Prevention of fire hazard situations on oil pipelines subject to the formation of asphaltene-resin-paraffin deposits

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Abstract. The article discusses the problem of ensuring fire safety at pipeline transport facilities for hydrogen sulfide-containing oil and oil and gas condensate raw materials, which during operation are subject to the formation of asphalt-resin-paraffin deposits. The effect of intensive accumulation of oil deposits on corrosion processes and the effectiveness of inhibitor protection has been established. To ensure fire and environmental safety in the oil and gas industry, it is critical to prevent local corrosive damage to oil pipelines. In modern conditions, the chemical method of removing asphalt-resin-paraffin deposits is one of the most promising. The paper proposes a new solvent composition for sediment removal. A fire risk assessment was carried out on the section of the main oil pipeline, during which an excess of the established standard value of the individual risk during local corrosion destruction due to untimely removal of asphalt-resin-paraffin deposits was revealed. A regression model was developed to assess the fire risk on the oil pipeline with the required volume of deposits solvent and its solvent capacity.

1 Introduction

The transportation of oil through pipelines is inevitably accompanied by the formation of asphalt-resin-paraffin deposits (ARPD) on the walls of the pipes. This is a serious problem that can lead to emergencies and fires. As ARPD deposits form inside the pipeline, favorable conditions are created for the development of metal corrosion [1].

Loss of containment caused by corrosion is a particular hazard. When a pipeline ruptures, oil is released, which can ignite in the presence of an ignition source. Given that oil is highly flammable and its vapors form an explosive mixture with air, the likelihood of fire or explosion is extremely high.

Therefore, in order to ensure fire safety at the facilities of the oil and gas complex, it is necessary to regularly diagnose the condition of pipelines, carry out a set of measures aimed at preventing local corrosion damage, including the accumulation of ARPD on the walls of pipelines and take timely measures to remove them.

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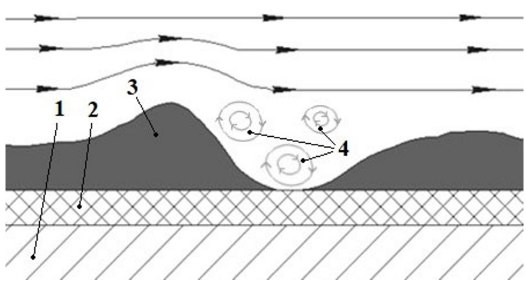
Due to the variety of field operating conditions and differences in the physical and chemical properties of oil, it is necessary to apply an individual approach and improve the existing methods of sediment removal. Among the many existing methods, a special place is occupied by chemical, which, due to its effectiveness and simplicity in technology, has become widespread. For optimal results, it is necessary to carefully select the solvent components and justify their effectiveness.

Thus, the solution of the fire safety problem is inextricably linked with the need to improve the chemical method of removing asphalt-resin-paraffin deposits, which involves research work.

2 Experimental results

Corrosion inhibitors are used to protect trunk oil pipelines from the corrosive fluid flow environment, which create a protective film on the inner surface of the pipeline. During prolonged exposure to hydrodynamic vortices, local destruction of the inhibitory film occurs [2], which contributes to the exposure of the metal surface (Figure 1).



1 - oil pipeline wall; 2 - corrosion inhibitor protective film; 3 - ARPD layer; 4 - vortices

Fig. 1. Formation of vortices behind the convex growth of ARPD deposits.

To verify the theoretical model of destruction of the protective film under the influence of turbulent flows, studies were carried out using the gravimetric method of analyzing the corrosive reaction of metal plates with an aggressive medium, as well as the method of molecular spectroscopy. Table 1 shows the results of the gravimetric test method with average values of corrosion rates for each parallel experiment.

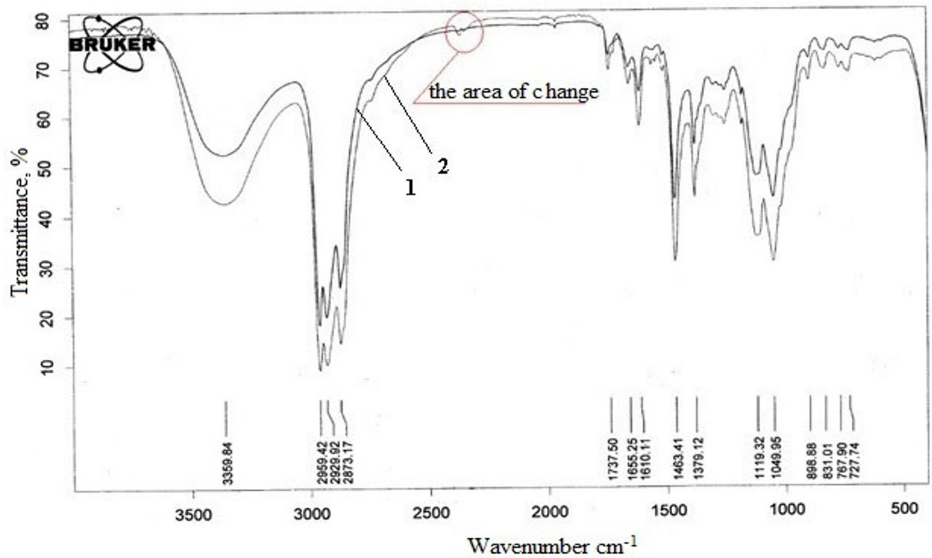
Table 1. Corrosion test results.

Test medium	**Test limits**	**Experience no.**	**Corrosion rate, g/m²· hour**	**Average corrosion rate, g/m²· hour**	**Corrosion rate, mm/year**
model water with corrosion inhibitor	without wave effects	1	0.773	0.7245	0.81
		2	0.676		
	with wave effects without wave effects	1	1.094	1.0205	1.14
		2	0.947		

Studies have shown that after exposure to hydrodynamic waves, the rate of corrosion processes increased by 40%. This supports the hypothesis that turbulent fluid flow causes hydrodynamic cavitation, which destroys the protective inhibitory coating and accelerates corrosion.

Spectral analysis revealed characteristic changes in the IR spectrum of the test compound in an important range of wave numbers from 2800 to 1800 cm^{-1} (Figure 2), which indicates a significant change in the concentration of inhibitor molecules in the solution.

This region of the spectrum is characteristic of triple bonds and some other functional groups that are rarely found in organic molecules [3].



1 - plot for the stock solution; 2 - graph for the solution exposed to wave action

Fig. 2. Infrared spectra plots of the investigated corrosion inhibitor SNPH before and after hydrodynamic impact.

The results obtained indicate that hydrodynamic effects significantly disrupt the mechanism of action of the inhibitor, preventing the formation of a protective film on the metal surface. This may be due to several factors [4]:

- mechanical destruction of the forming film;
- difficulty of adsorption of inhibitor molecules on the surface;
- desorption of already adsorbed molecules;
- violation of the structure of the formed protective layer.

Thus, to increase the efficiency of protection in turbulent flows, the development of new approaches and methods for ensuring fire safety is required.

Hazardous pyrophoric deposits are formed on metal surfaces during operation of pipelines transporting hydrogen sulfide-containing oil [5]. These deposits are a complex mixture including products of hydrogen sulfide corrosion, iron sulfides, mechanical impurities, resinous and other organic substances.

Of particular danger is the ability of such deposits to spontaneously burn when in contact with air oxygen. Importantly, this can occur even at the lowest ambient temperatures. The mechanism of spontaneous combustion is due to the presence of active iron sulfides in the sediments and their porous structure, which contributes to rapid oxidation with the release of a large amount of heat [5-6].

Based on the analysis, the following sequence of events can be distinguished, leading to a fire hazard situation during the accumulation of ARPD (Figure 3)

In order to avoid fire hazardous situations as a result of the accumulation of ARPD, it is necessary to apply and improve methods for the removal of deposits.

The chemical method of removing deposits using organic solvents ARPD was studied, tests were carried out using the "baskets" method, which is based on the process of weighing sediment samples before they are placed in a dissolving medium and then in mesh baskets. When analyzing the results of the study, the effectiveness of the solvent is evaluated according to three indicators: detergent, dispersing and solvent.

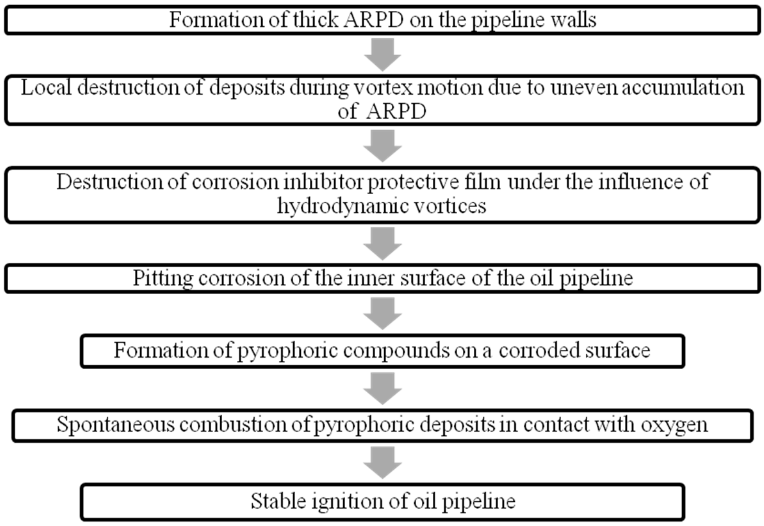


Fig. 3. The process of initiating a fire hazard situation as a result of the formation of ARPD in the oil pipeline.

Table 2 shows the results of the average efficiencies of the tested solvents, which showed the best dissolution capacity for each sample of deposits.

Table 2. Results of mean efficacy values of test solvents.

Name of the Pilot	Sample of Deposits	Detergent Method, %	Dispersing Ability, %	Dissolving capacity, %	Dissolutio n time, min
R-4	Sample 2	98.49	23.99	74.5	240
R -7	Sample 1	98.85	30.99	67.86	165

During the study of the chemical method of removal and laboratory tests using the "baskets" method, new complex solvents were obtained. The highest solvent and detergency for the sample of deposits Sample 1 showed solvent R-7, and for the sample of deposits Sample 2 - solvent R-3 [1].

The effectiveness of the developed solvents is due to their unique composition, where the ratio of naphthenic and aromatic hydrocarbons plays a key role. Each component in the solvent composition has a specific function: aromatic hydrocarbons effectively cope with the dissolution of polar components of asphalt-resin-paraffin deposits (asphaltenes and resins), while naphthenic hydrocarbons act on non-polar paraffin [1, 7].

3 Fire risk assessment

As part of the study, a comprehensive fire risk assessment was carried out at the section of the main oil pipeline transporting hydrogen sulfide-containing oil and oil and gas condensate raw materials subject to the formation of asphalt-resin-paraffin deposits.

The study included analysis of two pipeline operation scenarios:

1. Use of ARPD solvent for pipeline cleaning. In this case, effective removal of deposits helps to prevent local corrosion, which increases the reliability of the structure (case No. 1).
2. Absence of ARPD solvent, which leads to accumulation of deposits and destruction of the corrosion inhibitor protective film, increasing the risk of emergencies (case No. 2).

To assess the probability of emergencies, statistical data on the frequency of depressurization of pipelines of various types of damage were used in accordance with regulatory requirements (Appendix No. 6 to Order No. 533).

Using the specialized TOXI+Risk software package, collective and individual risk indicators were calculated for both operating scenarios. The results of the calculations are presented in Table 3 and allow a comparative analysis of the effectiveness of various approaches to the operation of the main oil pipeline from the point of view of fire safety.

Table 3. Quantitative fire risk assessment indicators for the considered linear section of the oil export pipeline.

Case under consideration	**Number at the same time people**	**Number risking**	**Coefficient presence**	**Collective risk, people/year**	**Individual risk, 1/year**
case No. 1	1	1	1.00	$2.3 \cdot 10^{-7}$	$2.3 \cdot 10^{-7}$
case No. 2	1	1	1.00	$1.43 \cdot 10^{-8}$	$1.43 \cdot 10^{-6}$

When using the ARPD solvent for pipeline cleaning and corrosion protection, the individual risk value was $2.3 \cdot 10^{-7}$, which fully complies with the requirements of the legislation (Federal Law No. 123, Article 93) and is within acceptable limits.

However, the situation changes in the absence of purification from ARPD. Accumulation of deposits leads to the destruction of the protective film of the corrosion inhibitor under the influence of hydrodynamic vortices. In this case, the individual risk increases by more than 6 times and reaches a value of $1.43 \cdot 10^{-6}$, which exceeds the standard indicators.

The results obtained indicate the critical impact of fire safety methods at the pipeline facility. Exceeding the standard values of individual risk in the absence of cleaning from ARPD requires the mandatory introduction of additional fire protection measures to ensure the safe operation of the main oil pipeline.

4 Regression

During the research work, the relationship between the fire risk and the parameters of the efficiency of removal of asphalt-resin-paraffin deposits in the oil pipeline was established. Linear regression analysis, a statistical method that predicts the value of a dependent variable (regressant) based on one or more independent variables (regressors or predictors), was used [8].

The study identified the following variables for statistical analysis:

- Y (regressant) - fire risk value (10^{-6})
- X_1 (regressor) - volume of solvent required for injection into the pipeline (m^3)
- X_2 (regressor) - solvent solubility (in fractions)

Particular attention was paid to the case when the oil pipeline does not use a solvent to remove ARPD. This scenario is characterized by maximum fire risk values and serves as a baseline for comparing the effectiveness of different cleaning methods.

Table 4 presents the data obtained during the study for statistical analysis of the dependence of the variable Y between two independent variables X_1 and X_2.

Then the regression model for the pipeline under study will take the form:

$$Y = a + b_1 \cdot X_1 + b_2 \cdot X_2 = 1.4487 + 0.00455 \cdot X_1 - 2.2126 \cdot X_2 \quad (1)$$

The results of the regression analysis made it possible to establish the following patterns in the assessment of fire risk at the studied facility:

- The basic value of the fire risk (constant *a*) in the absence of the impact of the factors under consideration (Xn) is $1.4487 \cdot 10^{-6}$. This indicator exceeds the normative values, which indicates the initially increased danger of the object.
- Coefficient b_1 demonstrates that with an increase of parameter X_1 by 1, the fire risk value increases by 0.00455. The coefficient b_2 indicates that as the X_2 parameter increases by 1, the fire risk value decreases by 2.2126, which confirms the effectiveness of using solvents with a higher solubility.

5 Conclusion

Studies have shown a critical safety problem for the oil export pipeline associated with the formation of asphalt-resin-paraffin deposits.

Mechanism of dangerous phenomenon:

- Uneven formation of ARPD causes hydrodynamic vortices.
- Vortices break the corrosion inhibitor protective film.
- Pyrophoric compounds are formed in the hydrogen sulfide-containing feedstock.
- Upon contact with oxygen, self-ignition occurs, leading to fire

To solve the problem, complex solvents based on naphthenic and aromatic hydrocarbons have been developed for two different types of sediment samples.

The fire risk assessment confirmed the danger of the situation: in case of destruction of the protective film due to uneven accumulation of ARPD, the individual risk exceeds the regulatory values, which requires additional safety measures. Regression analysis showed that the developed solvents reduce the fire hazard.

Thus, the results of the study are of great practical importance for the development of risk management systems for the operation of oil pipelines subject to the formation of ARPD.

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