Causes of corrosion cracking of pipe metal and methods for their protection

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Abstract. The article is devoted to studying the problem of corrosion cracking of pipelines and methods of their protection. An analysis of the main factors that determine the phenomenon of corrosion cracking is given. The article deals with the issue of identification of corrosion cracking based on the "carbonate theory". The main methods of protection of metal structures from corrosion cracking are given.

1 Introduction

One of the complex and dangerous types of destruction of main pipelines, in particular, gas pipelines, is stress corrosion cracking, which occurs under the influence of tensile mechanical stresses and a corrosive environment. This is one of the local types of corrosion, which also refers to stress corrosion or mechanochemical corrosion.

In the 1970s, American scientists proposed the term "Stress corrosion cracking in carbonate-bicarbonate solutions" to identify this type of corrosion-mechanical failure [6]. In order to describe the phenomenon of corrosion cracking, the following terms are used in the literature: carbonate corrosion cracking; stress corrosion cracking; stress corrosion.

Corrosion cracking is a complex process and depends on many factors: the composition of the corrosion medium, the chemical and phase composition of the material, the nature and magnitude of internal stresses, and the magnitude of tensile stresses applied from outside.

According to the adsorption-electrochemical theory of corrosion cracking proposed by G.V. Karpenko, in the initial period of stress corrosion on the steel surface in the most active areas, specific selective adsorption of molecules or ions from the electrolyte occurs, causing the Rebinder effect (the effect of adsorption strength reduction) and facilitating the formation and growth of initial microcracks. The second period of crack development is associated with the electrochemical process, namely with the anodic dissolution of the metal in the crack. It should be noted that during stress corrosion proceeding with hydrogen depolarization, the second period is also associated with metal hydrogenation in the cathode regions, which can lead to hydrogen embrittlement. In general, the formation of a crack during corrosion cracking is associated with the localization and strengthening of the

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anodic process in a narrow region of the steel surface, while the rest of the metal surface remains cathodically protected [2].

2 Materials and methods

For pipelines transporting a gaseous medium, corrosion cracking remains the most dangerous type of stress corrosion [7, 12]. Stress corrosion cracking mainly affects straight-seam and spiral-seam pipes with film and rubber-bitumen insulation, especially in places where the continuity of the coating is broken, there are defects or delaminations. It has also been recorded that the majority of corrosion cracking cracks are formed near gas compressor stations. This is due to the high temperature and pressure of the pumped product in this section of the pipeline, as well as increased vibration caused by the operation of pumping stations. Disruption of the integrity of the insulation of the lower generatrix of the pipes can occur under the action of the hydrostatic pressure of groundwater as a result of an increase in their level. Under the exfoliated insulation, conditions may arise for the occurrence of electrochemical corrosion, which also contributes to the development of corrosion cracking cracks. These cracks are localized on the outer surface of pipes with cathodic protection and propagate intercrystalline along the grain boundaries or transcrystalline along the body of the grain. [5].

The development of a crack, which occurs inter- or transcrystalline, goes through three stages:

- Stage of crack initiation.
- During this stage, a carbonate-bicarbonate environment is also formed in areas of the pipe surface with damaged insulation.
- Stage of stable crack growth.
- Corrosion erosion of the cavity of the nucleated crack in the pipe occurs here.
- Stage of mechanical blasting.

The first stage of crack formation is called the incubation period, when cracks are not visible visually. When calculating the durability of the pipe material, only the duration of the first and second stages of crack development is taken into account due to the instantaneous, uncontrolled flow of the third stage of mechanical fracture. After conducting numerous studies of the phenomenon of corrosion cracking on a large number of samples of emergency metal, Professor A.G. Gareev proposed a formula for predicting this type of fracture, which makes it possible to calculate the effective cracking rate [7]:

$$v_{эфф.} = \frac{\sigma}{\sigma_t \cdot (t-b)} \cdot a \cdot \delta \cdot e^{\frac{-Q}{RT}} v_{эфф.} = \frac{\sigma}{\sigma_t \cdot (t-b)} \cdot a \cdot \delta \cdot e^{\frac{-Q}{RT}}, \quad (1)$$

Where T is the absolute temperature; R is the universal gas constant; k is the pre-exponential normalizing factor; δ is the pipe wall thickness; a is an empirical coefficient characterizing SCC parameters; t is the time until the failure of the gas pipeline; b is the duration of the stage of formation of the near-electrode medium; σ are stresses; σ_t is the yield strength of steel.

At the initial stages of crack development in steels of the ferrite-pearlitic class, intergranular crack development with further transcrystalline propagation can be observed.

Many authors have noted that to describe the mechanism of corrosion cracking, the “carbonate theory” is most widely used, according to which a corrosion crack will develop provided that the rate of dissolution of the crack tip exceeds the rate of development of corrosion processes on the pipe surface and the rate of dissolution of the crack walls [1].

The carbonate-bicarbonate environment provokes corrosion cracking, damaging the grain boundaries. It is this phenomenon that explains the intergranular development of a crack. As a result of cathodic protection, alkalization of ground electrolytes occurs in the places where the protective film is destroyed:

$$H_2O \xrightarrow{I_{к.з.}} 2H^+ + OH^-, \tag{2}$$

$$CO_2 + OH^- \leftrightarrow HCO_3^- \tag{3}$$

$$HCO_3^- + OH^- \leftrightarrow CO_3^- + H_2O \tag{4}$$

As a result of the chemical interaction of carbon dioxide with hydroxyl ions on the surface of the pipeline in places where the integrity of the anti-corrosion insulation is broken, under the action of cathodic protection currents, salts of carbonic acid are formed, such as carbonates and bicarbonates (formulas 2-4).

Carbonate-bicarbonate ions interact with cations of alkali and alkaline earth metals contained in soils and form salts of the corresponding metals on the surface of the underground pipeline, which are cathodic deposits.

As a result of these reactions, an alkaline environment with pH = 12 in terms of the hydrogen index is formed on the pipe surface in places where there is no or broken insulation and in the crack itself, which creates the main conditions for the occurrence of corrosion cracking. Carbonates and bicarbonates can passivate steel in the presence of oxygen and are used in industry as anodic corrosion inhibitors. However, discontinuity of the insulating coating on the surface of the pipeline increases localized corrosion.

In contrast to corrosion fatigue, cracks caused by corrosion cracking are not rigidly linked to stress concentrators [8]. On the contrary, in some cases, geometric stress concentrators, including welds, risks and scratches, dissolve in the fracture site. In this case, the crack initiation occurs away from the stress concentrator on a practically defect-free surface and develops without noticing the concentrator. In addition, the development of cracks occurs at stresses below the working ones in the pipe wall. The time to stress corrosion cracking progressively increases with decreasing tensile stresses for all types of steel prone to this process. In some cases, the statistical period from the onset of corrosion cracking to depressurization of the gas pipeline can be on the order of ten years. In this regard, corrosion cracking is a rather long process [3].

During operation, single cracks or their systems appear on the supporting surface of the pipeline along the lower generatrix under the exfoliated insulation. Accordingly, the crack develops from the outer surface of the pipe with the formation of a viscous fracture on its inner surface in the direction perpendicular to the plane of action of the ring tensile stresses, which are maximum at internal pressure [12].

3 Results

The main technological methods for combating corrosion cracking in pipelines include lowering the temperature of the pumped product, increasing the thickness of the pipe wall, using combined protective coatings with an aluminum sublayer, modifying cathodic protection, heat treatment, using surface hardening, and using corrosion cracking inhibitors [11, 13].

It is known that lowering the temperature leads to a decrease in the corrosion rate of the metal inside the crack. Similarly, an increase in temperature leads to a deterioration in the protective properties of the coating and its further delamination. Anode polarization curves taken in a carbonate-bicarbonate medium at different temperatures have peaks in the anodic dissolution current densities, which increase with temperature and capture most of the cathodic protection potentials. This phenomenon explains the characteristic confinement of corrosion cracking to compressor stations [1].

One of the methods to prevent corrosion cracking is to reduce the pressure in the pipeline, which helps to reduce the most dangerous hoop tensile stresses in the pipe wall, but this method is costly due to a decrease in the productivity of the pipeline.

One of the technological methods to prevent corrosion cracking is to increase the thickness of the pipe wall in a dangerous section twenty to twenty-five kilometers long from gas compressor stations. For these areas, it is recommended to use reinforced type protective coatings [9]. Combined protective coatings with an aluminum sublayer, which are obtained by sputtering, provide high adhesion of the polymer coating to the sublayer, as well as additional tread protection [11].

Cathodic protection is a method of electrochemical protection of a material from an external direct current, which consists in its cathodic polarization to a potential that stops or slows down the anodic process on the metal. [13]. This method is widely used to protect main pipelines. The protective action coefficient Z determines the effectiveness of cathodic protection:

$$Z = \frac{v_0 - v_1}{v_1} \cdot 100\% \tag{5}$$

Where Z is the protective action in percent; v_1 is the corrosion rate in the absence of cathodic protection; v_2 is the corrosion rate in the presence of cathodic protection.

The entire surface of the metal is subjected to cathodic polarization. It should be noted that the presence of cracks can lead to a shift in the polarization potential at the crack tip. The deeper the crack, the greater the potential difference between the pipe surface and inside the crack. One way to prevent stress corrosion cracking is to strictly adhere to cathodic protection regimes, including maintaining polarization potentials in a certain range (-0.85 V) - (-1.1 V). The quality of cathodic protection directly depends on the condition of the pipe surface before applying the protective coating. During the manufacture of pipes, deposits in the form of mill scale are formed on their surfaces. The presence of such deposits prevents the adhesion of the coating to the pipe surface and can lead to delamination of the insulation and direct contact of the corrosive environment with the metal surface [10].

The effect of corrosion deposits in the form of scale and rust on the surface of a pipe made of 17G1S steel on the effectiveness of cathodic protection is shown in Table 1 [1].

Table 1. Influence of the surface condition on the effectiveness of cathodic protection.

Surface condition	**Relative value $I_{pro.}$**
Cleaned to a metallic sheen	1
Surface of steel with scale	1.7
scale+rust	13
Rust	20

These tables indicate the importance of preparing the pipe surface before applying protective coatings. In addition, in the presence of products of gas and electrochemical corrosion in the form of scale and rust, the value of protective currents sharply increases. Metal areas under these deposits may be in an unprotected state [1].

Often on pipelines with cathodic protection, the phenomenon of cathodic undermining of the coating occurs. As noted, there is an alkaline environment in places where insulation is broken, and there are no products of electrochemical corrosion. At the same time, the protective effect of the insulation is preserved, due to the sufficient thickness, density and mechanical strength of the coating. However, with porous and mechanically weak coatings, oxygen penetration can be enhanced, which can lead to the appearance of corrosion products under the coating. On the surface of the pipe, cross-mechano-electrochemical phenomena begin to act under the influence of tensile stresses and a corrosive environment: on the one hand, corrosion increases stress due to a change in the size of the section of the part, on the other hand, stresses increase the corrosion rate [4].

Heat treatment is used to protect materials from stress corrosion cracking by creating more stable structures and relieving internal stresses. To increase the resistance of steels to corrosion, surface tempering is used, which prevents the occurrence of corrosion-mechanical cracks. Materials made of carbon and low-alloy steels with sorbitic and ferrite-pearlite structures have the highest resistance to stress corrosion. Corrosion cracking of welds is one of the main problems of welded metal structures. The main task is to reduce the magnitude of tensile residual stresses, which can be achieved by annealing. In this case, welding stresses are almost completely eliminated. However, this method is not applicable for large structures [13].

Stress corrosion cracking occurs only in the presence of tensile stresses, while compressive stresses increase the resistance of steel to this type of fracture. This is actively used to combat corrosion cracking [13]. For example, shot blasting or sandblasting of products can create compressive stresses on the steel surface. Various methods of surface hardening in many cases slow down the formation of cracks. Hardening is most effective for carbon and low alloy steels. As a result of such treatment, residual compressive stresses appear on the metal surface in the surface layers.

To combat corrosion cracking, the method of inhibitor protection is currently actively used. When selecting corrosion cracking inhibitors, many factors that affect the rate of stress corrosion cracking must be considered. In general, the efficiency of the inhibition process depends on the composition of the medium, material, and operating conditions (temperature, pressure). The defining indicator of a corrosion cracking inhibitor is its protective effect (more than 90%). Both inorganic inhibitors (chromates, nitrites, phosphates, etc.) and organic inhibitors are used to protect against stress corrosion.

4 Discussion

Of the described methods for increasing the resistance of steel to corrosion cracking, it can be noted that by choosing the right protection methods already known, it is possible to significantly increase the resistance of the material to corrosion and mechanical stress. For example, it is advisable to use a combination of inhibitor protection and surface treatment.

5 Conclusion

The development of stress corrosion cracking depends on three main factors: the presence of a corrosive environment, tensile loads, and cathodic polarization. If one of these factors is eliminated, the process of corrosion cracking will slow down. Therefore, to prevent corrosion cracking of main pipelines, it is important to identify sections of the pipe with a broken coating and re-insulate them.

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