Aspects of protection against carbon dioxide corrosion of gas production facilities

*Dmitry Zapevalov, Ruslan Vagapov**

LLC «Gazprom VNIIGAZ», Center of construction technologies, repair and corrosion protection, 142717, Moscow region, Russian Federation

Abstract. The modern stage of development of many onshore and offshore gas and gas condensate fields is associated with objects in which carbon dioxide (CO₂) gas is present in the production. The presence of CO₂ in the produced gas in combination with other factors stimulates the intensive development of corrosion processes, which requires careful and reasonable attitude both to assess the degree of aggressiveness of the media and to choose technical solutions to ensure reliable and safe operation of hydrocarbon production facilities. The authors analyzed the existing approaches to the assessment of the danger of corrosion produced media, selection and implementation of protection against corrosion in the presence in them of aggressive CO₂.

1 Introduction

The reliable operation and long life of equipment and pipeline systems are the most important tasks for the development of an oil and gas fields. The presence of corrosive components in transported fluids may negatively affect metal. Together with hydrocarbons, the mineralized stratal water containing corrosive gases (carbon dioxide, hydrogen sulfide, etc.) are transported to the surface [1].

Carbon dioxide corrosion is one of the most significant factors causing the destruction of steel equipment and pipelines in the oil and gas industry. The main danger of carbon dioxide corrosion is the formation of local corrosion damage in the form of corrosion cavity and pitting, which depth is very significant in comparison with the general corrosion. The practice of using corrosion inhibitors has shown the success of this method to prevent carbon dioxide corrosion. Hydrocarbon fields can be effectively protected with the use of corrosion inhibitors that form and keep protective film on the corroded steel surface [2].

Considering the variety of operating conditions and their impact on the process of carbon dioxide corrosion, the most important issue is choosing the most effective and technological inhibitor for the given conditions. The article presents the main requirements for corrosion inhibitors used in onshore and offshore gas production.

It is known that the operating conditions of gas and gas condensate fields are different from each other, which affects also on the corrosive activity of the media, its estimation methods and the selection of corrosion protection agents (corrosion inhibitors, etc.).

Carbon dioxide corrosion is characterized by extreme localization of the corrosion process with the formation

of pits and other local forms of corrosion damage. At the same time, the rest, with the exception of the local area with corrosion, a part of the surface of the equipment and pipelines can corrode much less. Unfortunately, it is impossible to predict the place and time of occurrence of carbon dioxide corrosion, which makes this type of corrosion very dangerous and unpredictable.

In a gas pipeline, corrosion may occur:

- in the lower part of the pipe when moisture accumulates (six hours of corrosion);
- in the upper part of the pipe, moisture condensation (top-of-line corrosion);
- in places of moisture accumulation (cracks, gaps, stagnant zones).

2 Determining the aggressiveness of the environment

An important criterion of the degree of aggressiveness of the environment is the partial pressure of CO₂. There are several gradations of media for this indicator with similar parameters: NACE SP 0106-2006 [3], GOST R 51365-2009 [4] и STO Gazprom 9.3-011-2011 [5]. In our article [6] we gave a detailed analysis of the gradations of the danger of carbon dioxide corrosion existing in the regulatory documents. Most documents provide the following basic procedure for determining the corrosivity of environments from internal corrosion in the presence of carbon dioxide:

- environmental conditions containing CO₂ with a partial pressure of more than 0.2 MPa are defined as highly aggressive;
- environmental conditions with a partial pressure of CO₂ in the range of 0.02 (0.05) - 0.2 MPa is

* Corresponding author: R_Vagapov@vniigaz.gazprom.ru

characterized in the range from weakly corrosive to corrosive;
– environmental conditions with a partial pressure of CO₂ less than 0.02 (0.05) MPa are considered non-corrosive.

In all normative documents, it is noted that the presence of other factors (temperature, gas humidity, salinity, pH of the aqueous phase, etc.) increases the aggressiveness of the media, since these factors can increase the corrosion rate and, together with CO₂, lead to the formation of local corrosion damage. The main catalyst for carbon dioxide corrosion is the presence of moisture (formation or condensation water).

At the same time, the determination of CO₂ partial pressure allows only a preliminary assessment of the corrosivity of the environment, and in the presence of other factors, it is necessary to conduct practical experiments to determine the corrosion rate of the steels used in operational media, for example, simulation tests in laboratory conditions.

According to the requirements of regulatory documents, a medium with a corrosion rate higher than 0.1 mm / year refers to systems with high corrosivity, which requires the use of corrosion protection, for example, corrosion inhibitors [7].

So, in the standard NACE SP 0106-2006 [3] for protection against internal corrosion of pipelines and pipeline systems are recommended:

- dehydration (prevention of moisture loss or removal of moisture);
- the use of internal coatings;
- the use of chemical reagents (corrosion inhibitors, etc.).

In offshore production conditions at the subsea production complex or offshore platform, technological methods for preventing moisture deposition or its removal immediately after the fluid leaves the well are often difficult to implement and/or economically impractical. Moisture removal operations are usually carried out ashore (onshore complex), and a corrosive environment is transported via an underwater pipeline, requiring the use of protection from corrosion. The use of internal coatings in the field pipelines also has its limitations.

Gas fields and pipelines, including offshore facilities, can be effectively protected with the use of corrosion inhibitors that form and keep protective film on the corroded steel surface.

3 Simulation test

The approaches for the selection of modeling environments which based on the analysis of produced or condensation waters of gas fields containing carbon dioxide are were considered in our article [8]. When choosing model aqueous environments for the assessment of corrosivity and subsequent corrosion studies, it is recommended to use the method of statistical analysis of water probes from a particular field of gas. As a model medium (aqueous phase) for testing corrosion inhibitors, it is necessary to choose model

water variants that showed the greatest corrosive aggressiveness (taking into account the simulation of actual operating conditions).

A specific feature of corrosion at gas facilities, unlike oil, is that the content of the aqueous phase is insignificant, especially at the initial stages of operation, and the nature of its origin has a condensation character: droplet moisture occurs on the walls to create the necessary temperature and pressure conditions. As noted earlier, the peculiarity of corrosion processes on a gas pipeline consists in the possibility of so-called “top-of-line corrosion” in the upper part of the pipeline during condensation of moisture [9]. This is especially actually given the fact that the carbon dioxide corrosion is mainly local defects.

3.1 Onshore

Table 1 presents the data of our simulation tests under conditions of moisture condensation on steel samples in the presence and in the absence of CO₂ [6]. It can be seen that under conditions of moisture condensation in the presence of CO₂ at 20–25 ° C, the common corrosion rate of steel is 0.01–0.015 mm/year, and the maximum values of the local corrosion rate (on the same samples) are from 0.3 mm/year and above.

Table 1. The rate of general and local corrosion, measured on the same samples under conditions of moisture condensation on samples of carbon steel in the presence and absence of CO₂, temperature 20° C.

Aggressive medium	Rate of common corrosion, mm/year	Rate of local corrosion, mm/year
Presence of 0.1 MPa CO ₂	0.01 – 0.015	0.3 – 0.9
Presence of CO ₂ (from 0.075 MPa and below)	0.01 – 0.02	0.3 – 0.7
Absence of CO ₂ (presence of N ₂)	0.01 – 0.02	Local corrosion is absent

From the data of table 1 it can be seen that serious corrosion losses can occur at partial pressures of CO₂ from 0.075 MPa and below: the common corrosion rate of steel is 0.01-0.02 mm/year; maximum values of local corrosion rate (on the same samples): 0.3 - 0.7 mm/year.

In this regard, it should be noted that even with low values of the partial pressure of CO₂ can be potentially corrosive. The degree of development of corrosion processes, including local ones, may be low, but the localization of the corrosion process poses a serious threat to the integrity and safety of equipment and

A typical appearance of steel samples after the test under moisture condensation in the presence of CO₂ in all the above cases is shown on figure 1: local corrosion damages are visible across the sample surface.

For comparison, table 1 presents data from similar tests under conditions of moisture condensation in the

absence of CO₂ (during the experiment it was replaced by N₂). From these data it can be seen that the rate of common corrosion of steel is 0.01–0.02 mm/year, local corrosion is absent.

Fig. 1. View of carbon steel samples after testing under conditions of moisture condensation in the presence of CO₂.

Testing is aimed at simulating possible operating conditions in order to measure the potential corrosion hazard (corrosion rate). Table 2 shows the test results under different conditions: in the liquid or vapor phases, in an aqueous and/or hydrocarbon environment, under conditions of moisture condensation, under autoclave conditions (at elevated temperature and pressure). Conducting such a complex test allows to determine the corrosivity of the environment.

Table 2. Corrosion test data under different corrosion test

Test type	Test conditions / measurement conditions	Rate of corrosion, mm/year
Aqueous phase	Without hydrocarbon	0.7 – 0.8
	With hydrocarbon	0.17 – 0.39
Vapour phase	Without contact with aqueous phase	0.008 – 0.013
Under moisture condensation	Common corrosion	0.010 – 0.015
	Local corrosion	0.3 – 0.9
Autoclave test (aqueous phase)	Under elevated pressure and temperature	0.13 – 0.44

From table 2 it can be seen that:

- in the vapor phase, in the absence of moisture, corrosion will not develop;
- in conditions of moisture condensation, intense local corrosion occurs;
- in conditions of a constant film of moisture (in places where moisture can accumulate), common corrosion will intensively flow, turning into local one over time.

3.2 Offshore

In practice, the media consists of hydrocarbon and water parts. The water portion is a water-alcohol or water-glycol solution due to the use of methanol or monoethylene glycol (MEG) as inhibitors of hydrate formation. MEG is primarily used at offshore facilities. Both aqueous and glycol solutions should be used as test media in addition to hydrocarbons in determining corrosivity and selecting corrosion inhibitors.

Data from the table 3 show that with an increase in the concentration of MEG in the solution, the corrosion rate of carbon steel decreases at 20°C: 0.3, 0.4, 0.85 mm/year at 50%, 75% and 100% water in tested solutions (water:MEG) accordingly. The highest rate of corrosion is observed at 60°C: from 0.5–1.5 mm/year depending on water content of a mixture of water and MEG. A similar trend to increase corrosion rate with temperature is observed in autoclave tests (under elevated pressure and temperature).

Table 3. Corrosion test data of carbon steel under different corrosion conditions for offshore facilities in the presence of CO₂.

Test type	Temperature	Rate of corrosion, mm/year
Water	20°C	0.85
	60°C	1.5
Water:MEG (3:1)	20°C	0.4
	60°C	0.9
Water:MEG (1:1)	20°C	0.3
	60°C	0.5
Water:Hydrocarbon (5:1)	60°C	0.8
	75°C	0.25
Autoclave test (aqueous phase)	60°C	0.42
	75°C	0.25

Table 4 presents the data of simulation tests under conditions of moisture condensation on steel samples in the presence and in the absence of CO₂ (“top-of-line corrosion”). Under conditions of moisture condensation in the presence of CO₂ at 20–25°C, the common corrosion rate of steel is 0.01–0.09 mm/year, and the maximum values of the local corrosion rate (on the same samples) are from 0.3 to 1.2 mm/year and above. Condensation of both the aqueous phase and the aqueous solution of MEG causes high local corrosion of carbon steel.

Table 4. The rate of general and local corrosion, measured on the same samples under conditions of moisture condensation (water:MEG) on samples of carbon steel in the presence of 0,1 MPa CO₂, temperature 20° C.

Aggressive medium	Rate of common corrosion, mm/year	Rate of local corrosion, mm/year
Water:MEG (1 :1)	0.01 – 0.09	0.9 -1.2
Water	0.01 – 0.015	0.3 – 0.9

A typical appearance of carbon steel samples after the test under moisture condensation (Water-MEG mixture) in the presence of CO₂ is same as it is shown on figure 1: local corrosion damages are visible across the sample surface.

4 Corrosion inhibitors

The operating conditions of gas and oil fields are different from each other, which affects also on the requirements to corrosion inhibitors.

The inhibitors applied during the operation of gas equipment and pipelines should satisfy a number of protecting and technological requirements:

- they should be soluble or dispersible at least in one of solvents (water or brine; alcohol; hydrocarbons);
- they should not create emulsions in mixture of water and condensates;
- they should ensure a highly protective effect;
- they should prevent the formation of pitting;
- they should be stable to lower temperature;
- they should be non-toxic;
- they should have strong after-effects.

Inhibitors for oil fields cannot be used in gas fields without modification: the active basis of the corrosion protection reagent may remain the same, but additives are needed that determine the inhibitor's technological parameters: solubility, freezing point, tendency to form an emulsion, and others.

The results of our tests of the technological properties of corrosion inhibitors showed in [10] that inhibitors may have their limitations on technological properties that must be considered when choosing an inhibitor for gas fields.

Examples of results on the determination of the effect of an inhibitor on the separation time of a hydrocarbon-water emulsion when a complete emulsion separates or does not occur in the presence of a corrosion inhibitor are shown on figure 2.

Fig. 2. Photo of the results of the separation of the emulsion "hydrocarbon-water".

Examples of precipitation in solutions of corrosion inhibitors in alcohol are shown on figure 3, which limits the use of solutions of such inhibitors at low ambient temperatures (to minus 50-60°C) .

Fig. 3. Precipitation in a solution of a corrosion inhibitor in alcohol at a negative temperature.

4.1 Onshore

The results of laboratory tests showed the possibility of a significant reduction in corrosion of carbon steel by corrosion inhibitors in the presence of carbon dioxide under conditions simulating the corrosive environment of gas condensate wells and field pipelines. According to the requirements of regulatory documents for onshore facilities [7], corrosion rate at the presence of corrosion inhibitors must be less than 0.1 mm/year.

The tests have shown [10] that the introduction of inhibitors helps to reduce the corrosion rate, however, not all inhibitors at the same time provide a reduction in the corrosion rate to 0.1 mm/year.

According to the results of our laboratory and autoclave tests aimed at determining the protective and technological properties, the most effective corrosion inhibitor (corrosion rate less 0.1 mm/year) for the gas

field was selected, where its field tests were carried out. These tests confirmed its high protective properties: the corrosion rate is significantly below the threshold value of 0.1 mm/year. The mode of supply of the inhibitor to the pipelines of the gas collection system is constant dosing [11].

4.2 Offshore

According to the requirements of regulatory documents for offshore facilities [12], corrosion rate at the presence of corrosion inhibitors must be less than 0.1 mm/year.

The results of our laboratory tests are presented in table 3. Not all inhibitors can provide a reduction in the corrosion rate to 0.1 mm/year in all tested conditions. Some inhibitors can be effective and reduce the corrosion rate to values less than 0.1 mm/year.

Table 5. Test data of corrosion inhibitors under different corrosion conditions for offshore facilities

Test type	Temperature	Type of corrosion inhibitor	Rate of corrosion, mm/year
Water	20°C	Inhibitor 1	0.05
		Inhibitor 2	0.04
	60°C	Inhibitor 1	0.125
		Inhibitor 2	0.082
Water:MEG (3:1)	20°C	Inhibitor 1	0.09
		Inhibitor 2	0.06
	60°C	Inhibitor 1	0.1
		Inhibitor 2	0.09
Water:MEG (1:1)	20°C	Inhibitor 1	0.085
		Inhibitor 2	0.057
	60°C	Inhibitor 1	0.27
		Inhibitor 2	0.07

The results of laboratory, autoclave and field tests confirm, that for onshore and offshore gas production facilities it is possible to select corrosion inhibitors that are effective in protecting against carbon dioxide corrosion. In each case, depending on the operating conditions, adjustment of the formulation is required to bring the technological indicators of corrosion inhibitors to the required level.

5 Conclusions

- Presented data suggested that the selection of model media for testing, justification of the choice of test methods, the results of tests on the effectiveness of

corrosion inhibitors, should be accord to the operating conditions of gas onshore and offshore fields. Simulation tests should include all possible factors of corrosive effects.

- Inhibitor protection is one of the most appropriate and cost efficient ways to address the problem of carbon dioxide corrosion.
- For gas production onshore and offshore facilities it is possible to select corrosion inhibitors that are effective in protecting against carbon dioxide corrosion.
- Corrosion inhibitors must correspond to both protective and technological properties. The requirements for corrosion inhibitors at gas facilities are different compared to oil facilities, which are due to the specific operating conditions of gas onshore and offshore fields in which they are used.

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