Laboratory assessment of the efficiency of corrosion inhibitors at oilfield pipelines of the West Siberia region I. Objective setting

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Abstract

This paper starts a series of publications dealing with the laboratory assessment of the performance of corrosion inhibitors for oilfield pipelines. Typical corrosion and inhibitor protection conditions in oilfield pipelines of the West Siberia region and existing approaches to the laboratory simulation of corrosion situations in oilfield pipelines are discussed. The simulation conditions and capabilities of laboratory test methods are compared.

Key words: corrosion inhibitors, corrosion tests, oilfield pipelines.

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Introduction

Corrosion inhibitors provide a powerful tool for managing the internal corrosion of pipelines in oil production and transportation systems [1-10]. They are widely used by the majority of oil companies. The efficiency of their application directly depends on the choice of chemicals. Selection of the most efficient inhibitors for practical use requires them to be tested under conditions close to the real-life environment. Typically, it is based on pilot testing, *i.e.*, laborious, time taking, and expensive activities that do not ensure that the most appropriate inhibitor will be selected out of a large number of commercially available chemicals. Pilot testing is a mandatory stage in wide-scale application of inhibitors; however, it should be preceded by lab testing to reject the worst and identify the best promising chemicals. This series of publications is dedicated to the lab assessment of the efficiency of corrosion inhibitors at pipelines of West Siberia oil fields.

Selection of the test methods is critical to inhibitor testing [11–19]. These should be simple, accessible methods that match specific types of pipelines. Such matching assumes analysis of the following issues at the work organization stage:

- typical conditions of corrosion occurrence and inhibitor protection at oilfield pipelines, including:
 - chemical composition of the corrosive aqueous phase within the transported fluid;
 - phase composition of the transported fluids;
 - hydrodynamic modes of pipeline operation;
 - temperature modes of pipeline operation;
 - condition of the metal pipeline surface;
- existing approaches to lab simulation of the corrosion environment at oilfield pipelines, including the methods for:
 - corrosive fluid preparation for testing;
 - specimen preparation for testing;
 - corrosion inhibitor efficiency testing with due account of:
 - implemented hydrodynamic and temperature modes;
 - reported data on benchmarking of the test results with the results of pilot testing and/or pipeline operation experience;
 - availability of instrumentation;
 - data reproducibility;
- compliance of the conditions to be simulated with the capabilities of test lab methods.

All these considerations defined the structure of this publication.

1. Typical conditions of corrosion and inhibitor protection of oilfield pipelines in West Siberia region

The chemical composition of the corrosive aqueous phase within the *transported fluid* is the major factor that defines the corrosion situation at oilfield pipelines. General characteristics of the formation water chemical composition at West Siberia fields are given in Table 1.

Analysis of these data makes it possible to classify corrosion developing in oilfield pipelines of West Siberia region as carbon dioxide (CO₂) attack.

It is essential that the concentration of O₂ solution in the water of oil pipeline products (C_{O_2}) is low and ranges within 0.02–0.06 mg/l. Such C_{O_2} considerably reduces the corrosive properties of formation water and increases the efficiency of corrosion inhibitors. However, this is not always observed and so can cause acceleration of the corrosion rate. For example, in water lines of reservoir pressure maintenance systems, C_{O_2} can cover a wider range from 0.02 to 6–8 mg/l. This fact should be considered in development of the model electrolyte formulation.

The phase composition of the transported fluid is obviously different for different service of the pipelines. Presence of hydrocarbons has its effect on the corrosion kinetics and the efficiency of the pipeline protection with inhibitors.

Electrochemical processes of metal corrosion develop in the aqueous solution, while oil that contacts the metal surface can produce hydrophobic films preventing corrosion. On the other hand, the inhibitor concentration in formation water, C_{in} , and hence the pipeline

Indicator	Value at gas fields
HCO ₃ , g/l	0.06 – 3.0
Ca ²⁺ , g/l	0.05 - 1.5
Mg^{2+} , g/l	0.016 - 0.25
Cl ⁻ , g/l	3.2 - 30.0
$Na^+ + K^+$, g/l	0.3 - 10.0
SO_4^{2-} , g/l	0.0008 - 0.10
Total mineralization	5.7 - 25.0
pH	4.7 - 7.0
Dissolved gases:	
O ₂ , mg/l	0.02 - 0.06
CO ₂ , mg/l	33 - 130
H_2S , mg/l	0.002 - 0.011

Table 1. Formation fluid composition in the West Siberia fields of OJSC TNK-BP

protection efficiency, depend on the inhibitor distribution between the aqueous phase and hydrocarbon phases. Besides, the inhibitor can be adsorbed on the interface between aqueous and hydrocarbon phases in quantities that considerably affect the inhibitor concentration and protective properties.

It becomes obvious that the phase composition of the transported fluid is critical for simulation of the corrosion situation at oilfield pipelines. Data characterizing the presence of the hydrocarbon phase in fluids transported by water lines, oil pipelines handling products with high watercut, and pipelines handling products with low watercut are presented in Table 2.

Pipeline service	Temperature range, °C	Presence of hydrocarbons	Wall shear stress, Pa	
Water lines	0-20	_	< 5.2	
Oil pipelines with high watercut	0-50	+	< 168.7	
Oil pipelines with low watercut	0-40	+	< 4.4	

Table 2. Operational conditions in pipelines of various service

Hydrodynamic modes of pipeline operation constitute an important factor that should be simulated in lab tests. In stagnant sections and pipelines with low flow rates, *e.g.* water lines, inhibitors dispersible in water can form a separate phase thus hindering the protection in the aqueous phase. High flow rates of the fluid are also hostile for protection since the inhibitor adsorption films can be washed away from the metal surface.

It is commonly accepted that the key hydrodynamic value characterizing conditions of the fluid transportation in the pipeline is the wall shear stress [20]. This is a characteristic related to the surface that perfectly defines the impact of the flowing fluid on generation and stability of the adsorbed film of a corrosion inhibitor. The maximum values of the wall shear stress for oilfield pipelines of the West Siberia fields are given in Table 2.

In lab simulation of corrosion development and inhibitor protection in pipelines, methods and conditions should be selected that are characterized by wall shear stresses close to real ones. Subject to hydrodynamic conditions in the oil pipelines with high watercut and oil pipelines with low watercut, various flow structures are implemented: stratified flow, emulsion flow, or slug flow. Stratified flow and emulsion flow (oil emulsion in water) are the most hazardous ones in terms of the corrosion. It is these conditions that are subject to simulation in corrosion inhibitor efficiency assessment.

The temperature mode of pipeline operation, according to the analysis, can change from 0 to 50°C. Correlation of typical temperature ranges requiring lab simulation with service of pipelines is given in Table 2.

The condition of the pipeline internal surface can be different since steel can be either passive or active. Simulation of both conditions is required in the course of sample preparation for the tests, since inhibitors that efficiently stabilize the passive state of the metal may not have due effect on the actively dissolving metal and the other way round.

2. Methods for lab simulation of corrosion situation at oilfield pipelines

In order to estimate the effect of hydrocarbons on the protective properties of the film that is developed by inhibitors on the metal, it is expedient to use two-phase systems "hydrocarbons – aqueous electrolyte" to simulate the corrosion situation in pipelines with high watercut of the product and in oil pipelines with low watercut.

Fluids transported by field pipelines are characterized by relatively low C_{O_2} values (Table 1), therefore de-aeration of the corrosive fluid is significant in its preparation for testing. It should be carried out using an inert gas or carbon dioxide, and C_{O_2} should be monitored using an oxygen analyzer.

Preparation of steel samples for testing is an important aspect in the lab simulation of the corrosion situation at oilfield pipelines and inhibitor lab testing. According to [20, 21], preparation of samples for tests is limited to abrading of their surface followed by polishing, degreasing, and drying. In compliance with the recommendations in [22], in

order to simulate active metal, the surface of samples should be activated by acid etching before the tests.

A brief description of the most popular methods of testing the efficiency of corrosion inhibitors for oilfield pipelines is given in Table 3. It provides the key characteristics and assessment of the feasibility of applying the methods for simulation of West Siberia field pipeline conditions.

The static test, *i.e.*, corrosion testing in the absence of a corrosive fluid flow, is recommended [22] for preliminary qualitative and comparative assessment of inhibitors. The test duration can vary widely, depending on the test conditions. This test involves the weight loss method or electrochemical methods to define the corrosion rate, shows good reproducibility of the results and does not require high qualification of the personnel. If no autoclave treatment is used, the temperature of the tests normally does not exceed 80°C. It can be easily performed on standard lab equipment if the weight loss method of corrosion rate measurement is used.

The "wheel test" [14, 23–25] features low rates of the corrosive fluid flow. It is combined with the weight loss method of corrosion rate measurement. Flat steel samples are placed into vessels containing a mixture of brine solution, inhibitor and hydrocarbon, saturated with a gas with the required C_{O_2} and C_{H_2S} values. The vessels are mounted on a special wheel-shaped facility (Fig. 1). Its rotation ensures periodical wetting of the metal surface with the fluid. As a rule, the test duration is 24 hours at t < 80°C. The test shows poor reproducibility of the results and requires expensive equipment that is not manufactured in Russia.



Fig. 1. General view of the wheel facility [25].

The bubble test [20, 24–26] is an unsophisticated test carried out in a glass vessel with tubes for carbon dioxide bubbling. This test can be easily prepared and perfectly fits

for quick delivery of a large number of tests. In practice, a set of test vessels combined on a rack is often used. Each vessel is connected to an automated corrosion rate measurement system using the linear polarization resistance method (Fig. 2). The cells are equipped with special tubes for insertion of a measuring probe. This makes it possible to sink the electrodes directly into the aqueous phase, bypassing the hydrocarbon phase, which prevents them from wetting with hydrocarbons and ensures a better reproducibility of the test. As required, the weight loss method for determination of the corrosion rate can be arranged in the cell. The capabilities of the bubble test are restricted by the fact that the corrosion fluid flow rate against the samples which is provided by a magnetic stirrer is smaller than the flow rates that can be found in pipelines. The approximate value of wall shear stress in the test vessel is 1.2 Pa. The results of the test are not always well reproducible and hence a large number of parallel tests if required. The test is easily implemented using standard lab equipment. "Expert-004" corrosion meters developed at the Institute of Physical Chemistry and Electrochemistry of the Russian Academy of Sciences can be used for corrosion monitoring.



Fig. 2. General view of the facility for parallel bubble tests in 6 cells [26].

Inhibitor testing in a glass U-tube cell is specified in [22, 27]. Figure 3 demonstrates a standard laboratory device for such tests. A test medium flow is generated in a double chamber vessel using a stirrer activated through a hydraulic seal. The chamber where the witness samples are placed is equipped with a thermometer. The test medium is saturated with carbon dioxide which is injected through a special tube. The velocity of the fluid that flows past the witness corrosion samples normally does not exceed 1 m/s. This is much more than the flow rate in the bubble test but less than the rate measured in real pipelines (up to 6 m/s). The wall shear stress in the cell is up to 5.5 Pa.

As a rule, this facility is used along with the weight loss method to determine the corrosion rate. The test results are well reproducible. The temperature of the tests normally does not exceed 80°C. The laboratory test facilities are fabricated by OJSC NII Neftepromkhim.



Fig. 3. General view of the facility for test in U-shaped glass cell.

The rotating cylinder electrode (Fig. 4) [20, 21, 23, 28–33] allows high velocities of turbulent flow to be achieved. The facility design is similar to that used in electrochemical tests with rotating disc electrode, the difference being that the cylinder side surface, rather than its flat end surface, serves as the electrode. Using an appropriate drive system, one can achieve flow velocities that reach or even exceed the real values typical of pipelines. Normally, the fluid flow is turbulent. Due to ease of use, relatively low equipment cost and good reproducibility, this method is currently the most popular for corrosion inhibitor testing. The corrosion rate is determined by the weight loss method and/or from polarization curves. Using the appropriate drive system that ensures rotating rates up to 10000 rpm, wall shear stresses up to 90 Pa can be achieved on the electrode. Typically, the temperature during the test is less than or equal to 80°C.

Rotating cylinder electrode facilities are not made in Russia. However, rotating disc electrode facilities can be easily modified to fit cylinder electrodes. Rotating cylinder electrode facilities are produced by LLC Econics-Expert and LLC NTTs Amplitude. A serious disadvantage of these devices should be pointed out: they are not designed for long (more than 6 hours) continuous operation. This time is not always sufficient for accurate and objective assessment of the inhibitor protective capacity. Potentiostats of nearly any grade can be used to monitor the corrosion rate by the polarization curve method.



Fig. 4. Cylindrical electrode.

The rotating cage test is carried out using a special facility (Fig. 5) [23, 28]. It has the form of a plastic holder with flat samples that is installed on the axis of a motor whose rotation speed is normally 160 rpm. During the test, the holder is inserted into a sealed cell with a model fluid. To enhance flow turbulence, holes are made in the upper and bottom plates of the holder. The method assumes that the corrosion rate is measured by the weight loss method. According to the rotation velocity and the fluid volume in the cell, various modes of interaction between the samples and the gas and liquid environments can be implemented, from a homogeneous stream where the whirlpool does not touch the samples to a turbulent flow where the gas-liquid mixture affects the samples. At the same time, the corrosive fluid flow rate can achieve and even exceed the real values typical of pipelines. The shear stress in the cell can be up to 150 Pa. Equipment for this type of tests is fabricated by Process Measurement and Control Systems (UK).



Fig. 5. Rotating cage facility.

The impingement method is used for corrosion survey in a fluid flow and for assessment of corrosion inhibitor performance [21, 23, 24]. The test facility consists of a central cell with four extensions equipped with spray nozzles. An impeller is installed into the cell; the thrust rod of the former is connected to an electrical motor *via* magnetic transmission. Fluid is pumped from the cell by the impeller through nozzles, washes the samples and returns to the cell. Classically, the test is used in conjunction with the weight loss method of corrosion measurement and its reproducibility is rather good. The shear stress in the cell can reach 1000 Pa if an appropriate nozzle diameter is used. A considerable disadvantage of the method is the instrumentation complexity. Facilities for this type of tests are not manufactured on industrial scale.

The recirculating flow loop facility (Fig. 6) [20] makes it possible to simulate the turbulent flow mode and flow rates similar to the real operational conditions in field oil pipelines in a laboratory environment with the best accuracy. A standard laboratory flow loop has a maximum effective pressure up to 4 atm. It consists of two vessels where the test fluids are treated before the testing, a centrifugal pump with a fluid flow control valve, and a device for heating or cooling of test fluids. The test cell contains samples whose configuration simulates the conditions of the pipe walls. The method allows electrochemical measurements to be carried out in order to define the corrosion kinetics, and the weight loss to be determined. The capabilities of the flow loop are restricted since the same recirculation test fluid is used and accordingly, the absence of the adverse effect of the corrosion products in the fluid on the test results can be guaranteed for a short period of time only (up to 24 h). The achievable shear stress is defined by the geometry and the fluid flow rate. It can reach 225 Pa, which allows the full range of conditions typical of oilfield pipelines to be simulated. The tests have good reproducibility. Equipment for assessment of corrosion inhibitor performance in recirculating flow loop is not manufactured on commercial scale. However, the required facility that is capable of simulating the corrosion situation in water lines, oil pipelines with wet products and oil pipelines with low watercut can be assembled from standard industrial and sanitary equipment.



Fig. 6. Recirculating flow loop.

3. Analysis of compliance between simulated conditions and capabilities of lab test methods. Selection of base test methods

Benchmarking of the corrosion conditions in oilfield pipelines and the capabilities of lab tests is given in Table 3. Analysis demonstrates that the U-shaped cell test, rotating cage test, impingement test, and recirculating flow loop test should be used to assess the efficiency of protection by inhibitors. The rotating cage test, impingement test, and recirculating flow loop test should be used for simulation of inhibitor protection for oil pipelines that carry wet products. The U-shaped cell test, rotating cylinder electrode test, rotating cage test, impingement test, and recirculating flow loop test should be used to simulate the corrosion situation in oil pipelines with small watercut. However, the impingement test requires complicated instrumentation. Facilities of this type are not manufactured on commercial scale, so this method was not reviewed at further work stages.

At the same time, analysis of publications prompts us to include the bubble test into the list of base methods for lab assessment of inhibitor performance. In fact, publications [23, 34–36] compare the results of lab testing of six inhibitors against the results on their performance under natural conditions in oil and gas pipelines. The tests were carried out in a model electrolyte under static conditions using the bubble method, the rotating cage method, on the wheel facility, on rotating disc and cylinder electrodes, and also by the impingement method. The capability of inhibitors to suppress uniform and pitting corrosion was estimated. It was found that the rotating cage method provided the most accurate data on the efficiency of corrosion inhibitors in oil pipelines. The bubble method was ranked second and the rotating cylinder electrode was the third.

Still, it remained unclear to what extent the identified regularities are valid for environments other than the applied model fluid, *e.g.* those simulating the oil production systems of West Siberia region. However, the high rating of the bubble test did not allow us to ignore this method at subsequent work phases.

4. Conclusion

Considering all the above, the rotating cage method, the bubble method, the rotating cylinder method, the U-shaped glass cell test and the recirculating flow loop test were proposed for application as the base test methods for simulation of the corrosion situation in water lines. It was decided to use deaerated model water solutions with $t \le 20^{\circ}$ C as the corrosive fluid.

Simulation of the corrosion situation in oil pipelines carrying wet products was performed using the rotating cage method, the recirculating flow loop test, and the bubble test as the base methods. It was decided to use deaerated two-phase systems (hydrocarbons (5%) – aqueous electrolyte) with equilibrium inhibitor distribution and $t < 50^{\circ}$ C as the corrosive fluid.

In simulation of the corrosion situation in oil pipelines with low watercut, it was decided to use the rotating cage method, the rotating cylinder electrode method, the U-cell test, the recirculating flow loop test, and the bubble test as the base methods. It was decided to use deaerated two-phase systems (hydrocarbons – aqueous electrolyte) with equilibrium inhibitor distribution and $t < 50^{\circ}$ C as the corrosive fluid.

It was also concluded to perform the corrosion tests on air-oxidized passive samples and samples activated through acid etching.

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Test method	Corrosion rate measurement method	Temperature range, °C	Wall shear stress, Pa	Reproducibility of results	Accessibility	Requirements for - staff qualification	Method applicability for simulation of corrosion situation		
							Water lines	Oil pipelines with high watercut	Oil pipelines with low watercut
Static test	Weight loss or electrochemical method	<80	0	high	When using the weight loss method, the corrosion rates can be easily measured on standard lab equipment.	Does not require high staff qualification	-	_	-
Wheel test	Weight loss method	<80	close to 0	low	Requires expensive equipment not manufactured in Russia	Does not require high staff qualification	_	_	_
Bubble test	Polarization resistance or gravimetrical	<80	<1.2	low	Can be easily implemented on standard lab equipment	Does not require high staff qualification	_	_	_
Test in U-cell	Weight loss method	<80	<5.5	high	The test facility is manufactured by OJSC NII Neftepromkhim. The cost of the facility is around 70k rubles	Does not require high staff qualification	+	_	+
Rotating cylinder electrode test	Weight loss method or polarization curves method	<80	<90	high	Facilities for the rotating cylinder electrode are not manufactured in Russia. However, rotating disc electrode facilities can be easily modified to fit cylindrical electrodes. Such facilities are manufactured by Econics-Expert, LLC NTC Amplitude, <i>etc</i> .	The test requires high staff qualification	+	_	+

Table 3. Characteristics of methods for determination of corrosion inhibitor efficiency and applicability assessment.

Test method	Corrosion rate measurement method	Temperature range, °C	Wall shear stress, Pa	Reproducibility of results	Accessibility	Requirements for – staff qualification	Method applicability for simulation of corrosion situation		
							Water lines	Oil pipelines with high watercut	Oil pipelines with low watercut
Rotating cage test	Weight loss method	<80	<150	high	Equipment is made by Process Measurement and Control Systems (UK). The cost of the facility is 7750 £. However, the facility is not complicated and can be easily reproduced in Russia based on a specimen	Does not require high staff qualification	+	+	+
Impingement test	Weight loss method	<80	<1000	high	Facilities for this test are not produced commercially.	Does not require high staff qualification	+	+	+
Recirculating flow loop test	Weight loss method or polarization curves method	<80	<225	high	Equipment is not produced commercially. However, the facility can be assembled on the basis of construction and sanitary equipment. The cost of materials is around 300k rubles.	Does not require high staff qualification	+	+	+