Catode and Anode Processes in Sulfur Corrosion Destruction of Metal Constructions of Prolonged Exploitation in an Aggressive Environment

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Abstract. The analysis of the literature and the practical data show that the existing scientific and technical and technological developments concerning the provision of reliable cross-mechanical stability and durability of the pipelines of the oil and gas industry are largely contradictory and uncertain; there was a need for a systematic study of the causes, conditions and mechanisms of corrosion damage of long-term equipment, features of cathodic and anodic processes in hydrogen sulfide destruction, in particular sulfur-hydrogen metal degradation. From the analysis of corrosion processes, we can draw the following conclusions: a) corrosion always destroys the anode, i.e. the electrode with a more negative potential; b) the cathode is not destroyed by corrosion and there is a process of depolarization, that is the removal of electrons; c) during hydrogen depolarization, electrons are neutralized by hydrogen ions and hydrogen gas is released from the cathode surface; d) during oxygen depolarization, the electrons are removed by oxygen dissolved in the electrolyte, which enters from the air or together with the environment; e) depolarization leads to a significant convergence of the values of the potentials of the electrodes and reduce the corrosion rate. Despite the large number of literature sources describing the experimental works, there is no single view of the mechanism of cathode and anode processes in the hydrogen sulfide degradation of oil and gas pipelines. This is explained by the multiplicity of factors affecting this mechanism, the complexity and insufficient study of individual elementary physicochemical processes, and therefore requires additional theoretical and experimental studies.

1. Introduktion
The analysis of the literature sources [1-13] and the practical data show that the existing scientific, technical and technological developments to ensure reliable cross-mechanical stability and durability of the oil and gas pipelines are largely contradictory and uncertain; there are no quantitatively justified recommendations on practical methods and techniques to increase the corrosion-mechanical stability of equipment operating in operational-aggressive environments under alternating temperature and pressure conditions and their introduction into production at oil and gas enterprises; there was a need for a systematic study of the causes, conditions and mechanisms of corrosion damage of long-term operated equipment, features of cathode and anode processes in hydrogen sulfide destruction, in particular sulfur-hydrogen metal degradation [1, 3, 6-10, 14].

The corrosion rate of the pipes is strongly influenced by the presence of hydrogen and sulfur in technological environments. It has been established [3, 5, 7] that samples with a hydrogen content of 10
ml/100g and above collapse brittle with many cracks in the fracture zone. In particular, metal flooding plays a significant negative role in the operational reliability of long-term oil and gas pipelines in chemical-aggressive environments at alternating loads [2, 3-5, 8]. Therefore, the problem of corrosion of metal equipment and pipe structures is relevant and of great practical importance.

**The purpose of the work** is to study the cathode and anode processes in the hydrogen sulfide destruction of metal structures during prolonged operation in aggressive environments.

2. Results of analytical studies and their discussion

It is known [1-5, 14-18] that the processes of anodic dissolution of the metal, which are accompanied by the generation of hydrogen ions, develop in the crack. The cathodic processes are characterized mainly by the recovery of hydrogen and subsequent hydrogen saturation of the metal. During the electrode reaction of the recovery of hydrogen evolution in the form of ions, which are in the volume of solution adjacent to the metal surface in the form of hydrated hydroxonium ions $H_2O^+(H_2O)$, there is a reaction with the electrons of the metal with the formation of hydrogen molecules, which then pass into oil and gas phase. Since water is always present in the work environment, it is usually not considered as a reaction component, which in simplified form looks like $2H^+ + 2e^- \rightarrow H_2$.

This reaction takes place in several sequential stages. The first stage is the delivery of $H^+$ ions from the volume of the solution to the metal surface. Let us take the following notation: $(H')$ are hydrogen ions that are closest to the metal surface. Then we present this stage as $H^+ \rightarrow (H')$.

It should be noted that in the case of oil and gas pipelines, mixtures containing CO$_2$ and H$_2$S may be a source of hydrogen ions. Moreover, particles $(H')$ are discharged on the metal surface with the formation of adsorbed atomic hydrogen: $(H') + e^- \rightarrow N_{ads}$.

This reaction is called the Volmer reaction and indicates the charge transfer in the process of hydrogen evolution, because during this reaction, electrical charges are transferred through a double electric layer at the interface of the "metal-electrolyte solution".

At the contact of metal of pipes of the technological equipment with the working medium-electrolyte, two cases of corrosion processes are possible [17-19]:

1) The metal has a negative electrode potential according to the reaction:

$Me^+ + e^- + nH_2O = Me^' \cdot nH_2O + \Theta$, where $Me^-$ - ion-atom; $e^-$ - electron; $Me^' \cdot nH_2O$ – hydrated ion; $\Theta$ – excess electron.

This reaction takes place under the condition that the hydration energy is greater than the binding energy of the metal ion atom with half-free electrons.

2) The metal has a positive electrode potential according to the reaction:

$Me^' \cdot nH_2O = Me^+ + nH_2O$, where $Me^'+ nH_2O$ – ion-atom; $Me^+$ - cation; $nH_2O$ – water.

This reaction takes place under the condition that the hydration energy is greater than the binding energy of the metal ion-atom with half-free electrons.

Depending on the value of the electrode potentials, metals are placed in a series of stresses relative to the hydrogen potential, which is taken as “zero”, i.e. the potential ratio makes it possible to compare the corrosion resistance of metals. They can evaluate the effectiveness of protective coatings, select materials for the protection of equipment, including pipeline structures, which are operated in corrosive environments, to ensure their reliability and durability.

Attention should be paid to the existence of two types of electrochemical corrosion, which can occur in the case of corrosion damage to metal structures, in particular with hydrogen and oxygen depolarization [3, 5, 14, 18]. Corrosion with hydrogen depolarization is characterized by the release of hydrogen gas. This type of corrosion destroys the majority of metals in acids and other acidic processing media of oil refineries.

In the case of corrosion with oxygen depolarization, an influx of oxygen is required for the operation of the galvanic cell, which enters the technological mixture in different ways. According to this mechanism, steels, aluminum and other alloys corrode in neutral environments.

The following conclusions can be drawn from the analysis of corrosion processes:

1) corrosion always destroys the anode, ie the electrode with a more negative potential;
2) the cathode is not destroyed by corrosion and it undergoes a process of depolarization, ie removal of electrons;
3) during hydrogen depolarization, the electrons are neutralized by hydrogen ions and gaseous hydrogen is released from the cathode surface;
4) during oxygen depolarization, electrons are removed by oxygen dissolved in the electrolyte, which enters from the air or together with the environment.

Thus, depolarization leads to a significant convergence of the values of the electrodes and reduce the corrosion rate.

It is known [3-7, 10-13, 19, 20] that when a microcrack is formed, processes of anodic metal solution develop, which is accompanied by the generation of hydrogen ions. The mechanisms of hydrogen evolution can be realized according to the Folmer-Tafel reactions [20]: (H') + e⁻ → H_ads, followed by recombination of adsorbed atomic hydrogen with the formation of adsorbed molecular hydrogen: H_ads + H_ads = (H₂)_ads. But there is another Folmer-Geirowski mechanism, in which there is an electrochemical recombination of atomic hydrogen present on the surface with discharged H⁺ ions with the direct formation of (H₂) ADC (electrochemical desorption reaction): H_ads + (H⁺) + e⁻ → (H₂)ads.

Both mechanisms are presented in figure 1 [17].

The association of atomic hydrogen with defects in the structure of the metal, such as pores, traps, dislocations, can slow down their movement during plastic deformation, which leads to hydrogen embrittlement of the metal.

**Figure 1.** The reaction scheme of the cathodic evolution of hydrogen: a) by the Volmer-Tafel mechanism; b) by the Volmer-Geirowsky mechanism.

The authors of [1,4,5,19] believe that the formation of hydrogen atoms adsorbed on the metal surface is due to the reaction of the discharge of hydroxyl ions:

H₃O⁺ + e⁻ → H_ads + H₂O

and the parallel restoration of other donors - protons:

H₂S + 2e⁻ → 2H_ads + S_ads⁻;

HCO₃⁻ + 2e⁻ → H_ads + CO₃²⁻.

The most probable ways of molecular hydrogen formation: electrochemical desorption:

H_ads + HCO₃⁻ + 2e⁻ → H₂ + CO₃²⁻;

and recombination

2H_ads → H₂.
In this case, any of the steps (5-9) may be limiting.

![Diagram of corrosion mechanism](image)

**Figure 2.** The mechanism of corrosion of low carbon steel in a chemically active medium containing sulfur and hydrogen, and the formation of blisters in the cathodic release of hydrogen by the Volmer-Tafel mechanism.

Considering that in the technological mixture, which is transported through oil and gas pipelines [3,5,7,10,19], hydrogen, oxygen, sulfur (H₂S), anions HCO₃⁻, SO₄²⁻, chlorine ions Cl⁻ and others are always present in the elementary state or in the form of chemical compounds, the corrosion process of the surfaces of pipelines in the presence of external and internal alternating loads can be described by the following reactions:

**cathode reactions**

1. H₂O + e⁻ = H_H₂ + OH⁻
2. H₂O + H⁺ + OH⁻
3. SO₄²⁻ + 8H_H₂ + H⁺ = HS⁻ + 4H₂O

**(corrosion initiation)**

1. HS⁻ + H⁺ = H₂S
2. H₂S + e⁻ = H_H₂ + HS⁻
3. SO₄²⁻ + 8H_H₂ + H⁺ = HS⁻ + 4H₂O
4. H₂O = H⁺ + OH⁻

**(corrosion stimulation)**

1. 5H₂S + e⁻ + SO₄²⁻ = 6HS⁻ + 4OH⁻

**(standard cathode reaction)**

4Fe + SO₄²⁻ + 4H₂O = FeS + 3Fe(OH)₃ + 2OH⁻.

The above reactions show that the main corrosion agents in the technological environment of the oil and gas production, which initiate and catalyze the corrosion process, are HS⁻, SO₄²⁻ ions, H₂S, oxygen and hydrogen molecules.

It is known [2,14,17,20] that the carbon gas present in the working environment causes the following reactions:

- in solution [14]:
  \[
  \text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{H}^+ + \text{HCO}_3^- \leftrightarrow \text{H}_2\text{CO}_3;
  \]
  \(\text{(10)}\)

- at the active centers of the metal surface [16]:
  \[
  \text{CO}_{2\text{solution}} \leftrightarrow \text{CO}_{2\text{ads}};
  \]
  \(\text{(11)}\)

  \[
  \text{CO}_{2\text{ads}} + \text{H}_2\text{O} \rightarrow \text{H}_2\text{CO}_3\text{ads}.
  \]
  \(\text{(12)}\)

However, the following reactions can occur in parallel, which shift the pH of the medium to the acidic region:

\[
\text{Fe} + \text{HCO}_3^- \rightarrow \text{FeCO}_3\text{ads} + \text{H}^+ + 2e^-;
\]
\(\text{(13)}\)
Fe(OH)$_3$ + HCO$_3^-$ → FeCO$_3$ + H$_2$O + 2OH$^-$; \hspace{1cm} (14)

FeCO$_3$ + HCO$_3^-$ → [Fe(CO$_3$)$_2$]$^{2-}$ + H$^+$. \hspace{1cm} (15)

During long-term interaction of the solution with the metal surface, chemical and electrochemical reactions develop, which subsequently take place both on the metal surface and in the near-surface layers. The longer dissolved CO$_2$ or CO act on the metal, the more intense this process, for example, under the influence of temperature, the more corrosion products are formed in the volume of the solution and on the metal surface. Along with the accumulation of metal oxidation products on the surface, is the next solution under the action of HCO$_3^-$ ions (see reaction 15), which, in turn, affects the pH of the medium and leads to the creation of favorable conditions for other reactions, in particular (14).

Also, at a temperature of 60-80°C and above, pH ≈ 6-8 and partial pressure of CO$_2$ equal to 1.5-2.0 MPa, reactions can occur, which lead to the formation of a dense film of siderite [17]:

2Fe$_3$O$_4$ + H$_2$O = 3($\gamma$-Fe$_2$O$_3$) + 2H$^+$ + e$^-$. \hspace{1cm} (16)

The presence of Fe$_3$O$_4$ in the oxide film can probably be explained by the previous decomposition of Fe(OH)$_3$ by reaction:

Fe + CO$_3^{2-}$ → FeCO$_3$ + 2e$^-$. \hspace{1cm} (17)

Analysis of corrosion processes concerning technological environment of oil-refining allows to systematize reactions that describe the change in the ratio of oxide-hydroxide and carbonate component of the film:

Fe + 2H$_2$O → Fe(OH)$_2$ + 2H$^+$ + 2e$^-$; \hspace{1cm} (19)

Fe + 2H$_2$CO$_3$ → Fe(HCO$_3$)$_2$ + H$_2$; \hspace{1cm} (20)

Fe(HCO$_3$)$_2$ → Fe$^{2+}$ + 2HCO$_3^-$; \hspace{1cm} (21)

HCO$_3^-$ → H$^+$ + CO$_3^{2-}$; \hspace{1cm} (22)

Fe$^{2+}$ + CO$_3^{2-}$ → FeCO$_3$ + H$_2$. \hspace{1cm} (23)

At the same time, there may be reactions that cause changes in the composition of the film in accordance with its protective properties and increase the permeability:

H$_2$CO$_3^{ads}$ + e$^- $ = H$_{ads}$ + HCO$_3^{ads}$; \hspace{1cm} (24)

H$_3$O$^+$ + e$^- $ ↔ H$_{ads}$ + H$_2$O; \hspace{1cm} (25)

H$_2$O$_{ads}$ + e$^- $ ↔ H$_{ads}$ + H$_2$O. \hspace{1cm} (26)

The above data indicate the important role of carbon dioxide corrosion in the damage of metal of oil and gas pipelines.

The brittle delamination of the metal with absorbed hydrogen formed according to the above mechanisms and reactions is shown schematically in figure 3 [14].

![Figure 3](image-url)

**Figure 3.** Schematic representation of the process of corrosion cracking of metal by local anode dissolution (a) and as a result of hydrogen embrittlement (b)

Corrosion of iron in hydrogen solutions of hydrogen sulfide proceeds according to the total equation:

Fe + H$_2$S = FeS + H$_2$. \hspace{1cm} (27)
The recombination of atomic hydrogen released on the corroded surface is slowed down by the formation of iron sulfides, which facilitates the penetration of atomic hydrogen into the metal and its intense flooding, which results in slow destruction, especially under stress.

It should be noted that despite the large number of literature sources describing the experimental works, there is no single view of the mechanism of cathode and anode processes in the hydrogen sulfide metal degradation of oil and gas pipelines. This is due to the number of factors influencing this mechanism, the complexity and insufficient study of certain elementary physicochemical processes [4, 6-10, 12, 13, 15].

3. Conclusions
1. Analysis of the literature sources and practical data show that the existing scientific, technical and technological developments to ensure reliable corrosion-mechanical stability and durability of the pipelines in the oil and gas industry are mostly contradictory and uncertain; there was a need for a systematic study of the causes, conditions and mechanisms of corrosion damage of long-term equipment, features of cathodic and anodic processes in hydrogen sulfide fracture, in particular sulfide-hydrogen metal degradation.

2. The following conclusions can be drawn from the analysis of corrosion processes:
   a) corrosion always destroys the anode, i.e. the electrode with a more negative potential;
   b) the cathode is not destroyed by corrosion and it undergoes a process of depolarization, i.e. removal of electrons;
   c) during hydrogen depolarization, electrons are neutralized by hydrogen ions and gaseous hydrogen is released from the cathode surface;
   d) during oxygen depolarization, electrons are removed by oxygen dissolved in the electrolyte, which enters from the air or together with the environment;
   e) Depolarization leads to a significant approximation of the values of the electrode potentials and reduce the corrosion rate.

3. Despite the large number of literature sources describing experimental works, there is no single view on the mechanism of cathode and anode processes in hydrogen sulfide metal degradation of oil and gas pipelines. This is due to the number of factors influencing this mechanism, the complexity and insufficient study of single elementary physicochemical processes, and therefore requires additional theoretical and experimental studies.

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