Surfactants for improving the safety of oil plant equipment operation

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Abstract. The phenomenon of oil acidification is explained by the accumulation in its flow of electrostatic charges formed during pumping of water-oil emulsion through lined pipelines. Negative charges are accumulated by the water phase, and positive charges are concentrated in oil. These processes occur both in pipelines lined with polymeric materials and in steel pipelines that have only external insulation. The purpose of the studies was to determine the corrosion rate of the pipe steel in the stored charge sub-commercial water having different values of pH and redox potential, as well as to evaluate the possibility of using surfactants to reduce the redistribution of electrostatic charges.

1. Introduction
In process of water-oil mixture pumping through lined field pipelines static charge accumulates - negative on pipeline surface and positive in oil. Since formation water is an electrically conductive electrolyte and its potential is equal to that of the pipe, a potential difference is accumulated between the water and the oil. The process of changing charges is directly related to the formation of direct and reverse type emulsions due to electrostatic repulsion forces between globules. Accumulation of charges in the oil phase takes place by the mechanism of formation of so-called carbocations - organic molecules with high molecular weight, which attach ion with positive charge. The charge on the molecule is redistributed across all atoms, and the total charge of the molecule varies slightly. Carbocations in the environment of the dielectric oil phase can exist for a long (several days) time [1-2].

Electrostatic charges, accumulating in the volume of water, change its hydrogen pH index and redox potential Eh. Increasing the concentration of negative ions in the aqueous phase reduces its corrosive activity, which is a positive development. Oil, which has accumulated a large amount of positively charged ions, poses a great danger to oil preparation and processing plants. After settling oil is supplied via main pipelines to oil refineries, where residual moisture is removed and carbocations are broken down first at electric demineralization plants, and then at high temperature in column of atmospheric-vacuum tube [3-15]. The water condensate in the oil refining has a pH of about 1, so no unit is without the crude oil first snapping.

Acidulation of oil cannot be referred only to use of acids for layer hydraulic fracturing, and formation of emulsions - only influence of pumps and the natural surfactants (S). Therefore, we tried to explain this phenomenon by accumulating static charge when pumping oil through pipelines.
An important indicator of the change in the composition of the water-oil mixture is the aqueous electrically conductive phase. The change in the characteristics of the aqueous phase is directly related to its Eh and corrosion activity. Accumulation of negative charge by water phase is equal in amount of electricity to accumulation of positive charge by oil.

2. Experimental

The purpose of the studies was to determine the corrosion rate of the pipe steel in the stored charge sub-market water having different values of pH and Eh, as well as to evaluate the possibility of using surfactants to reduce the redistribution of electrostatic charges.

The change in Eh water was carried out in a specially designed laboratory plant that simulates the movement of an oil-water emulsion through a lined pipeline. The corrosion rate of the metal samples was determined by three methods: gravimetry, linear polarization resistance and polarization curve removal [16-21].

Gravimetric analysis for determination of depth corrosion index was performed on samples of steel C22 in accordance with GOST 9.502-82.

Parameters were recorded by linear polarization resistance using Monikor-2M corrosion rate indicator.

To implement the method, the following parameters were established: polarization of the working electrode into the cathode and anode regions from the corrosion potential ± 10 mV; Value of factors ba and bk 120 mV; Duration of polarization - 30 s in cathode and anode regions.

Anode and cathode polarization curves were collected using IPC-Pro M potentiostat. Polarization of the working electrode to the cathode region was conducted to a potential of -1.5 V, to the anode region to 0.5 V; The potential scanning rate was 0.5 mV/s. A sample of steel C22 was selected as the working electrode.

This method is based on Stern Weight principle received theoretically by differentiation of the equation of a polarizing curve near the stationary potential of corrosion (ΔE<10-20 mB). In general, this principle is read as follows: the corrosion current density is inversely proportional to the polarisation resistance of the electrode surface measured near the stationary corrosion potential.

Corrosion current density is calculated by formula:

\[ i_k = \frac{\Delta i}{\Delta E} \cdot \frac{b_a \cdot b_k}{2.3 \cdot (b_a + b_k)} \]  

where

- \( i_k \) - corrosion current density, mA/cm²;
- \( \Delta i \) - emerging anode or cathode current density at displacement of potential (ΔE) by 10-20 mV, mA/cm²;
- \( b_a \) - constant showing the slope of the taphel portion of the anode polarization curve, mV;
- \( b_k \) - constant showing the slope of the taphel portion of the cathode polarization curve, mV;
- \( \frac{b_a \cdot b_k}{2.3(b_a + b_k)} \) - Stern Weight coefficient.

The tests were carried out in the following environments:

1. control environment;
2. the activated water;
3. solution I;
4. solution II;
5. solution III.

River water mixed with diesel fuel was used as the control medium and then permanent in the separation funnel. Activated water was obtained by circulating in a 10 % water-cut plant for 1 hour. Solutions I, II, III were prepared by circulating the mixture for 1 hour with addition of an antistatic agent in an amount of 10, 20 and 50 mg. Per 1 litre of water respectively.
3. Results and discussion
Samples after gravimetric tests are shown in Figure 1.

![Figure 1. Samples after gravimetric tests in a moving environment. Exposition (from left to right), h: 12, 24, 48, 60, 72.](image)

The polarization curves of C22 in the test media are shown in Figure 2.

![Figure 2. Polarization diagrams of steel C22 in investigated media. 1 - control medium; 2 - activated water; 3 - solution I; 4 - solution II; 5 - solution III.](image)

From the tables 1, 2 it is visible, with increase in concentration of antistatic (solution I → solution III) the oxidation-reduction potential of water increases and at concentration of 50 mg/l reaches Eh values of not loaded liquid. Furthermore, the addition of an antistatic agent does not significantly
increase the pH of the aqueous component of the emulsion. Thus, the acidity of the oil will not change in this case either.

Table 1. Parameters of investigated media.

| Environment                     | pH   | Eh, mV (SHE) | \(E_{corr}, \text{V (SHE)}\) | \(\beta_a\) | \(\beta_k\) |
|---------------------------------|------|--------------|-------------------------------|-------------|-------------|
| Control environment             | 8.0  | 444          | -0.40                         | 0.19        | -0.25       |
| The activated water             | 8.4  | 419          | -0.29                         | 0.15        | -0.20       |
| Solution I                      | 8.2  | 426          | -0.38                         | 0.18        | -0.24       |
| Solution II                     | 8.1  | 431          | -0.36                         | 0.18        | -0.23       |
| Solution III                    | 8.1  | 443          | -0.31                         | 0.14        | -0.21       |

Based on the modern theory of electrokinetic phenomena, an expression for the current of electrification under the turbulent mode has been obtained:

\[
I = -0.04 \pi \text{Re}^{0.75} \nu_0 \varepsilon \varepsilon_0 \zeta,
\]

where \(I\) - current intensity of the electrification, A; 
\(\text{Re}\) - Reynolds number; 
\(\nu_0\) - average velocity of liquid movement in the pipe, m/s; 
\(\varepsilon\) - dielectric constant of the liquid; 
\(\varepsilon_0\) - absolute dielectric constant; 
\(\zeta\) - electrokinetic potential, V.

It is assumed that the difference between the redox potential of the charged and uncharged liquid is numerically equal to the electrokinetic potential of this medium that occurs when the liquid moves relative to the solid.

The current of electrification, which can be calculated according to the given formula, superimposed on the corrosion current, changes the corrosion rate of the pipeline metal. Besides, the higher the values of electrokinetic potential, the more important the current of electrification is. Currents from static electricity are opposite in the direction of corrosion currents, so the current shift of polarization curves occurs towards the decrease of its values. Thus, the greater the difference has the redox potential of the charged liquid as compared to the non-charged potential, the lower the corrosion activity the medium in question has.

Table 2. Corrosion rate of steel samples C22 in test environment.

| Environment                  | Corrosion rate, mm/year | Gravimetric analysis | Polarization resistance method | Polarization curve removal method |
|------------------------------|-------------------------|----------------------|-------------------------------|----------------------------------|
| Control environment          | 0.070                   | 0.045                | 0.048                         |
| The activated water          | 0.007                   | 0.004                | 0.004                         |
| Solution I                   | 0.009                   | 0.005                | 0.006                         |
| Solution II                  | 0.048                   | 0.024                | 0.039                         |
| Solution III                 | 0.061                   | 0.033                | 0.046                         |

4. Conclusions

1. In case of joint transportation of oil and water, as a result of redistribution of charges, water is charged negatively, at the same time its corrosion activity is sharply reduced, but acidity of oil is increased.
2. Due to accumulation of static charge by water phase pH increases from 7 to 8, Eh decreases from 445 to 420 mV.
3. The use of surfactants (antistatic additives) in an amount of 50 mg/L reduces the redistribution of charges, while the corrosive activity of water remains at the same level, pH and Eh are also practically unchanged, i.e. the accumulation of static charges is excluded.

4. Use of antistatic additives will make it possible to prevent emulsion formation when water-oil mixture is pumped through lined pipelines and significantly reduce corrosion rate at oil preparation and processing plants.

References

[1] Tyusenkov A S and Rubtsov A V 2020 IOP Conf. Ser.: Mater. Sci. Eng. 734 012165

[2] Latypov O R, Bugai D E and Boev E V 2015 Method of controlling electrochemical parameters of oil industry processing liquids Chem. and Petroleum Eng. 51(3) 283–5

[3] Nasibullina O A and Gareev A G 2019 Destruction patterns of X70 steel sample, possessing cracks of corrosion-mechanical origin, under cyclic loading Mater. Sci. Forum 946 20–4

[4] Nasibullina O A, Gareev A G and Rizvanov R G 2018 Investigation of the hydrogen stratification of the metal of the active gas Solid State Phenomena 284 1302–6

[5] Yakhin A V, Karetnikov D V, Cherepashkin S E and Rizvanov R G 2019 Evaluation of the properties of alternative construction combined tube joints from heat exchanger tube grids made of steel 2Cr18Ni10Ti Chem. and Petroleum Eng. 55(7-8) 681–6

[6] Nasibullina O A and Gareev A G 2019 Materials Science Forum 946 381–6

[7] Rizvanov R G, Mulikov D Sh, Karetnikov D V, Fairushin A M and Tokarev A S 2018 IOP Conf. Ser.: Mater. Sci. Eng. 317 012077

[8] Karetnikov D V, Rizvanov R G, Fairushin A M and Kolokhov K S 2013 Welding International 27(7) 557–60

[9] Rizvanov R G, Abdeev R G, Matveev N L, Ryskulov R G and Shenknekht A F 2000 Chem. and Petroleum Eng. 36 3

[10] Ibragimov I G and Vil'danov R G 2007 Welding International 21(2) 139–41

[11] Kulakov P A, Bogdanova D D and Afanasenko V G 2019 IOP Conf. Ser.: Mater. Sci. Eng. 272 032072

[12] Kulakov P A and Afanasenko V G 2019 Influence of minimally permissible quantity of source materials on the probability of failure of a pump–tank system Chem. and Petroleum Eng. 54 681–6

[13] Kuzeev I R, Ibragimov I G, Bayazitov M I, Davydov S N and Khairudinov I R 1985 Chem. and Technology of Fuels and Oils 22(3) 111–3

[14] Afanasenko V G, Boev E V and Kulakov P A 2019 IOP Conf. Ser.: Mater. Sci. Eng. 560(1) 012003

[15] Kulakov P A, Apparov I H Y and Afanasenko V G 2018 IOP Conf. Ser.: Mater. Sci. Eng. 451(1) 012201

[16] Tyusenkov A S and Nasibullina O A 2019 IOP Conf. Ser.: Mater. Sci. Eng. 687 066016

[17] Tyusenkov A S and Nasibullina O A 2019 IOP Conf. Ser.: Mater. Sci. Eng. 687 066021

[18] Tyusenkov A S 2017 Chemical resistance of steel 13CrV (rus 13ХФА) J. of Chem. Technol. and Metallurgy 52(4) 766–72

[19] Mirkhaydarova K A, Tyusenkov A S and Rizvanov R G 2018 Gas Corrosion of Pyrolysis Furnace Coils Solid State Phenomena 284 1297–301

[20] Nasibullina O A and Tyusenkov A S 2019 IOP Conf. Ser.: Mater. Sci. Eng. 537 022018

[21] Nasibullina O A and Tyusenkov A S 2019 IOP Conf. Ser.: Mater. Sci. Eng. 537 022023