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INFLUENCE OF COMPONENTS PRODUCED WATER ON THE RATE OF CORROSION OF OIL EQUIPMENT

Background

The premature failure of oilfield equipment is caused, as a rule, by its surface corrosion. The destruction of the equipment is closely associated with high corrosiveness of working media that are constantly present in the oilfield equipment. Corrosiveness of the medium is due to solid impurities, dissolved acid gases, salt ions, and anaerobic and aerobic microorganisms involved in metal depolarization or dissolution. Treatment of the working medium to reduce its aggressiveness is one of the most effective ways to reduce the rate of corrosion. This can be achieved by removing corrosive agents from the medium, or weakening their ability to interact with the metal of the equipment.

Aims and Objectives

To reduce the rate of corrosion of metal equipment in contact with formation water, it is necessary to identify main factors that exert effect on corrosion. For this purpose, the components of formation water shall be tested.

Methods

Reading polarization curves was used as the basic test method. Parameters of polarization curves were processed to determine the rate of corrosion of metal coupons. Specially prepared model of formation water was used for lab testing. Electrolytic potential of the metal surface was measured against silver chloride reference electrode.

Results

Studies showed that the most important factor affecting the rate of metal corrosion is the concentration of chlorides in the formation water. It was stated that the concentration of 353 mg/dm^3 was critical, and the rate of corrosion of steel 20 in the model formation water sharply increases at higher concentrations.

Key words: corrosion rate, formation water, polarization curves, statistical analysis, oil field equipment, solution components

Currently, as the oil production is intensified, the well stream is watered to one or another extent, therefore water is almost always present in the working medium of the oilfield equipment [1, 2, 3]. Operating experience shows that presence of water in any aggregate state promotes corrosion processes that result in shortened service life and lower safety of the oilfield equipment.

In the field, water is usually in the same formations as the recovered oil and gas [4, 5]. Here, phases are naturally separated by density: gas is in the highest position, oil is under gas, and water is below. Also, self-contained water-bearing horizons may be above or below pools in the section of oil and gas fields [6, 7, 8]. Depending on their position in relation to oil-bearing/gas bearing stratum the underground waters are subdivided into:

1) Formation waters. They embed in one formation with oil and are recovered together with oil. Formation waters may be also classified as:

a) bottom edge waters embedded in the lower parts of the oil stratum and «supporting» oil pool;

b) bottom waters filling reservoir pores under the pool;

c) intermediate waters related to water-bearing strata embedded in the very oil-bearing formation;

2) Top and bottom waters related to aquifers and occurring above or below oil-bearing bed;

3) Connate, or relict, waters that have remained since the time when oil and gas deposit was formed, and that are found exactly in the producing formations of the oil and gas part of the field. This water usually holds immobile during oil travel within formation, therefore, it is sometimes called interstitial water. Interstitial water may occur in the form of adsorbed,

capillary or film water. The forms of interstitial water are essential for the development of oilfields as they exert substantial effect on the oil recovery [9, 10, 11, 12, 13].

Chemical composition of formation waters in the oil and gas fields is usually formed under active influence of oil and gas, and hampered water exchange. Therefore, formation waters have wide variety of their chemical properties. The composition of formation waters depends also on the geological age and chemical composition of rocks, oil and gas, so within different oil and gas fields, and even within one field, formation waters may differ greatly in their chemical composition, concentration of dissolved mineral salts and different oil and gas components. The composition and properties of formation waters change as the oil and gas field is being developed. During oil recovery the formation pressure is lowered, the temperature changes, and the contact with formation waters of other horizons is formed, which often leads to degassing and disturbance of ionic balance of the formation water [12].

Depending on their chemical composition, formation waters may be classified into four types by certain typical criteria [14]: calcium-chloride, magnesium-chloride, sodium-bicarbonate, and sodium-sulfate.

Formation water may be attributed to one of these types by testing chemically the proportion of quantities of separate ions (in mg-eq.). Each water type is in turn subdivided into three groups, depending on anion predominance: sulfate, chloride, and bicarbonate. Each of these groups usually includes three sub-groups subdivided according to cation predominance: calcium, sodium, and magnesium [15].

Sodium-bicarbonate and calcium-chloride waters are most common for oil deposits. Calcium chloride waters are usually characterized by high salinity, and their density varies widely and can reach 1.2 g/cm^3 . They contain a very large amount of Ca^{2+} , Na^+ , Mg^{2+} and Cl^- , and not too much CO_3^{2-} , HCO_3^- . In some fields these waters contain a large amount of iron ions (up to 300 mg/l).

Sodium-bicarbonate waters have somewhat lower salinity, and their density rarely exceeds 1.07 g/cm^3 . The composition of the main components of sodium bicarbonate water includes Na^+ и Cl^- ions, and they also contain a small amount of Ca^{2+} ions.

Most often found in fresh waters are HCO_3^- , Ca^{2+} , Mg^{2+} ions. With increase in the total salinity of water the concentration of SO_4^{2-} , Cl^- , Na^+ , Mg^{2+} , K^+ ions increases. Highly mineralized waters contain large quantities of Cl^- , Na^+ ions, rarer Mg^{2+} ions, and very rarely Ca^{2+} ions. In water, the concentration of one of the main anions and one of the main cations always prevails over the concentration of other ions, so the natural waters are classified by chemical composition, depending on the anions and cations prevailing therein. The presence of salts in the injected formation water can cause the formation of corrosive components. For example, the reaction of calcium sulfate CaSO_4 with methane may form H_2S , contributing to the development of local corrosion processes [6].

The model of formation water (MFW) in accordance with GOST 9.502-82, composition No. 3 was used as a test corrosive liquid.

How the main ions of salts being the part of the formation water model influenced the corrosion rate of the material was determined by the methods of design of experiment. Steel 20 was selected for testing. Matrix of design shown in Table 1 was made (initial ion content is given in the line MFW No.1).

Table 1 - Compositions of formation water models (matrix of design)

No. MFW	Component concentration by mass, mg/dm ³		
	<i>Na₂SO₄</i>	<i>NaHCO₃</i>	<i>CaCl₂</i>
1	213.0	138.0	333.0
2	320.0	138.0	333.0
3	213.0	207.0	333.0
4	320.0	207.0	333.0
5	213.0	138.0	500.0
6	320.0	138.0	500.0
7	213.0	207.0	500.0
8	320.0	207.0	500.0

Voltammetric characteristics of the coupons of steel 20 in the model formation water of different composition were recorded by linear polarization method using a potentiostat «IPC Pro-M». Polarization scan was built in the range from minus 300 to plus 300 mV of steady potential at 100 mV/s. Next, the rate of corrosion of coupons in components of model formation water was calculated (Table 2).

Table 2 - Results of electrochemical testing of steel 20 in the model formation water of different composition

No. MFW	/ Component concentration by mass, mg/dm ³			Rate of corrosion of steel 20, mm/year
	<i>Na₂SO₄</i>	<i>NaHCO₃</i>	<i>CaCl₂</i>	
1	213.0	138.0	333.0	0.593
2	320.0	138.0	333.0	0.318
3	213.0	207.0	333.0	0.273
4	320.0	207.0	333.0	0.350
5	213.0	138.0	500.0	0.365
6	320.0	138.0	500.0	0.380
7	213.0	207.0	500.0	0.400
8	320.0	207.0	500.0	0.450

It is clear from the table 2 that MFW No. 8 has the highest corrosiveness in relation to steel 20.

Statistic analysis was conducted to determine the most aggressive component of the corrosive medium. Two-factor central composite design (Design of Experiment Module Experiment (DOE)) was used for a more thorough study of the area of the experimental values. Intervals of varying the rate of corrosion of steel 20 were determined from 0.2 to 0.4 mm/year. The following factors were studied: the number of sulfates, chlorides and bicarbonates in the MFW. The lower and upper levels of the amount of salt components in the model formation water were determined for the test purposes: sulfates - 213...320 mg/dm³, bicarbonates -

138...207 mg/dm³, chlorides - 333...500 mg/dm³. After that the model was chosen, and the matrix of design was made.

Figure 1 demonstrates the selection of the model - quadratic type. Figure 2 shows the matrix of design.

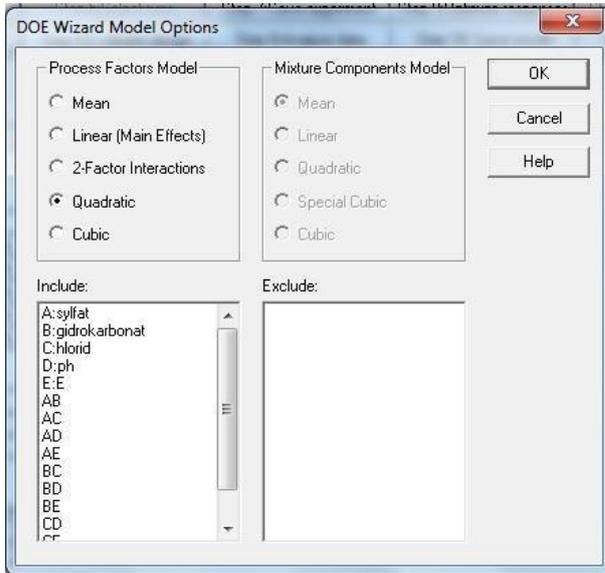


Figure 1 - Selection of the type of model

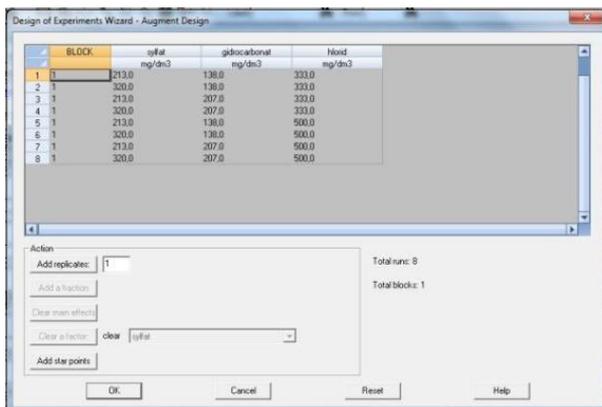


Figure 2 - Matrix of design

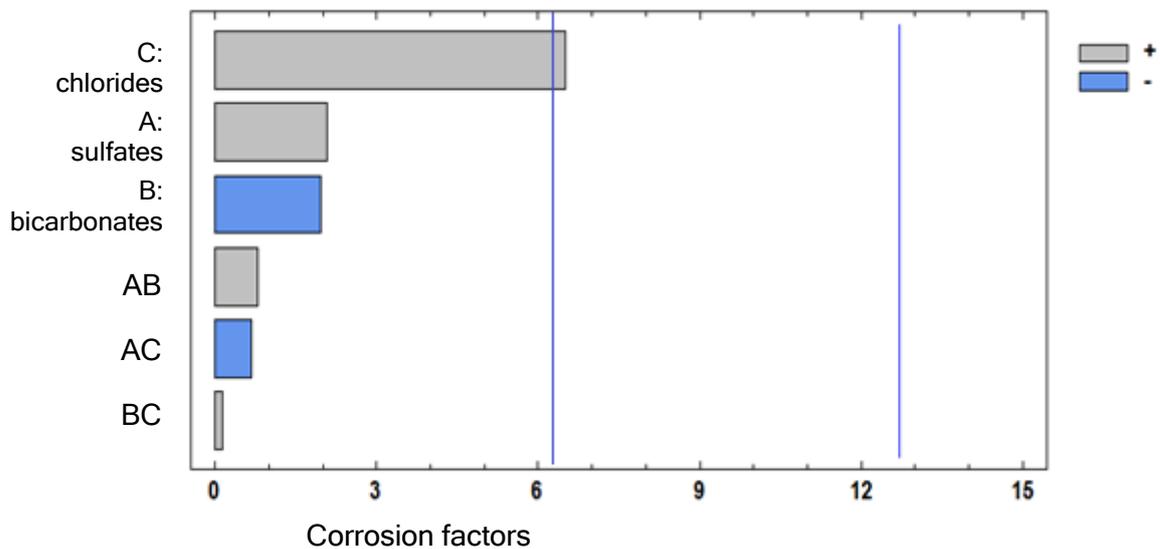


Figure 3 - Standardized Pareto chart for corrosion rate

To determine the most significant salt influence on the corrosion rate of the steel 20 in the components of the model formation water, it is convenient to use a standardized Pareto charts (Figure 3).

Pareto chart clearly shows that the chlorides exert statistically significant effects. This is demonstrated by that the respective columns intersect the vertical line which represents up to 95 % of significance of the test. The plot of corrosion factors deviation from the normal distribution also supports this conclusion (Figure 4).

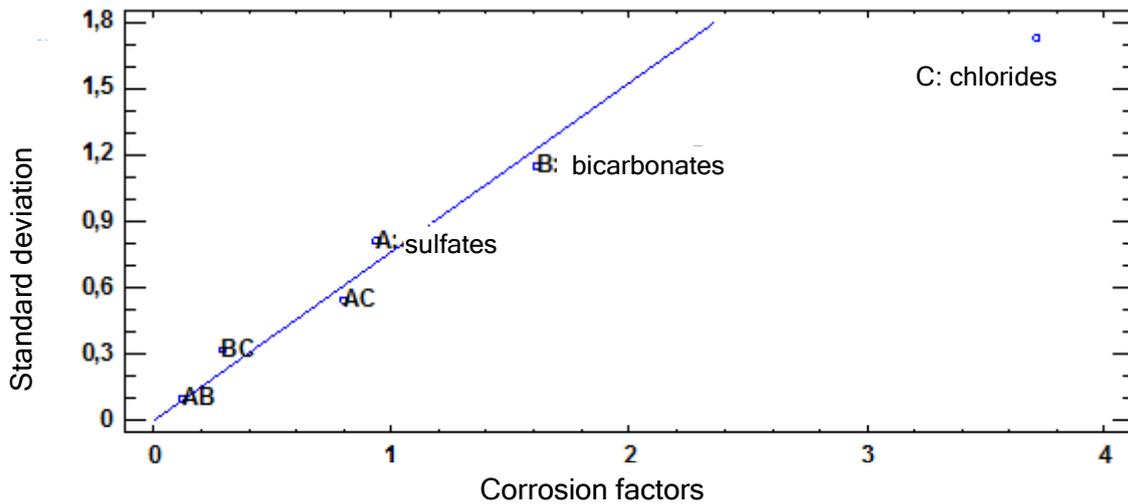


Figure 4 - Corrosion factor deviations from the normal distribution

It is clear from figure 4 that chlorides are away from the line of normal distribution, indicating the statistic significance of their effect on the response, i.e., the rate of corrosion.

Figure 5 shows the plot of the surface of response.

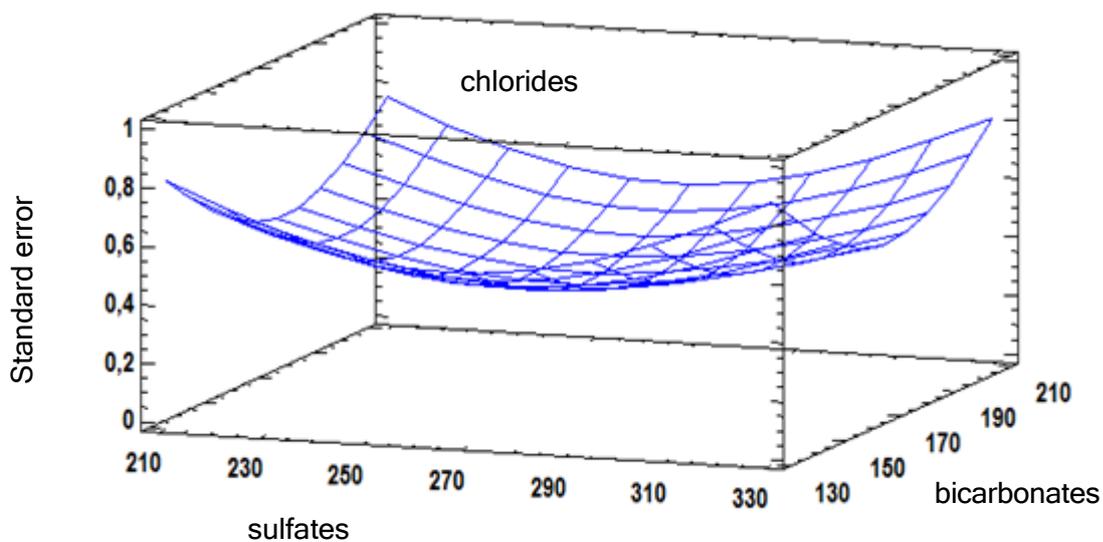


Figure 5 - The plot of the surface of response for the rate of corrosion of steel 20 in the model formation water

This 3D plot has a concavity with peaks: for “sulfates” factor 207 mg/dm³; for “bicarbonates” factor 159 mg/dm³; and for “chlorides” factor 353 mg/dm³. The plot shows the composition of formation water at which the minimal rate of corrosion 0.276 mm/year is achieved. Further increase in chlorides in the formation water contributes to sharp acceleration of corrosion.

Thus, using the program complex STATGRAPHICS Centurion XVI.I it was stated that chlorides as components of the model formation water exerted statistically significant effect, i.e. they had the greatest influence on the rate of corrosion of steel 20. Moreover, the amount of MFW components contributing to maximum rate of corrosion was determined. Reduction in the amount of the most significant components (chlorides) results in slower corrosion of the oilfield equipment.

Conclusion

The studies found that the most significant factors in determining the kinetics of corrosion processes on the surface of oilfield equipment are composition of formation water and the concentration of salt ions such as sulfates, carbonates and chlorides. The corrosion rate of the steel 20 coupons at different content of these ions was determined. By means of design-of-experiment methods it was stated that the main factor contributing to the high rate of corrosion of equipment was a significant concentration of chlorides (up to 95 % significance). Increasing the amount of chlorides in the formation water contributes to a dramatic increase in corrosion rate. When their content in the formation water is in excess of 353 mg/dm³, the corrosion rate of steel 20 exceeds 0.276 mm/year.

Thus, the use of highly efficient methods to reduce the concentration of active chlorine ions, for example, by the use of complexing scale inhibitors, reduces the rate of corrosion of oilfield equipment in the formation water.

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