The influence of total sediment of petroleum products on the corrosiveness of the metal of the tanks during storage

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Abstract. Storage tanks for petroleum products must comply with the requirements of technical, technological and environmental safety. The corrosion rate increases with prolonged storage of petroleum products in tanks. To prevent the destruction processes for reliable operation of tanks caused by metal corrosion some solutions are needed. Active formation of general sludge occurs in the storage of fuel oil, which contains corrosion-active substances, because of the incompatibility of fuels. The paper assesses the effect of total oil sludge in tanks on the corrosion process and on the reliability of tanks. Studies of the formation of a common sediment caused by incompatibility when mixing petroleum products are conducted. The paper proposes a solution which allows to reduce the formation of total oil sludge and to ensure reliable operation of reservoirs.

1 Introduction

Increasing the capacity of tank farms leads to an increase of accident risk level, as a consequence, the condition of the tanks should be technical supervision [1]. Ensuring the reliability and safety operation is an urgent problem. The requirements of technological, technical, physicochemical and environmental safety should be complied with tank farms of crude oil and petroleum products respectively.

Metal corrosion is the most dangerous and unpredictable process of destruction of tank structures.

![Percentage of corrosion](image)

*Fig. 1. The percentage of corrosion.*

Corrosive damage is a surface defect of the metal and cause a local decrease in the wall thickness with the formation of corrosion products on the surface; a concentration of stresses occurs at the sites of formation of certain defects. The statistical studies of various types of corrosion are shown in Fig.1 [2]. This statistical ratio can be considered approximate, since in real conditions certain types of corrosion are found in various combinations [3-5].

Corrosive damage to the internal surface of tanks according to the degree of exposure to the corrosive components of petroleum products is divided into several zones; this is the roof, the bottom and the lower belt. Inspections of tanks after storage of petroleum products revealed that the bottoms and the lower zone of tanks are most susceptible to corrosion, and the intensity of corrosion under the influence of the vapor-air mixture is 4 to 5 times lower [6]. Depending on the type of stored oil product, the corrosion rate of the bottom and the lower belt is 0.4 mm / year or more. The corrosion rate of light oil storage tanks can reach 0.5 mm/year [7].

The most dangerous types of corrosion are pitting and pitting, because due to the small size of the ulcers and their filling with corrosion products, such destruction is difficult to detect and repair in time. After 3 ... 5 years of storage of petroleum products, ulcers appear on the bottom and the lower belt, up to 4 ... 5 mm in depth, so overhaul is often required [8].

2 The effect of petroleum products on the corrosion of metal tanks during storage

Petroleum products are corrosive, because they contain sulfur and oxygen-containing compounds. Their number depends on many factors: type of fuel, methods of processing and the origin of oil. Metal ions are transferred to fuel during storage as a result of corrosion processes occurring in fuel storage tanks.
At the same time, as a result of corrosion effects, the service life of these technical means decreases, the risk of loss of petroleum products increases, the environmental situation worsens, and the fuel is contaminated with corrosion products. Corrosion products are a kind of abrasive, causing premature wear and failure of the rubbing parts of fuel equipment and cylinder-piston group of internal combustion engines and other types of equipment [9].

Corrosion of metals in petroleum products has its own characteristics. Corrosion aggressiveness is manifested mainly by impurities, such as water, sulfur-containing and oxygen-containing compounds, hydrogen sulfide and mineral salts [10].

Sulfur and sulfur compounds have a corrosive effect on metals as a result of direct interaction with metals or as a result of the effect of oxidation products of these compounds on metals [11].

Oxygen-containing compounds contained in petroleum products also affect their corrosivity and are naphthenic acids. They enter petroleum products with feedstock or are formed in petroleum products as a result of oxidation of commodity fuels during their storage and use. It should be noted that sulfur compounds are more aggressive for metals and alloys than the products of auto-oxidation of naphthenic acids [8].

Corrosion can be carried out by a chemical mechanism in the presence of chemically aggressive substances in the oil product, namely sulfur, hydrogen sulfide, water. However, studies indicate that often the occurrence of corrosion of internal surfaces of tanks occurs through an electrochemical mechanism due to the presence of a film of water on the inner surface of the tank, containing dissolved oxygen, mineral acids and salts. Under production conditions during transportation and storage of oil products, they are constantly saturated with water and condensed on a metal surface [12, 13].

Chromatographic and spectrophotometric studies have shown that water condensates selected from storage and fuel systems contain low molecular weight oxidation products of hydrocarbons: carboxylic acids, ketones, aldehydes, alcohols. Water-soluble oxidation products of sulfur compounds — mainly sulfonic acids — were also found in condensates of sulfur-containing fuels [14]. Consequently, water condensates that collect on metal surfaces are electrolyte solutions that promote electrochemical corrosion of metals in low acidity conditions.

Manifestations of "incompatibility" when mixing petroleum products are associated with the emergence of strong intermolecular interactions caused by changes in the structural group composition and the relative ratio of concentrations of high molecular compounds of petroleum products, which leads to the formation of associates of molecules, bulk colloidal particles of various shapes and structures. When mixing, it is necessary to take into account the formation of static electricity in tanks [15].

It is also worth noting that, due to the high polarity, water can interact with insoluble low-stable compounds, hydrate them and transport them to metal surfaces. Due to its high surface activity, water collects in the hydrocarbon environment fine particles of contaminants into large aggregates, which quickly settle to the bottom of the reservoir. [14].

The total precipitate contained not only a mixture of asphaltenes, resins and paraffins, but also nitrogen, sulfur, oxygen and metals [16].

The active formation of sediment accumulates at the bottom of the tank and increases the corrosion activity and at the same time creates an additional load on the stress-strain state of the lower belt of the tank.

Therefore, it is necessary to prevent the precipitation of the total sediment due to incompatibility by determining the compatibility of the fuels before mixing. Existing methods for assessing the stability and compatibility of petroleum products do not have high accuracy and have a large error.

For an accurate assessment of the compatibility and stability of petroleum products, it is necessary to develop a new exact method that will make it possible to determine the compatibility of several types of fuels at once and in the necessary proportion before mixing in tanks [17]. This task becomes possible through the use of GOST R 50837.6 "Method of determining the total sediment" with a change in the method of testing, which will determine the compatibility and stability of petroleum products.

4 Results

The principal difference of the new method is that to determine the compatibility of several types of petroleum products, first of all, it is necessary to perform tests to determine the total sediment with preliminary chemical aging (Total Sediments Accelerated - TSA) according to the method of GOST R 50837.6 for each component of the mixture. Further, after determining the total sediment for each of the components, the fuel data should be thoroughly mixed in the required proportion and then tests should be performed to determine the total sediment of the prepared mixture of petroleum products according to the method. Knowing the values of the total sediment of each of the fuels separately, and after obtaining the result of the total sediment of the prepared mixture, it is possible to draw conclusions about their compatibility.

Studies were carried out to determine the compatibility and stability of petroleum products by the
laboratory method presented, oil products were mixed in an accumulator tank in an equal proportion, after sampling was carried out according to GOST 2517 and the total sediment content of the resulting product was checked.

Fig. 2. Comparison of the obtained results on the determination of compatibility before mixing and after transportation and mixing in tanks.

The linear chart (Fig. 2) shows the obtained values almost coincides in critical points and fully meet the requirements of reproducibility according to GOST R 50837.6, which means the method for determining the compatibility of petroleum products is applicable in practice.

5 Conclusion

Corrosion of the internal surfaces of the tank is the dominant factor affecting the standard life of the tank. The rate of corrosion damage to the metal of a tank depends on many factors related to both the properties of the metal and the properties of the environment, external influences and the conditions of protection of the tank [18]. One of these factors is the active precipitation of the total sediment due to incompatibility when mixing petroleum products. When storing high-sulfur petroleum products, it is necessary to combat sedimentation, since this leads to the occurrence of the corrosion process on the bottom and lower zone of the tanks.

In order to timely detection and elimination the formation of a general precipitate, an algorithm has been developed for conducting laboratory tests to determine compatibility when mixing petroleum products. Since the material damage caused by corrosion can be enormous, it is necessary to study all aspects of this problem.

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