Abstract. At the present stage of gas field development, the products of many mining facilities have increased content of corrosive CO₂. The corrosive effect of CO₂ on steel equipment and pipelines is determined by the conditions of its use. CO₂ has a potentially wide range of usage at oil and gas facilities for solving technological problems (during production, transportation, storage, etc.). Simulation tests and analysis were carried out to assess the corrosion effect of CO₂ on typical steels (carbon, low-alloy and alloyed) used at field facilities. Gas production facilities demonstrate several corrosion formation zones: lower part of the pipe (when moisture accumulates) and top of the pipe (in case of moisture condensation). The authors have analyzed the main factors influencing the intensity of carbon dioxide corrosion processes at hydrocarbon production with CO₂, its storage and use for various technological purposes. The main mechanism for development of carbon dioxide corrosion is presence/condensation of moisture, which triggers the corrosion process, including the formation of local defects (pits, etc.). X-ray diffraction was used for the analysis of corrosion products formed on the steel surface, which can have different protective characteristics depending on the phase state (amorphous or crystalline).

Keywords: oil and gas facilities, carbon dioxide, media corrosiveness, carbon dioxide corrosion, corrosion rate

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In recent years, the problem of carbon dioxide corrosion (CDC) in gas fields has become relevant. In the Russian Federation in recent years at a number of gas facilities, problems of corrosive nature have arisen due to the increased content of carbon dioxide in the produced products [1]. Taking into account corrosion risks (including due to the CDC) plays an important role in the processes of ensuring the reliable and safe operation of enterprises for hydrocarbons extraction [2 – 3]. To control the technical condition of gas production and underground storage
facilities, a set of measures is used, including diagnostic surveys and corrosion monitoring [4].

Carbon dioxide (CO$_2$) can be in several states of aggregation: gas, liquid and supercritical (SCS). The so-called “triple point” connects all three states of CO$_2$ ($P_{cr} = 7.38$ MPa and $T_{cr} = 31.1$ °C), depending on change on which the type of aggregate state is determined.

At gas production facilities, the partial pressure is relatively low, and CO$_2$ is in gaseous aggregate state. It should be noted that CO$_2$ is not only a component in the composition of produced products, but can also be used at oil and gas facilities for technological tasks. In this case, the above-mentioned special properties of CO$_2$ can be effectively used, including in SCS. Among the most commonly used are the use of CO$_2$ to intensify oil or gas production at the later stages of field exploitation and as a buffer gas in underground gas storage (UGS) facilities [5]. It should be also mentioned about the injection of excess CO$_2$ into underground storage facilities in order to reduce its emissions into the environment [6 – 7]. For these purposes, both the infrastructure for pumping gas into underground reservoirs and pipelines for transporting it from the places of CO$_2$ separation to the disposal site are being arranged [8]. For such purposes, underground caverns are used after the end of the exploitation of oil or gas fields, geological cavities with aquifers [9 – 10].

In all of the above cases, aggressive CO$_2$ comes into contact with steel equipment and pipeline systems, which in the presence of an aqueous phase and other factors intensifying corrosion (temperature, etc.) can lead to the development of corrosion damage. In the first place, the most dangerous forms of local defects typical for CDC will develop. In this regard, the article discusses topical issues of assessing the corrosiveness of carbon dioxide media and the resistance of various steels in the conditions of CDC at oil and gas facilities.

### RESULTS AND DISCUSSION

Let us consider the corrosiveness of the medium of gas production facilities in conditions of increased CO$_2$ content. The analysis shows that the most corrosive type of equipment at gas production facilities are downhole equipment and field pipelines. Under such conditions, corrosion can occur [12]:
- at the pipe bottom when moisture accumulates (bottom-of-line corrosion, BOL corrosion);
- at the pipe top in case of moisture condensation (top-of-line corrosion, TOL corrosion);
- in places where moisture accumulates (cracks, gaps, stagnant zones, elevation differences, etc.).

The main condition for corrosion process development is the presence of moisture when reactions of its interaction with steel in the solution volume (BOL) or in a thin film of moisture on steel (TOL) occur. TOL corrosion in contrast to the corrosive conditions of oil facilities is typical for gas fields. When leaving the well, water vapor in the gas phase condenses on the pipe inner surface due to the temperature difference between the wet gas flow and the environment, which leads to the appearance and TOL corrosion development. BOL corrosion will be typical in sections of the pipeline system when the water phase is in constant contact/movement with the inner surface of the pipeline steel [13 – 14].

Results of the autoclave tests (Table 1) show that with an increase in CO$_2$ partial pressure the corrosion rate of steel St20 mainly grows, as well as with an increase in temperature. It should be borne in mind that with an increase in temperature deposits can form including the form of corrosion products. The resulting solid sediments (iron carbonates, etc.) at 80 – 90 °C may have certain protective properties, because they form more tightly packed than at lower temperatures. Probably, it is precisely with this that the fact that at 80 – 90 °C is not observed a stronger increase, as in other types of corrosion, increase in the rate of CDC. This test simulates BOL corrosion conditions.

Our TOL tests in the presence of CO$_2$ showed that at a low (less than 0.1 mm/year) rate of general corrosion, carbon steel X65 (API 5L) undergoes severe lo-
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General corrosion rate (mm/year) of steel St20 according to the results of autoclave tests

| Partial pressure CO\textsubscript{2}, MPa | Temperature and mineralization of the aquatic environment, °C | \(K_{loc,aver}\) | \(K_{loc}\text{max}\) |
|------------------------------------------|-------------------------------------------------|-----------------|-----------------|
|                                         | 30 \, 60 \, 80 \, 90 \, 3 \% NaCl \, 0.5 \% NaCl |                 |                 |
| 0                                       | 0.073 \, 0.065 \, 0.063 \, 0.065 \, 0.120 \, 0.093 \, 0.108 | 0.269 \, 0.241 \, 0.240 \, 0.522 \, 0.338 \, 0.490 \, 0.476 | 0.299 \, 0.387 \, 0.265 |
| 1                                       | 0.221 \, 0.203 \, 0.241 \, 0.240 \, 0.590 \, 0.539 \, 0.553 |                 |                 |
| 4                                       | 0.201 \, 0.196 \, 0.365 \, 0.331 \, 0.590 \, 0.539 \, 0.553 | 0.269 \, 0.241 \, 0.240 \, 0.522 \, 0.338 \, 0.490 \, 0.476 | 0.299 \, 0.387 \, 0.265 |

Table 1. Скорость общей коррозии (мм/год) стали Ст20 по результатам автоклавных испытаний

Table 2. Результаты испытаний по определению локальных скоростей коррозии, рассчитанных по средней \((K_{loc,aver})\) и максимальной \((K_{loc, max})\) глубине коррозионных повреждений на стали X65 в среде CO\textsubscript{2} и конденсации влаги
cesses not only for gaseous, but also for other aggregate states of CO$_2$. According to [16], for each of the aggregate states of CO$_2$ there is a critical value of water content for the beginning of corrosion localization: 80 % humidity – for gas; 60 % – for liquid and SCS. The authors carried out the tests on steel X65 at 25 – 35 °C and increased values of CO$_2$ pressure (4 – 8 MPa).

Analysis of the effect of various salts (in low concentration) showed that they insignificantly affect the corrosion rate in the vapor phase [17]. An increase in the rate of localized corrosion will be influenced by an increase in water content in the test chamber, which will remain approximately the same when the mineral composition changes and the medium mineralization remains unchanged. An increase in local corrosion is possible only if, as a result of the dissociation of salt in water, its acidification and/or the formation of acid gases occurs.

The test results confirm that gas facilities operated in conditions of CO$_2$ presence in the extracted products are subject to increased corrosion hazard in the water and vapor phases, especially to local corrosion typical for CDC.

Corrosion products formed on the metal surface play a certain role in the protection of steels from corrosion. Tests carried out in an aqueous medium (Figure a) to determine the phase composition of the film formed on steel after autoclave tests showed that siderite (FeCO$_3$) is formed predominantly during CDC, and mackinawite (FeS) can form in the presence of hydrogen sulfide impurities, both independently and together with FeCO$_3$.

In addition to the amount of CO$_2$, CDC in the aqueous environment is influenced by its mineral composition. UGS facilities and CO$_2$ storage sites are often located in aquifers [18]. The authors of [19] provide data on the effect of saline water and its composition (up to 35,000 ppm Cl$^-$, 10,000 ppm Ca$^{2+}$ and 10,000 ppm Mg$^{2+}$) on the corrosion resistance of steel X65 (0.11 % Cr) in the conditions of SCS corrosive gas formation. Simulation tests were carried out in an aqueous electrolyte saturated with CO$_2$ (60 °C, 10 MPa). The main initiator of corrosion localization was the presence of chloride anions in water which contribute to the formation of iron carbonate (in the form of deposits of corrosion products). The addition of Ca$^{2+}$ and Mg$^{2+}$ has a different effect on the properties of corrosion deposits, their morphology and coprecipitation together with iron carbonate on steel. The resulting local corrosion defects had a depth of 20 – 50 μm.

As in our tests (Figure a) at a CO$_2$ pressure of 0.8 MPa, in the study [20], siderite was obtained in a NaCl solution at 80 °C saturated with CO$_2$ (but at a higher pressure of 15 MPa). However, with the addition of other salts, for example, CaCO$_3$, the layer of corrosion products turned out to be more porous and less resistant to chloride anions, which provoke the nucleation and development of pits, in contrast to the denser siderite layer.

Identified experimental diffraction pattern of corrosion products after autoclave tests on steel X65:

\[
\begin{align*}
\text{a} & - P_{CO_2} = 0.8 \text{ MPa, temperature } 80 \degree C, 3 \% \text{ NaCl; } \\
\text{b} & - P_{H_2S} = 0.15 \text{ MPa, temperature } 60 \degree C, \text{ salinity of the water phase } 1 \text{ g/l} \end{align*}
\]

(arrow indicates an X-ray amorphous gallo, asterisk indicates X65 steel signal)

Identифицированная экспериментальная дифрактограмма продуктов коррозии, полученных после автоклавных испытаний на стали X65:

\[
\begin{align*}
\text{a} & - P_{CO_2} = 0.8 \text{ МПа, температура } 80 \degree C, 3 \% \text{ NaCl; } \\
\text{b} & - P_{H_2S} = 0.15 \text{ МПа, температура } 60 \degree C, \text{ минерализация водной фазы } 1 \text{ г/л} \end{align*}
\]

(стрелкой указано рентгеноаморфное галло, звездочкой – сигнал от стали X65)
Tests of carbon steel X65 at 25 – 60 °C and a pressure of 2.0 – 14.5 MPa showed [21] that the corrosion rate at first can reach up to 28 mm/year, then decreasing to 1 mm/year. The formation of corrosion products can inhibit the corrosion process over time, but their protective properties will depend on the temperature of the environment. At higher temperatures, denser and less porous films were formed, mainly consisting of siderite. The steel surface also plays a role: presence of cementite at the interface led to formation of loose films of corrosion products.

The temperature factor can also intensify the corrosion processes. Investigation of the effect of temperature (35 °C and 50 °C) at SCS (8 MPa CO₂) for steel X65 (0.11 % Cr) showed [22] that the development of local defects is observed: the rate of local corrosion can reach 0.3 – 0.9 mm/year (at 35 °C), increasing to 0.9 – 1.7 mm/year (at 50 °C). It is also noted that an increase in local corrosion occurs with an increase in the amount of water.

An important role in the corrosiveness of CO₂, both in the gas and in SCS, is played by the presence of impurities in it, such as SO₂, H₂S, etc.

TOL corrosion tests in a CO₂ environment with small additions of H₂S (50 ppm) on steel X65 showed (Table 3) that the local corrosion rate reaches 0.90 – 1.37 mm/year. On the samples, pits are observed, up to 50 – 100 μm in depth, which were formed during 30 days of the test. Difference in the rate of local corrosion, which was at CDC (Table 2), is leveled in the presence of H₂S. This is apparently due to the higher corrosivity of H₂S compared to CO₂.

It is also noted in [23] that even small additions of H₂S (21 ppm) to the aqueous CO₂ medium lead to a change in the corrosion mechanism from carbon dioxide to hydrogen sulfide. In this case, composition of the corrosion products also changes: only mackinawite is formed on the steel (without traces of siderite). According to the authors, the formed FeS film on steel X65 is not capable of being a barrier to the penetration of corrosive components to the steel surface. This may be due to the small thickness of FeS layer which directly depends on H₂S content. According to the results of the autoclave tests in an aqueous H₂S-containing medium (Figure b), mackinawite crystals were also found on steel X65, but their content does not exceed 40 %. The diffractogram shows that there is an X-ray amorphous gallo: the content of amorphous compounds reaches 60 %. The morphology of mackinawite (density, absence/presence of pores), as well as its thickness, will affect the barrier properties of the formed corrosion products in relation to H₂S corrosion. Fully crystallized substances will form a more densely packed film of corrosion products.

In [24], results of the studies at a temperature of 35 °C and in SCS (8 MPa CO₂) for steels X65 (0.11 % Cr) and

| Type of sample | \(K_{\text{dyn.}}\), mm/year | \(K_{\text{loc. aver.}}\), mm/year | \(K_{\text{loc. max.}}\), mm/year | Photo of sample after removal of corrosion products | Depth of corrosion damage, micron |
|----------------|----------------------------|---------------------------------|-------------------------------|-----------------------------------------------|----------------------------------|
| Base metal     | 0.0208                     | 0.978                           | 1.371                         | ![Photo](image)                                | 114, 106, 88, 80, 60, 70, 68, 48, 48, 54, 68, 82, 78, 82, 100, 98, 82, 68, 76, 66, 46 |
|                | 0.0200                     | 0.926                           | 1.264                         | ![Photo](image)                                | 66, 60, 66, 58, 60, 64, 76, 54, 98, 58, 58, 56, 66, 68, 62, 120, 82, 88, 64, 88, 60, 76, 92 |
| Weld           | 0.0179                     | 0.886                           | 1.121                         | ![Photo](image)                                | 54, 56, 74, 68, 72, 100, 70, 36, 80, 54, 82, 78, 82, 44, 62, 80, 72, 64 |
|                | 0.0156                     | 1.056                           | 1.317                         | ![Photo](image)                                | 86, 92, 62, 90, 60, 88, 70, 70, 86, 72, 90, 64, 70, 74, 64, 92, 76, 74, 96, 94, 130, 70, 80, 94, 72 |
13Cr (13 % Cr) are given. The addition of two other aggressive gases (SO$_2$ and O$_2$) to CO$_2$ in the presence of moisture leads to a synergistic effect in corrosion process development. The general corrosion rate for both steels is equally high: 0.95 mm/year for X65 steel, and 0.65 mm/year for 13Cr steel. Pitting corrosion is even higher for both steels (X65 and 13Cr), and ranges from 7 to 80 mm/year. The presence of impurities leads to the formation of other corrosion products: iron oxides and iron sulfate instead of iron carbonate. Dissolution of SO$_2$ in an aqueous film leads to the formation of extremely corrosive sulfuric acid, the destructive effect of which is enhanced by the presence of a strong oxidizing agent in the form of O$_2$.

The presence of sulfur compounds (SO$_2$, H$_2$S) even in small trace amounts, negatively affects the corrosive situation in CDC, enhancing its development.

The use of high-alloy steels (with a high chromium content for corrosion protection) is not always able to provide protection against CDC. Tests of carbon (X65) and alloyed (13Cr) steels showed that at a temperature of 80 °C and high CO$_2$ pressure (13.5 MPa) the local corrosion rate can reach 15.6 and 0.32 mm/year, respectively [25]. Another work [26] provides comparative test results for similar steels X65, C75 and X20Cr13 in an aqueous medium saturated with SCS CO$_2$ at elevated temperatures (50 – 130 °C) and CO$_2$ pressure (9.5 – 21.5 MPa). The general corrosion rate for carbon steels (C75 and X65) reached 3.5 – 15 mm/year, local defects were observed on the metal surface. In corrosion-resistant steel X20Cr13, the general corrosion rate reaches 0.3 – 0.8 mm/year (there were no local defects). According to [27], in the presence of impurity gases in CO$_2$ in SCS, chloride anions from the aqueous medium play an important role in formation and development of local defects on alloyed steel 13Cr, which locally destroy the film of corrosion products.

In such aggressive conditions, high-alloy steels can be used for the protection of steel equipment and pipelines which, however, in some particularly aggressive conditions also require the use of anti-corrosion protection means [28]. Carbon and low-alloy steels that are not resistant to CDC, as well as some alloyed ones, can be protected by corrosion inhibitors or coatings. On carbon or low-alloy steels at 80 °C and 12 MPa CO$_2$ in the presence of inhibitors, the corrosion rate can decrease to 0.1 mm/year [29]. A decrease in corrosion tenfold compared to background values is observed. Although the initial background corrosion rate on low alloy steels is lower than on carbon steels, the inhibitor protects carbon steels better than low-alloy steels. This is explained by the morphology of corrosion products: on low-alloy steels they are thicker and more porous, which can negatively affect the adsorption of corrosion inhibitor.

Somewhat different results were shown by tests of a number of CDC inhibitors in an aqueous medium saturated with SCS CO$_2$ at elevated temperatures (50 – 130 °C) and CO$_2$ pressure (9.5 – 21.5 MPa) [26]. These conditions are more aggressive and, apparently, it is precisely with this that the use of inhibitors for carbon steels, although it leads to a significant decrease in corrosion rate, it does not fall below 1 mm/year: increased temperature conditions lead to a higher corrosive influence of environments on carbon steels (X65 and C75). Reagents more effectively inhibit CDC on alloyed X20Cr13 steel, reducing it below 0.1 mm/year.

Tests of carbon steel at 50 °C and 10 MPa showed [30] that in the vapor phase over 5 % NaCl the corrosion rate is 0.06 mm/year, and in the water phase – 0.62 mm/year. When SO$_2$ is added to this system, the corrosion rate increases by 5 – 14 times to 3.6 and 8.2 mm/year for the vapor and water phases, respectively. Tests of 3 inhibitors have confirmed that they are capable of protecting steel in such aggressive environments: the corrosion rate decreases to 0.13 – 0.18 mm/year, and for the most effective – to 0.07 – 0.09 mm/year.

Coatings can also be used for CDC protection. In [31], the possibility of using conversion coatings of a complex composition for the protection of pipelines transporting CO$_2$, including under conditions of acidification of the aqueous phase, is discussed. It is important for coatings to be non-porous. The authors of [32] report the use of a metal microstructured Ni–Co coating with corrosion resistance for protection in CO$_2$ conditions.

Conclusions

Analysis of the research results shows that when CO$_2$ is used, both in gas and SCS, the main corrosion factors will be the possibility of moisture condensation and the dissolution of CO$_2$, in which will trigger the CDC mechanism. To investigate such corrosion cases, it is important to exhibit TOL corrosion tests. The presence of impurity gases will affect the acceleration of corrosion process. An important factor of the protective effect is phase composition and morphology of corrosion products. Corrosion inhibitors and coatings can be used to protect steel against corrosion in the presence of CO$_2$ (in various states of aggregation).

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Rafael’ R. Kantyukov, Cand. Sci. (Eng.), Deputy General Director for Research, Scientific-Research Institute of Natural Gases and Gas Technologies – “Gazprom VNIIGAZ”
ORCID: 0000-0003-3339-4774
E-mail: vniigaz@vniigaz.gazprom.ru

Dmitrii N. Zapevalov, Cand. Sci. (Eng.), Head of the Corporate Scientific and Technical Center for Corrosion Monitoring and Protection, Scientific-Research Institute of Natural Gases and Gas Technologies – “Gazprom VNIIGAZ”
ORCID: 0000-0002-2867-1995
E-mail: D.Zapevalov@vniigaz.gazprom.ru

Ruslan K. Vagapov, Cand. Sci. (Chem.), Head of the Laboratory of Atmospheric and Internal Corrosion Protection, Scientific-Research Institute of Natural Gases and Gas Technologies – “Gazprom VNIIGAZ”
ORCID: 0000-0002-8467-4103
E-mail: R.Vagapov@vniigaz.gazprom.ru

Contributions of the authors:
R.R. Kantyukov – formation of the article concept, goals and objectives of the study, correction of conclusions.
D.N. Zapevalov – scientific guidance, revision and correction of the text, formation of conclusions.
R.K. Vagapov – analysis of research results, text formation, search and analysis of literature data, text formatting and design.