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Corrosion inhibitors for steel oilfield equipment[1]

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Abstract. The rate of corrosion and protection of steel are determined as a test environment using the model which produces water with the addition of inhibitors or corrosion inhibitors ($CaCl_2 \cdot 6H_2O$, $MgCl_2 \cdot 6H_2O$, NaCl, $CaSO_4 \cdot 2H_2O$). The proposed steel protection "Steel 20" was 77.8 % in comparison to the same conditions conducted for tests of commercially available corrosion inhibitors. The protective properties of the proposed corrosion inhibitor are not inferior with respect to the currently used inhibitors.

Key words. Petroleum recovery, concentrate, corrosion inhibitor, “Steel 20”, corrosion rate, hydrogen sulfide.

1. Introduction

Most of the oil and gas fields are characterized by a high water content, which greatly complicates the process of production, collection and treatment processes associated with the formation of stable emulsions of oil, deposits of inorganic salts and corrosive destruction of equipment and pipelines [1]. Destruction of oilfield equipment is determined by the physicochemical properties of water and hydrocarbon components of the system, their composition, quantity ratio, presence of dissolved gasses (hydrogen sulfide, carbon dioxide, oxygen, etc.). At higher flow velocities, ensuring intensive mixing phase emulsion system, it is formed by an oil-in-water or water in oil while defending their separation into two immiscible phases. In all cases, the corrosive environment is water. The most common problem for the oil industry today are carbon dioxide corrosion, hydrogen sulfide corrosion, hydrogen embrittlement, etc. The experience of corrosion indicates that the safe operation of process equipment can be achieved through the use of inhibitors. At the same time, compared to other methods of corrosion protection technology for inhibiting aggressive media they are relatively simple and do not require the use of significant

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logistical costs [2]. Corrosion inhibitors are classified to organic (95 %) and inorganic (5 %). Organic corrosion inhibitors—surfactants—can be classified as artificial and natural. Artificial surfactants are corrosion inhibitors obtained in chemical and petrochemical plants by methods of oxidation, suffocation, nitration, alkylation, etc. Corrosion inhibition has complex mechanism and depends on the formation of mono- or multidimensional protective layers on the metal surface. The protective nature of the surface layer depends on many factors: interaction between inhibitors and substrate, incorporation of the inhibitor in the surface layer, chemical reactions, electrode potentials, concentration of the inhibitor, temperature and properties of the corresponding surface, etc. The corrosion inhibitors as surfactants can be divided into two groups: the water-oil-soluble (WOS) surfactants and oil-soluble (OS) surfactants. Also, according to the mechanism of action of WOS and OS in nonpolar (hydrocarbon media) they are divided into corrosion inhibitors chemisorptions type donors, electron acceptors, corrosion inhibitors adsorption and dewatering agents. To protect steel pipes from corrosion in oil production, various types of surfactants [3–10] currently used are such IR as "Affinor," "SNPCH-1004." These reagents have proved decisive; however, the problem is the reagents' high expense. That is why there raises the question of development of new chemicals that exhibit not inferior protective qualities of new IR corrosion inhibitors and their costs are lower. In this regard, the aim of this work is to reduce the human-made hazards in the oilfield equipment, through the use of waste coolant concentrate obtained by membrane separation as a corrosion inhibitor.

2. Methods

The concentration of oil, grease and nonionic surfactant was determined by corrosion inhibitor spectrometry using "Kontsentratomer KN-3". The water content and solids was determined gravimetrically. The PH value (pH) of concentrate was determined by the potentiometric method. The density of the inhibitor was found using a technique based on GOST 3900 "Oil and oil products methods for determination of density". The essence of the method consisting in immersing the hydrometer in the tested liquid is to consider the effects of the hydrometer scale on the temperature determination and based on the results of the density at 20 °C. The concentrate solubility was determined in the following manner. Tests to determine the solubility, dispensability are performed in a transparent glass container with a stopper chemical at room temperature. They are prepared in the test inhibitor mixture solvent of various concentrations (0 to 50 %). For this purpose, the mixture is shacked and stirred vigorously to be dissolved or formed as emulsion structure. Both indicators are evaluated visually against a sheet of white paper in transmitted light periodically for a time interval of 1 hour to 7 days. Determination of the rate of corrosion and protection of metal with the use of waste coolant concentrate were performed according to GOST 9.506-87 "Inhibitors of metal corrosion in aqueous environments of oil" by gravimetric method. The method consists in determining the weight loss of metallic specimens during their stay in the inhibited and uninhibited test environments, followed by evaluation of the protective ability of the inhibitor to change the rate of corrosion. The aggressive environment conditions as produced in water-oil fields should be considered. As the metal samples we used metal plates of rectangular shape of dimensions of 70×35×0.5 mm which are made of "Steel 20" used for pipelines to pump oil. To activate the surface of the samples before the test, the plates were immersed for 1 minute in a 15 % solution of hydrochloric acid (HCl), then washed thoroughly with running water and distilled water and dried with filter paper. Just before the samples are weighed on analytical scales with an accuracy test of 0.0001, the samples were hung on the suspension and placed in a glass beaker with the test environment. The solutions were stirred by magnetic stirrers to create dynamic conditions. As used test medium, inhibited and uninhibited water reservoir model prepared according to the composition described in GOST 9.506-97 was used of volume of 130 cm^3. Such an inhibitor of corrosion was added to the emulsion concentrate of the spent coolant, and the corrosion tests were carried out for 24 hours to determine the mass loss of samples purified from surface corrosion products as gasoline, alcohol, and soft elastic corrosion, washed thoroughly with tap water and distilled water, dried with filter paper and weighed on a mathematical scales with an accuracy of 0.0001 g.

3. Results and discussion

Used coolant constitutes 3–10 % soluble, that involves industrial oils, as an idol, sodium nitrite, ethylene glycol, and other materials. In the machine construction companies, they use a coolant with the short life service which can be employed for a several month. After cleaning by using membrane methods [11–14], the waste coolant are used as a corrosion inhibitor. Their composition is presented in Table 1 for the second usage.

Table 1. Component composition of the waste coolant concentrate

No.	Ingredients	Content (%) ($P = 0.95$, $n = 2$)
1	Humidity	4.56
2	The organic part (oil and non-ionic surfactant...)	94.7
3	Contamination	0.74
Total		100

Currently used corrosion inhibitors are composed mainly of nonionic surfactant-quaternary ammonium; phosphites and phosphates; alkyl- and acryl zinc and other metals, nitrate oil, oxidized petrolatum, complete and incomplete (acid) esters oxy-propylation and oxy-methylation products. For comparison, the main properties of the spent coolant concentrate with commercially available corrosion inhibitors that are studied are the following physicochemical properties: pH, density, and solubility. The results of studies of physical and chemical properties compared with the most commonly used in the oil industry corrosion inhibitors are listed in Table 2.

Table 2. Physico-chemical properties of corrosion inhibitors

Corrosion inhibitor	Index		
	pH	Density (g/cm^3)	Solubility
Concentrate spent coolant	6.9±0.1	0.940±0.047	Emulsifies in water
“SHNPH”	6–9	0.880±0.044	Soluble in water, alcohols
“TNHC-7”	6–9	0.890±0.045	Soluble in water, alcohols
“NAPOR-1007”	6–9	0.890±0.045	Soluble in aromatic hydrocarbons, alcohols

Results showed that the investigated indicators concentrate waste emulsion coolant characteristics are close to the corrosion inhibitor properties of the brand “NAPOR-1007”.

Consequently, because of the similarity of physical and chemical properties, it was used as infrared and conducted tests on corrosion protective properties. Table 3 presents the model of produced water with a corrosion inhibitor and without inhibitor ($CaCl_2 \cdot 6H_2O$; $MgCl_2 \cdot 6H_2O$; NaCl, $CaSO_4 \cdot 6H_2O$), prepared according to GOST 9.506-87, see Table 3.

Table 3. Properties of the model of water formation

pH	ρ (g/cm^3)	Specific conductivity (mS/cm)	I (mol/dm^3)	Content (mg/dm^3)		
				Fe_{total}	O_2	H_2S
6.0±0.1	1.12	194±19	3.51	0.7±0.1	6.2±0.9	305±61

Indicators for the model with the produced water show the weakly acidic medium, which may be the result of the high content of hydrogen sulfide and sulfides. These conditions are sufficient to identify the corrosion properties of the medium, which has been investigated in our tests. According to the literature [14], the effectiveness of corrosion inhibitors can increase the input of the latter hydrophobic reagent. This condition results in reducing the hydrophobic character in polypropylene with the content range of 1 to 30 %. For application according to [15] it can be used in oil pipes under the earth as inhibitor of polyethylene corrosion. The comprehensive study shows that using these material is useful for protection of pipes. In other words, by calculation of total strain energy as well as the thermoelastic energy of material before any fracture or corrosion grows in the advanced materials, these inhibitors of polyethylene corrosion can prevent it from damage [16–18]. The results indicate that the optimal condition for the coolant are 9 pH and 10 % polypropylene glycol (PPG). With these conditions the test results show that the protection level for the steel 20 is about 78 %. We conducted comparative laboratory corrosion tests with corrosion inhibitor brands "SHNPH" and "TNHS-7" which are applied in oil gathering pipeline system, see Table 4.

Table 4. Results of laboratory corrosion tests of corrosion inhibitors

Corrosion inhibitor brand	Corrosion inhibitor dosage	The mean corrosion ratio (mm/year)	Protection degree (%)
"TNHS-7"	3.8	0.0383	72.0
"SHNPH"		0.0209	84.7
Concentrate spent coolant		0.0304	77.8

4. Conclusion

Due to hazards and environmental problems in the oilfield equipment, we developed an approach using the waste coolant which creates membrane separation as a corrosion inhibitor. The high degree of protection observed in the corrosion inhibitor brands "SHNPH" and modified concentrate coolant on the level of protection were only slightly inferior with respect to the present corrosion inhibitors. Results showed that the worst performance of corrosion and protection degree of the steel for the corrosion inhibitor "TNHS-7" brand occurs at a dose of $3.8\,g/dm^3$. The results demonstrated the effectiveness of corrosion inhibitors for steel oilfield equipment.

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