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CORROSION INHIBITOR PROTECTION METHODS IN AMINE GAS SWEETENING UNITS

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During the operation of amine-based gas sweetening equipment, general corrosion occurs on the units, as well as a more dangerous phenomenon — corrosion cracking. The general corrosion rate of carbon steel increases with the growth of amine concentration, temperature, the degree of saturation of absorbent solutions with acid gases, as well as due to the presence of mechanical impurities and the accumulation of thermal-chemical decomposition products of amines.

As a result of contact with oxygen, thiosulfate amine may form in an amine solution saturated with H_2S, while in the presence of carbon dioxide, aminoacetic acid, oxalic acid, formic acid, and other acids may be produced.

For desulfurization equipment made of low-carbon and alloy steels, the most hazardous case is corrosion cracking (CC), which usually develops in metals with high internal stresses, especially in welded joints [1]. Heat treatment reduces these internal stresses and significantly improves the metal structure. The main cause of this phenomenon is hydrogen embrittlement of the steel, which occurs due to the penetration of atomic hydrogen into the metal structure during electrochemical corrosion processes in the presence of H_2S and CO_2 in the amine solution.

First of all, for gas sweetening units operating with H_2S or H_2S and CO_2, it is necessary to select appropriate materials [2]. However, the most effective method of combating corrosion is the use of inhibitors, which are added to the circulating amine solution (the absorbent).

Several studies [3] have reported results of using inhibitors to protect desulfurization units from general corrosion. Unfortunately, until now, the most effective, low-cost, and practical methods of introducing inhibitors have not been widely applied in practice.

According to the data [4], corrosion inhibitors can be conditionally divided into three groups:

1. Adsorptive inhibitors — they bond with the steel surface, forming a monomolecular protective layer that shields the steel surface from the destructive action of the solution.
2. Precipitating inhibitors — they form a multilayer film on the steel surface, slowing down the corrosion process. H_2S itself can act as such an inhibitor, but its efficiency is insufficient.
3. Oxidizing passivators — they bond strongly with the steel surface and promote the formation of a stable iron oxide film, which practically eliminates corrosion on the steel surface (annual losses reduced to fractions of a millimeter).

Research conducted by American scientists showed that for amine gas sweetening units operating with H_2S and CO_2, the best inhibitor is a synergistic combination of two oxidizing passivators [5]:

a) Vanadium (V) compounds in amounts of 0.02–0.25 mM, mainly from the following group: $NaVO_3$ (I), V_2O_5, Na_3VO_4, KVO_3, NH_4VO_3, $VOCl_3$, or their mixtures;

b) Organic nitro compounds in amounts of 0.6–0.8 mM, mainly from the following group: p-nitrobenzoic acid (II); m-nitro- and 3,5-dinitrobenzoic acids; p- and m-nitrophenols; m-nitrophenylsulfonic acid and the salts of these acids.

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In the Amine Guard ST process developed by Union Carbide (USA), such mixtures of substances are used as inhibitors [6]. In Russia, only limited experimental data have been collected on the industrial testing of certain inhibitor types such as IFXANGAZ-1, VUS-2, and GAZ AMIN.

Industrial trials with IFXANGAZ-1 inhibitor in the hydrogen sulfide gas sweetening process at the Minnibaevsky Gas Processing Plant demonstrated that the corrosion rate of carbon steel samples exposed to hot monoethanolamine (MEA) solution decreased to 0.13 mm/year, which is not considered very low. According to the authors [7], the components of IFXANGAZ-1 (dialkyl (C_7–C_9) aminopropionitriles) themselves do not exhibit inhibitory activity; instead, the inhibitory effect results from the formation of thioamides when they interact with hydrogen sulfide.

The "A"-grade VUS-2 inhibitor was also tested industrially and was implemented in 1987 at the Salavatnefteorgsintez hydrodesulfurization unit GO-4.

Another effective sulfur-containing inhibitor is ethanolamine polysulfides (GAZAMIN inhibitor). The ability of MEA and DEA polysulfides not only to suppress general corrosion but also to prevent stress corrosion cracking of carbon steels in H_2S and SO_2-saturated alkanolamine solutions was confirmed in industrial trials at the Otradnensky, Janajolsky, and Shkapovsky Gas Processing Plants, as well as at "Shurtanneftgaz" LLC [8].

In gas absorption sweetening units exposed to aggressive environments containing H_2S and CO_2, modern adsorption-type corrosion inhibitors are generally solutions of one or more organic compounds (active bases) with high inhibitory properties, dissolved in hydrocarbon or water-alcohol solvents.

Corrosion inhibitors used in the oil and gas processing industry must meet the following requirements:

- provide protective action across a wide temperature and pressure range (from ambient up to elevated levels), as well as under conditions of high flow velocity and the presence of abrasive particles;
- have a low freezing point (at least –50 °C);
- be well soluble and/or dispersible in the working environments (water-soluble, hydrocarbon-soluble, water-dispersible, hydrocarbon-dispersible, or insoluble in both water and hydrocarbons);
- not affect the stability of oil-water emulsions;
- comply with fire and explosion safety, as well as sanitary standards;
- be compatible with other reagents used in the technological process and not negatively affect further oil and gas processing operations or product quality.

In addition, the development of effective corrosion inhibitors should consider:

- environmental impact,
- applicability at low concentrations (100–200 mg/L),
- chemical stability in corrosive environments.

All commercial corrosion inhibitors have their optimal field of application depending on the industrial segment, the composition of the corrosive environment, and the technological features of the equipment requiring protection.

Table I. [9] provides the composition of the most commonly used inhibitors across different sectors.

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Segment	Inhibitors	Composition	Medium
Oil and gas industry	corrosion inhibitors	linear amines and imidazolines dissolved in various solvents (kerosene, methanol, neonol, etc.)	oil emulsion
Chemical-technological protection of process equipment	corrosion inhibitors	oxidized fatty amines and imidazolines	oil products containing various impurities
Water treatment facilities	complex-action inhibitors	organophosphorus compounds	water
Circulating technical water treatment systems of industrial enterprises	complex-action inhibitors	phosphorus-containing components, sodium polyphosphates, zinc sulfates, etc.	water containing various impurities

The majority of inhibitors are applied during oil and gas production processes (in pressurized pipelines, gathering systems, production lines, and water injection pipelines), as well as during crude oil transportation. Therefore, the development of new corrosion inhibitors for aggressive environments containing hydrogen sulfide (H_2S) and carbon dioxide (CO_2), as well as the improvement of existing inhibitors, remains an urgent task in the oil and gas production and processing industry.

In summary, the most effective protection method against general corrosion and stress corrosion cracking observed in equipment during the amine-based gas sweetening process is the use of inhibitors. Research has shown that organic inhibitors with adsorption mechanisms and complex effects, forming a stable protective layer on the steel surface (compounds containing nitrogen, phosphorus, sulfur, and oxygen), provide high efficiency in practice. Their application reduces the aggressive impact of amine solutions, significantly decreases the rate of general and localized corrosion, and prevents stress corrosion cracking caused by hydrogen embrittlement of the metal. Therefore, the development and implementation of complex inhibitors that are compatible with existing technological conditions and environmentally safe represent a key scientific and technical solution ensuring the reliability and long-term efficient operation of amine sweetening units.

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