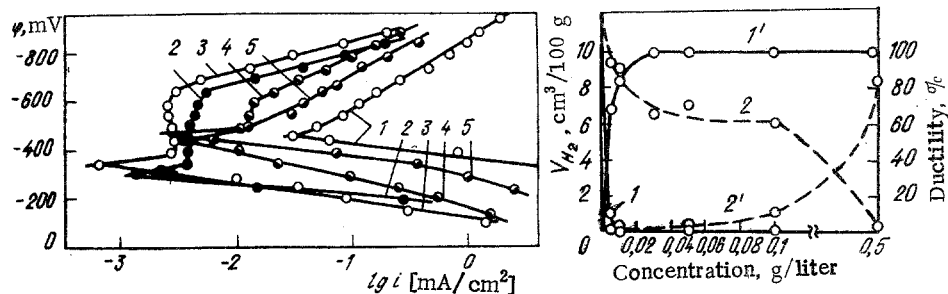


Fig. 4

Fig. 5

Fig. 4. Cathodic and anodic potentiostatic curves recorded in 0.5% NaCl + CH<sub>3</sub>COOH (250 mg/liter) + H<sub>2</sub>S (1500 mg/liter): 1) without inhibitor; 2) in the presence of diheptylamine; 3) diocetylamine; 4) dinonylamine; 5) didecylamine (500 mg/liter).

Fig. 5. The influence of inhibitors on hydrogen absorption (curves 1, 1') and ductility (curves 2, 2') of steel in 0.5% NaCl + CH<sub>3</sub>COOH (250 mg/liter) + H<sub>2</sub>S (1500 mg/liter): 1, 1') IFKhANGAZ-1; 2, 2') VISKO-904.

The decrease in the degree of hydrogen absorption in alkaline media is related to the different mechanism of the cathodic process in acid and alkaline media [5]. In an alkaline

TABLE 1. Influence of Hydrogen Sulfide on the Corrosion Rate of St.3 Steel in a 3% NaCl Solution

CH <sub>2</sub> S, mg/liter	Corrosion rate g/m <sup>2</sup> ·h	Test conditions
—	0,060	Solution previously deaerated with argon for 2 h.
45	0,194	
100	0,250	
360	0,320	
500	0,370	Test time 5 h.
1500	0,600	

TABLE 2. Relationship of the Protective Capacity of Amines (10 mg/liter) to the Number of Carbon Atoms in the Alkyl Groups [the solution: 0.5% NaCl + CH<sub>3</sub>COOH (250 mg/liter) + H<sub>2</sub>S (1500 mg/liter), pH = 3.6, t = 20°C]

Compound	Structural formula	Amount of hydrogen, cm <sup>3</sup> /100 g	Ductility, %	Protective effect, %
—	—	12,5	1	—
Diethylamine	(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> NH	11,3	1	15
Dibutylamine	(C <sub>4</sub> H <sub>9</sub> ) <sub>2</sub> NH	9,8	1	22
Diheptylamine	(C <sub>7</sub> H <sub>15</sub> ) <sub>2</sub> NH	1,8	40	66
Dioctylamine	(C <sub>8</sub> H <sub>17</sub> ) <sub>2</sub> NH	0,11	100	85
Dinonylamine	(C <sub>9</sub> H <sub>19</sub> ) <sub>2</sub> NH	2,1	40	65
Didecylamine	(C <sub>10</sub> H <sub>21</sub> ) <sub>2</sub> NH	12,0	1	5

TABLE 3. The Influence of Various Functional Groups on the Protective Effect of an Amine in 0.5% NaCl + CH<sub>3</sub>COOH (250 mg/liter) + H<sub>2</sub>S (1500 mg/liter) at t = 20°C

Heteroalkylated amine	Structural formula	Ductility with amine concn. of, mg / liter	
		100	500
Triethylamine	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N	1	17,4
1-Diethylaminoethanol	(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> NCH <sub>2</sub> CH <sub>2</sub> OH	11	84
Diethylaminoepoxypropane	(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> NCH <sub>2</sub> CHCH <sub>2</sub> O	28	44
Diethyl ester of diethylaminoethanephosphonic acid	(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> NCH <sub>2</sub> CH <sub>2</sub> PO(OC <sub>2</sub> H <sub>5</sub> ) <sub>2</sub>	5	44
Diethylamino-3-butanone	(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> NCH <sub>2</sub> CH <sub>2</sub> CCH <sub>3</sub>    O	56	98
1-Diethylamino-3-butanone hydrazone	(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> NCH <sub>2</sub> CH <sub>2</sub> CCH <sub>3</sub>    NNH <sub>2</sub>	72	87
Ethyl ester of diethylamino-propionic acid	(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> NCH <sub>2</sub> CH <sub>2</sub> COOC <sub>2</sub> H <sub>5</sub>	56	42

medium the major portion of the adsorbed hydrogen atoms on the surface of the metal occur as a result of reduction of water molecules and, as is assumed, in an energy respect differs from the hydrogen atoms discharging from H<sub>3</sub>O<sup>+</sup> ions in acid electrolyte solutions. It is assumed that in alkaline media the adsorbed hydrogen atoms possess increased energy and easily recombine into molecules, thereby retarding penetration of hydrogen into the metal. In addition, the less intense hydrogen absorption in alkaline media may also be explained [4] by competing adsorption between the hydrogen sulfide molecules and hydroxyl ions. With pH > 7 the latter start to displace hydrogen sulfide ions and retard penetration of hydrogen into the metal, i.e., to have an inhibiting action.

One of the methods of reducing corrosion and hydrogen embrittlement of steels in a hydrogen sulfide medium is the use of inhibitors [6]. Investigation of the degree of hydrogen absorption and also of the corrosion and electrochemical behavior of various nitrogen-containing organic compounds as inhibitors of hydrogen sulfide corrosion and hydrogen embrittlement (aliphatic, alicyclic, and heterocyclic amines and their heteroalkylated derivatives)

TABLE 4. The Results of Experimental Production Testing of IFKhANGAZ-1 Inhibitor in a Gas Sulfur Removal Unit in a 20% Monoethanolamine Solution

Point of location of samples	Conditions		Without inhibitor		With inhibitor (200 mg/liter)	
	p, Pa	t, °C	corrosion rate, mm/yr	ductility, %	corrosion rate, mm/yr	ductility, %
Bottom of "gas" absorber	5·10 <sup>6</sup>	30	0,384	28,5	0,011	100
Desorber	3,5·10 <sup>4</sup>	108—112	0,111	87,6	0,040	100
At the outlet of saturated solution heat exchanger	—	90	0,041	100	0,016	100
Acid-gas line	1·10 <sup>5</sup>	85	0,219	73,6	0,056	100

TABLE 5. The Protective Effect Provided by IFKhANGAZ-1 Inhibitor in the Hydrogen Sulfide Corrosion of Compressors

Without inhib.			With inhibitor			Protective effect, %
condi- tions		corrosion rate, mm/yr	medium		corrosion rate, mm/yr	
p, Pa	t, °C		p, Pa	t, °C		
7 · 10 <sup>5</sup>	20	0,9	7 · 10 <sup>5</sup>	40	0,07	92
1,6 · 10 <sup>6</sup>	20	3—5	1,6 · 10 <sup>6</sup>	30	0,03	90—95

TABLE 6. The Results of Production Tests of Steel under a Stress of 0.7σ<sub>y</sub>

Properties of the steel	Original samples	Without inhibitor	With IFKhANGAZ-1 inhibitor (200 mg/liter)		
			C-1	C-2	C-3
Tensile strength, MPa	450	408	459	449	430
Elongation, %	22,0	14,1	21,8	21,8	20,0
Reduction, %	64,0	39,0	66,4	64,0	64,0

Explanation: C-1 is the first stage of compression, p = (2.0-2.4)·10<sup>5</sup> Pa, t = 85-90°C; C-2 is the second stage, p = (6.3-7.0)·10<sup>5</sup> Pa, t = 84-90°C; C-3 is the third stage, p = (1.6-1.8)·10<sup>6</sup> Pa, t = 70-85°C.

showed that of the amines the most effective are aliphatic secondary amines and the least effective, the heterocyclic amines of the triazole series. The addition of these inhibitors (up to 500 mg/liter) maintained the ductility of steel at 35-39% of the original value.

Studying the mechanism of action of hydrogen sulfide corrosion inhibitors it is of interest to establish the interrelationship between the structural and protective properties of secondary amines. For this purpose a series of amines having a different number of carbon atoms in the alkyl agroup in their composition were selected (Table 2).

As may be seen, the amines containing alkyl groups with a chain length of eight carbon atoms most effectively prevent hydrogen absorption and corrosion. An increase in the length of the alkyl radicals above this value weakens the protective action of amines, which, apparently, may be explained by the reduction in solubility of such compounds and also by their poor adsorbability on the surface of steel as a result of screening of the reaction center of the molecule by the alkyl substituent.

This data is confirmed by the results of electrochemical investigations (Fig. 4). Of all of the studied amines, appreciable retarding of corrosion processes is provided by octylamine, which increases the overvoltage of the liberation of hydrogen by more than 150 mV at the same time reducing the self-solution current by about two orders of magnitude.

In view of the fact that hydrogen sulfide corrosion inhibitors must not only provide a high protective effect but also possess a number of technological and physicochemical properties (not influence the production, refining, and transportation of petroleum and gas, not coke and resinify at increased temperatures, not cause frothing of operating solutions of absorbents in drying and sulfur removal, etc.), amines may not always be used. In connection

with this, certain functional groups must be added to the composition to impart the necessary properties to them (Table 3).

Purposeful synthesis and broad investigations have made it possible to obtain a new class of effective hydrogen sulfide corrosion inhibitors, the IFKhANGAZ's, which are outstanding in their good technological and protective properties. Even an insignificant concentration of one of them, IFKhANGAZ-1 (30-50 mg/liter), prevents hydrogen absorption by a metal and restores its ductile properties, while in the presence of VISO904 (USA) even with 500 mg/liter the ductility of the steel remains at only about 80% (Fig. 5). This inhibitor has successfully passed experimental production tests in the Mubarek Gas-Processing Plant in Central Asia (Table 4).

A method of protecting compressors compressing petroleum casing head gas containing up to 2% hydrogen sulfide from corrosion cracking with the inhibiting composition has been developed. Without inhibitor protection the use of compressor station equipment was practically impossible (Table 5). The inhibiting composition also aids in maintaining the mechanical properties of steel, which prevents corrosion cracking of equipment (Table 6).

Therefore, the inhibiting composition based on IFKhANGAZ-1 provides a high protective effect (~95%). In steel not protected by the inhibitor there is a strong drop in the mechanical properties, especially elongation and reduction, but in the presence of the inhibitor they remain at the original level.

The investigation of the physicochemical properties of IFKhANGAZ-1 inhibitor showed that the inhibitor is quite heat resistant (up to 250°C), possesses low viscosity (8-10 St), a low solidification point (-75°C), and good solubility in hydrocarbons, and forms a stable emulsion with water. In addition, IFKhANGAZ-1 has high antifrothing and antifoaming qualities.

All of this provides a basis for recommending the hydrogen sulfide corrosion and hydrogen absorption inhibitor developed for protection of existing petroleum and gas industry equipment. At present IFKhANGAZ-1 is used in a number of facilities, in particular in a gas-cleaning plant in Central Asia and in the Pokrovsk Gas Compressor Station, Buzuluk.

#### LITERATURE CITED

1. Z. A. Iofa and Fang Long Kam, "The mechanism of the accelerating action of hydrogen sulfide on the reaction of discharge of hydrogen ions on iron," *Zashch. Met.*, No. 1, 17-21 (1974).
2. L. I. Antropov and V. F. Panasenko, "The mechanism of the inhibiting action of organic substances under conditions of hydrogen sulfide corrosion of metals," in: *The Results of Science and Technology, "Corrosion and Protection from Corrosion," Series [in Russian], No. 4, Vses. Inst. Nauch. Tekh. Inf., Moscow (1975), pp. 46-112.*
3. M. Smyalovski, "The influence of hydrogen on the properties of iron and its alloys," *Zashch. Met.*, No. 3, 267-291 (1967).
4. T. Zakroczymski, Z. Szklarska-Smialowska, and M. Smialowski, "The influence of promoters on the penetration of electrolytic hydrogen into steel," *Werkstoffe und Korrosion*, 27, No. 9, 625-630 (1976).
5. S. M. Beloglazov, *Hydrogen Absorption by Steel in Electrochemical Processes [in Russian]*, Izd. Leningrad. Gos. Univ., Leningrad (1975).
6. I. L. Rozenfel'd, *Corrosion Inhibitors [in Russian]*, Khimiya, Moscow (1977).