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TYPES OF CORROSION OBSERVED IN AMINE GAS SWEETENING UNITS, THEIR CHARACTERISTIC CHEMICAL REACTIONS, AND CORROSION-PRONE AREAS OF THE EQUIPMENT

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Abstract: The article analyzes the main types of corrosion observed in amine gas sweetening units, their chemical reaction mechanisms, and corrosion-prone areas of the equipment. The study highlights the carbonate corrosion of carbon steels caused by CO₂, the sulfide corrosion induced by H₂S, and the high-temperature acidic corrosion resulting from the thermal degradation of amines. The lower section of the absorber, the desorber, the reboiler, and the circulation pipelines and pumps were identified as the most corrosion-prone zones. It is emphasized that proper selection of technological and chemical protection methods is essential for minimizing corrosion in amine gas treatment systems.

Keywords: amine gas sweetening unit, corrosion, H₂S, CO₂, iron sulfide, carbonate corrosion, thermal decomposition, organic acids, equipment protection.

Introduction. Ensuring the long-term and safe operation of technological equipment in the oil and gas industry is one of the key engineering requirements. Amine absorption and regeneration systems used in gas processing are subject to corrosion caused by acidic gases such as CO₂ and H₂S. This process reduces equipment reliability and poses environmental risks. The article analyzes the main types of corrosion observed in amine environments, their chemical mechanisms, and influencing factors. The most severe metal degradation occurs in the lower part of the absorber, the reboiler, condenser, and pump–pipeline systems.

Ensuring the long-term, reliable, and safe operation of technological equipment used in the oil and gas industry is among the key requirements of modern engineering practice. In particular, the absorption systems applied in gas processing — such as absorption and desorption (regeneration) columns, heat exchangers, reboilers, pipelines, and other auxiliary equipment — are continuously exposed to acid gases (CO₂, H₂S). As a result, they are subjected to a high risk of corrosion. This phenomenon can lead to premature failure of technological units, the occurrence of technogenic accidents, a decrease in production efficiency, and the emergence of serious environmental problems.

It is known that elemental sulfur dissolves well in alkalis, including caustic soda (sodium hydroxide), resulting in the formation of sulfides, polysulfides, and thiosulfates [1–3]. These compounds are hazardous to metallic constructions, as they can initiate pitting corrosion, hydrogen embritlement (hydrogen sulfide cracking), and oxidation–reduction processes, all of which contribute to the further development of corrosion.

According to literature data, the dissolution of sulfur in aqueous hydroxide solutions of alkali metals occurs mainly through a disproportionation reaction mechanism [2, 4–6].

$$3S + 6OH^{-} = 2S^{2-} + SO_3^{2-} + 3H_2O$$
 (1)

Furthermore, the nucleophilic addition of sulfur to the sulfide and sulfite ions formed in the solution is also observed:

$$2S^{2-} + (2n-2)S = 2S_n^{2-}$$
 (2)

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$$SO_3^{2-} + S = S_2O_3^{2-}$$
 (3)

The authors [2,5] have shown that the rate of reaction (4) is relatively low. At the same time, the formation of thiosulfates proceeds through a faster reaction involving the interaction between sulfite ions and polysulfide ions, as follows:

$$SO_3^2 + S_n^2 = S_2O_3^2 + S_{n-1}^2$$
 (4)

Thus, the overall equation for the sulfur dissolution reaction can be expressed as follows:

$$2(n+1)S + 6OH^{-} = 2S_{n}^{2} + S_{2}O_{3}^{2} + 3H_{2}O$$
 (5)

The authors [2] proposed a stepwise mechanism for the dissolution of sulfur in aqueous alkaline solutions. This process exhibits an autocatalytic nature, proceeding through the formation of sulfide and unsaturated chain polysulfide ions [3].

It has long been known that elemental sulfur reacts with organic compounds to produce valuable products, and this property has been widely utilized in practice [7,8]. Among such reactions is the interaction of elemental sulfur with ethanolamines, which leads to the formation of polysulfides.

When primary and secondary ethanolamines are heated with finely dispersed, granulated, or molten sulfur, polysulfides are formed. It has been established that the mechanism of formation of these compounds is similar to that observed in inorganic alkaline solutions as described in source [2]. However, for the initiation of sulfur dissolution, i.e., for the disproportionation reaction to occur, the presence of hydroxide ions (OH⁻) in the medium is essential, as they are generated through the dissociation of water:

$$H_2O \leftrightarrow H^+ + OH^-$$
 (6)

Because ethanolamines are hygroscopic, even in small quantities they can retain up to about 0.5% of water by mass. This amount of moisture is sufficient for the reaction to occur.

At the same time, the direct interaction of sulfur with ethanolamines can also take place. According to the findings of the authors [7,8], at elevated temperatures, monoethanolamine (MEA) is capable of reducing sulfur to hydrogen sulfide (H₂S). Subsequently, polysulfidic sulfur compounds may form through reaction (2). The main types of corrosion observed in amine gas sweetening units and the characteristic chemical reactions associated with them are described in detail below [9,10].

1. Corrosion of steels under the influence of CO₂ ("carbon dioxide corrosion"). When carbon dioxide (CO₂) dissolves in water, it forms carbonic acid (H₂CO₃), which lowers the pH of the medium and thereby accelerates the corrosion of carbon steels. The carbonic acid corrosion of steel can be represented by the following chemical reactions:

$$CO_2 + H_2O \Rightarrow H_2CO_3$$
 (karbonat kislotasi) (7)

$$Fe + H_2CO_3 \rightarrow FeCO_3 \downarrow + H_2 \uparrow (8)$$

In this process, ferrous carbonate (FeCO₃) may initially form a protective film on the steel surface; however, under conditions of high flow velocity, elevated temperature, or low pH, this film becomes unstable, leading to intensified localized (pitting) corrosion.

2. Hydrogen Sulfide–Induced Cracking (H₂S Corrosion). Hydrogen sulfide (H₂S) reacts with iron to form iron sulfide (FeS). Although FeS exhibits slightly passivating properties, it is unstable and tends to crack or flake off under process conditions. This phenomenon is a critical issue in the oil and gas industry, particularly in production and pipeline transportation systems. The corrosion of steel under the influence of hydrogen sulfide can be represented by the following reaction:

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6.995, 2024 7.75

 $Fe + H_2S \rightarrow FeS \downarrow + H_2 \uparrow (9)$

Iron sulfide (FeS) is a dark brown-black, shiny crystalline compound. Over time, the porous protective layer of FeS deteriorates, which leads to an increase in the corrosion rate.

The mechanism of this corrosion process can be explained as follows: hydrogen sulfide gas reacts with the metal surface to form a thin iron sulfide (FeS) film — often referred to as a "protective screen" — and atomic hydrogen (H). The hydrogen atoms then diffuse into the metal lattice, where they recombine or become trapped at lattice defects, inclusions, or grain boundaries.

This condition causes an increase in internal pressure within the metal crystal lattice, leading to the formation of microcracks in the structure. This process is known as hydrogen cracking, hydrogen embrittlement, or, as commonly referred to by petroleum industry specialists, hydrogen sulfide cracking (H₂S cracking).

If the metal is subjected to significant mechanical stresses — that is, mechanical forces of varying magnitude and amplitude such as vibration, tension, expansion, or torsion — the cracking process accelerates. This phenomenon is referred to as sulfide stress corrosion cracking.

3. High-Temperature Amine Corrosion. At temperatures above 120 °C, amines begin to thermally decompose, forming organic acids such as acetic and formic acids. These acidic products cause intense corrosion of various parts of the desorber (regenerator) column. The process can be represented by the following simplified reactions:

 $RNH_2 + CO_2 \rightarrow RNHCOO^-$ (karbamat) (10)

 $RNHCOO^- + H^+ \rightarrow RNH_2 + HCOOH$ (chumoli kislotasi) (11)

Formic acid has the following corrosive effect on iron:

 $Fe + 2HCOOH \rightarrow Fe(HCOO)_2 + H_2 \uparrow$ (12)

This leads to severe acidic corrosion of the desorber column and heat exchangers.

4. Atmospheric and crevice corrosion occurs under the influence of O₂. When air comes into contact with the system, oxygen oxidizes iron, forming rust (Fe(OH)₃ and Fe₂O₃·H₂O):

 $4\text{Fe} + 3\text{O}_2 + 6\text{H}_2\text{O} \rightarrow 4\text{Fe}(\text{OH})_3\downarrow$ (13)

 $Fe(OH)_3 \rightarrow Fe_2O_3 \cdot H_2O$ (zang qatlami) (14)

The most corrosion-prone areas in the technological equipment.

- 1. The lower part of the absorber, which is in contact with the rich amine solution. (Here, the concentrations of H₂S, CO₂, and moisture are high, resulting in sulfide and carbon dioxide corrosion. If the amine solution is contaminated for example, containing organic acids acidic corrosion is also intensified.)
- 2. The desorber (regenerator) column and reboiler section, where the temperature reaches 100–125 °C. At elevated temperatures, amines undergo thermal decomposition, forming organic acids (e.g., HCOOH, CH₃COOH). As a result, acidic and high-temperature corrosion types develop.
- 3. The reflux condenser (cooling section). Acid gases (H₂S, CO₂) and water vapors condense in this area, forming acidic condensate, which leads to crevice and pitting corrosion.
- 4. Circulation pipelines and pumps of the amine solution. If the solution contains acidic impurities, the pH level decreases (shifting toward an acidic medium), which initiates corrosion. In addition, mechanical corrosion (erosion–corrosion) may occur on pump shafts and pipelines.

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5. Gas inlet and outlet sections of the unit (narrow nozzles and valves). In these zones, H₂S and CO₂ in the gas stream promote localized erosion–corrosion, particularly under high velocity and turbulent flow conditions.

Corrosion in amine gas sweetening units mainly develops in areas exposed to high temperatures, acidic gases (H₂S, CO₂), and stagnant zones of degraded or stagnant absorbents. Scientific and technical analysis of the identified corrosive agents and corrosion-prone zones makes it possible to apply effective corrosion protection methods, which, in turn, depend on the correct choice of technological, chemical, and structural approaches to solving the problem [9,10].

Conclusion.

Corrosion processes in amine gas sweetening units are complex and multifactorial, mainly driven by CO₂ and H₂S reactions, thermal degradation of amines, and increased acidity of the solution. The most critical corrosion zones are identified as the lower section of the absorber, the desorber, reboiler, condenser, and circulation pump system. To mitigate corrosion, optimizing process parameters, using inhibitors, maintaining amine solution purity, and selecting appropriate construction materials are essential. Effective control of these factors enhances equipment reliability and ensures safe and stable operation of the entire gas treatment system.

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