Protection with Steel Corrosion Inhibitors in Hydrogen Sulfide Environments

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ABSTRACT

Ensuring the reliability and durability of equipment and pipeline systems is one of the most important tasks in the development of oil and gas fields and in the further transportation and processing of hydrocarbons. Corrosion of steel equipment and pipelines, in addition to reducing their service life and increasing the cost of their repair, can cause serious damage to the environment. The article considers the literature data on inhibitors of hydrogen sulfide corrosion of carbon steel, including those recommended for use in similar conditions abroad.

Keywords: Corrosion, protection, inhibitor, hydrogen sulfide, sulfate reduction, bacteria, bactericide.

The high aggressiveness of operating media is determined by the presence of aggressive gases (hydrogen sulfide, carbon dioxide and oxygen) in them, as well as the presence of an aqueous phase and its physicochemical properties (pH, temperature and salinity).

The presence of corrosive gases in the product leads to corrosion destruction of steel equipment and pipelines in the process of production, purification, transportation and processing of hydrocarbon raw materials. When operating oil and gas fields containing large amounts of acid gases, there is a difficult problem of protecting gas production equipment from corrosion. Inhibitor protection is one of the most convenient and economical means of combating corrosion under these conditions [1].

The main danger for gas and oil pipelines is condensate formed when the temperature of oil and gas decreases, which consists of a two-phase system, in the water part of which corrosion processes occur. Characteristically, the surface area in contact with the vapor phase is often much larger than with the liquid.

Certain requirements are imposed on inhibitors in terms of technological and protective properties. Inhibitors must have high protective properties in hydrogen sulfide-containing water and vapor phases of at least 85% of total corrosion and at least 70% of hydrogen embrittlement and not have a negative impact on technological processes [2].

From the most general data, it follows that the method of anticorrosion protection of metals, in particular steel, based on the use of corrosion inhibitors - chemical compounds that are present in the corrosion system in small quantities, is very effective, since inhibitors significantly reduce the corrosion rate. The most difficult task of inhibitory protection against corrosion is the protection of the metal surface under conditions of hydrogen sulfide corrosion, when the real surface is a complex conglomerate of sulfides of variable composition [3].

These problems really arise in the conditions of chemical production, oil production and oil refining, when the source of free hydrogen sulfide and sulfides is both oil itself and oilfield waters. It is this hydrogen sulfide that is very aggressive and causes intense corrosion of oilfield equipment and pipelines. A feature of corrosion is its local nature due to the diffusion of hydrogen sulfide into intergranular zones. The process of hydrogen sulfide corrosion of steel is significantly enhanced in the presence of oxygen, carbon dioxide and sulfides on the steel surface. The combined effect of these factors leads to the spontaneous development of the processes of ionization of iron atoms on the surface and, ultimately, to through destruction of pipelines and equipment. Possible ways of inhibition by inhibitors of hydrogen penetration into the metal can be [4]:

- formation of a stable adsorption inhibitor film on the metal surface, which prevents the penetration of hydronium ions to the metal surface, their discharge to atomic hydrogen and diffusion deep into the metal;
- change due to the adsorption of the inhibitor on the active areas of the metal surface of the rate-limiting stage of the reaction of hydrogen evolution, for example, from recombination to the stage of discharge or electrochemical desorption;
- removal of atomic hydrogen from the metal surface, for example, by participating in hydrogenation reactions with adsorbed inhibitor molecules (hydrogenation of unsaturated compounds).

The main part of the inhibitors currently used in oil and gas production are organic nitrogen-containing compounds with long hydrocarbon chains (usually C10-C18), which, due to the combination of a lone electron pair on nitrogen atoms with aliphatic radicals of various lengths and a conjugated πelectron aromatic fragment cloud are the basis of many modern inhibitors of both hydrogen sulfide and carbon dioxide and atmospheric corrosion. They have also found wide application in neutral aggressive media [5].

For most nitrogen-containing inhibitors of the cationic type, which are chemically adsorbed on the surface of steel, or acetylene compounds, which undergo transformations on the surface, the most probable is the first way of inhibiting the penetration of hydrogen into the metal [6]. Thus, hexamethyleneimine derivatives, forming dense chemisorption (nitrogen-containing compounds) or polymer films (acetylene compounds) on the surface, prevent the penetration of hydronium ions to the metal surface. The inhibition of the cathode process leads to a decrease in the number of discharging hydronium ions and, accordingly, the fraction of hydrogen penetrating into the metal.

When studying the effectiveness of some nitrogen-containing corrosion inhibitors, it was found that such substances are able to increase the wettability of the protected metal surface with hydrocarbons (oil). Sometimes the coating of the inhibitor layer adsorbed on the metal with an oil film, which contributes to the thickening of the screening layer, predetermines the obtaining of a high protective effect. The basis for assessing the concentration of nitrogen-containing inhibitors in hydrocarbon condensate individually and as part of a mixture is the use of specific color reactions for their nitrogen-containing functional group, for example, the ability of nitrogen-containing inhibitors to form a pinkish-violet complex with methyl orange yellow and violuric acid.

Free hydrogen sulfide is the main "culprit" of hydrogen sulfide corrosion. It is formed due to the vital activity of sulfate-reducing bacteria, which are able to use hydrogen during hydrogen depolarization of microcathode sections of steel to reduce the sulfate-containing corrosion medium [7]. It is known, for example, that in a sterile environment containing up to 500 mg/l of hydrogen sulfide, the corrosion rate is low due to surface passivation (an iron sulfide film is formed), and when the system of sulfate-reducing bacteria is infected, the protective film loosens, and the corrosion rate increases sharply. This is due to the formation of colonies of microorganisms on the metal surface, which, releasing concentrated hydrogen sulfide, enhance electrochemical corrosion by increasing the conductivity between the cathodic formations of iron sulfide and the anode surface of the metal (i.e., due to depolarization in local areas of the surface), and also isolate the metal surface from exposure to conventional corrosion inhibitors.

Studies have shown that when the concentration of hydrogen sulfide in the volume of the medium is about 100 mg/dm3 under deposits of corrosion products and adhesive forms of bacteria, the concentration of biogenic hydrogen sulfide reaches 1400 mg/dm^3. This leads to an increase in the corrosion rate of local areas. Destructions in water conduits are ulcerative in nature and are located, as a rule, along the lower generatrix of pipes under a layer of corrosion products, they are characterized by the presence of mucus, stickiness and good adhesion to the surface. It is believed that the most favorable conditions for sulfate reduction in oil reservoirs are a temperature of 35–40 °C, the presence of hydrocarbon-oxidizing bacteria, the waste products of which serve as food sources for sulfate-reducing bacteria, and the presence of a sufficient amount of sulfates. With an increase in water cut, carbon dioxide content and sulfate-reducing bacteria, conditions are created for an increase in the accident rate of pipelines of oil gathering systems [8].

The active life processes of sulfate-reducing bacteria are catalyzed by iron ions. Therefore, the most favorable conditions for the formation of adhesive forms of bacteria are formed in the system of oil treatment and disposal of industrial wastewater. In addition to a sharp increase in the intensity of local corrosion, an active process of hydrogenation of the metal inevitably occurs under the biocenosis, which leads to its fragility and even faster disables the pipe wall or the bottom of the tank.

Recently, the production of special organic inhibitors has been expanding. Chlorinated phenols are widely used, which have a wide spectrum of action on bacteria and fungi. These are 2,4,5-trichlorophenol and pentachlorophenol. However, due to their high toxicity, their use is limited. Quaternary ammonium salts are successfully used, despite their relative harmlessness to fungi and less efficiency in the presence of protein. However, the ability of these compounds to destroy mucus and penetrate into cells makes possible the complex use of their preparations together with others (for example, with copper salts). The high solubility of these compounds in hydrocarbon fuel and water makes it possible to successfully use them in the protection of diesel fuel against microorganisms.

In addition, the following biocides are proposed: acylated alkyl dienes, oleates, butyrates, caproates, dimethylbenzenesulfonates, silver toluenesulfonates, as well as compounds containing boron, arsenic, tin, mercury, nitrofuran resins, a mixture of ethylene glycol monomethyl ether with glycerin.

Thus, the most effective hydrogen sulfide corrosion inhibitors that suppress the action of sulfate-reducing bacteria (as the main cause of this corrosion) are cationic-type inhibitors that can suppress the process of hydrogen evolution. Being adsorbed on the metal surface, they inhibit the hydrogen reduction reaction (RRR) and, thus, inhibit the action of sulfate-reducing bacteria as cathodic depolarizers [9], although not always. Sulfamide preparations, some aromatic alcohols, heterocyclic compounds, and some industrially used herbicides have been proposed as inhibitors of microbiological corrosion caused by sulfate-reducing bacteria.

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