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ASSESSMENT OF CORROSION MECHANISMS AND EQUIPMENT OPERATIONAL SAFETY IN PRIMARY OIL REFINING UNITS

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Abstract. This article examines the specific characteristics of corrosion processes observed in primary distillation units of oil refineries and the technological factors influencing them. The chemical composition of deposits (fouling) formed as a result of the interaction between chlorides, sulfur compounds, and ammonia in the raw material is analyzed using column equipment as an example. Furthermore, a comparative assessment of the corrosive aggressiveness levels during the operational mode and pre-repair shutdown periods of the units was conducted. The research results hold significant scientific and practical importance for extending the service life of equipment metals and ensuring technological safety.

Keywords: Corrosion, oil refining, hydrogen sulfide, deposits, hydrogenolysis, rectification columns, atmospheric corrosion, condensate, technological regime, operational safety.

Annotatsiya. Ushbu maqolada neftni qayta ishlash zavodlarining birlamchi distillash qurilmalarida kuzatiladigan korroziya jarayonlarining o'ziga xos xususiyatlari va ularga ta'sir qiluvchi texnologik omillar ko'ribBundan tashqari, jihozlarning ishlash rejimi va ta'mirlashdan oldin o'chirish davrlarida korroziv agressivlik darajasini qiyosiy baholash o'tkazildi. Tadqiqot natijalari metall uskunalarning xizmat qilish muddatini uzaytirish va texnologik xavfsizlikni ta'minlashda muhim ilmiy va amaliy ahamiyatga ega.

Kalit so'zlar: korroziya, neftni qayta ishlash, vodorod sulfidi, konlar, gidrogenoliz, rektifikatsiya ustunlari, atmosfera korroziyasi, kondensat, texnologik rejim, ekspluatatsiya xavfsizligi.

Аннотация. В данной статье рассматриваются особенности коррозионных процессов, наблюдаемых в установках первичной перегонки нефти на нефтеперерабатывающих заводах, и технологические факторы, влияющие на них. На примере колонного оборудования проведен анализ химического состава отложений (обрастаний), образующихся в результате взаимодействия хлоридов, соединений серы и аммиака в сырье. Кроме того, была проведена сравнительная оценка уровней коррозионной агрессивности агрегатов в период эксплуатации и предремонтных остановок. Результаты исследований имеют важное научное и практическое значение для продления срока службы металлов оборудования и обеспечения технологической безопасности.

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Ключевые слова: коррозия, нефтепереработка, сероводород, отложения, гидрогенолиз, ректификационные колонны, атмосферная коррозия, конденсат, технологический режим, безопасность эксплуатации.

INTRODUCTION.

In the oil refining industry, the corrosive degradation of technological equipment is considered one of the primary factors posing a serious threat to production efficiency and industrial safety. Under modern refinery conditions, apparatus and pipeline networks operate under the influence of aggressive environments such as hydrogen chloride, hydrogen sulfide, and various organic acids, in addition to high temperatures and mechanical loads. The complexity of these processes lies in the fact that thermal decomposition products within the raw material feedstock form corrosion-active deposits on the metal surface through condensation, which in turn leads to the acceleration of local corrosion types (pitting and ulcerous/grooving corrosion).

Corrosion processes observed during the operation of oil refinery equipment possess a number of specific characteristics. Construction materials are subjected to the simultaneous influence of various factors, which leads to the deterioration of the mechanical properties and corrosion resistance of the metal, and consequently, results in unexpected equipment failure.

Main Part. The corrosion state within a primary oil refining unit is determined by the raw material composition, the extent of anti-corrosion protection measures, and other simultaneously acting factors [1-10] such as the following:

- High temperatures, which, in addition to increasing the corrosion rate, can lead to the occurrence of intergranular corrosion (intercrystalline corrosion);
- The presence of weld seams and mechanical loads (usually cyclic in nature), which cause high internal stresses and result in stress corrosion cracking and corrosive fissuring;
- The presence of chloride and sulfur compounds in combination with water vapor, which can lead to general (uniform), pitting, and ulcerous (crevice) corrosion;
- The application of various reagents (alkalis, amines, etc.), which cause various forms of general and local corrosive degradation;
- Coking of apparatus and pipelines, which leads to localized destruction (degradation);
- The use of highly aggressive circulating water, which causes pitting and ulcerous corrosive degradation.

Accounting for the influence of all parameters that play a significant role in the mechanisms of processes occurring in such systems is extremely complex, and

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often impossible. However, an analysis of the equipment's material execution and operational conditions allows for the identification, with high probability, of apparatus and pipelines prone to corrosive degradation that require special attention during operation. Objective, reliable, and timely information regarding the condition of equipment, along with an understanding of the essence of the ongoing processes, is vital for ensuring the safe operational conditions of production facilities.

The equipment and pipelines of oil refinery (OR) technological units operate under conditions where the metal is affected by hydrogen, hydrogen sulfide, free sulfur, thiols, chlorides, hydrogen chloride, ammonium chloride and sulfide, moisture, and carboxylic and polythionic acids. The concentration of these compounds is determined by the processes of thermal decomposition and hydrogenolysis of the hydrocarbon feedstock. Deposits (fouling) are formed as a result of the condensation and cooling of gas-product mixtures in heat exchangers, air-cooled condensers, water coolers, compressors, and pipelines.

Hydrogen sulfide is formed during the decomposition of mercaptans, disulfides, sulfides, and thiophenes contained in the raw material. Significant liberation of H_2S is observed at temperatures of 180-200°C and occurs due to the interaction of free sulfur with hydrocarbons. Further formation of H_2S takes place at temperatures above 300°C.

Hydrogen chloride is formed as a result of the hydrogenolysis of organochlorine compounds [11]:

$$RCl + H_2 \longrightarrow RH + HCl \quad (1)$$

$$RCl + S + H_2 \longrightarrow RH + H_2S + HCl \quad (2)$$

Ammonia formation occurs as a result of the hydrogenation (gidrirovanie) of nitrogen-containing hydrocarbons. Ammonia is also introduced into primary oil refining units as a neutralizing agent.

During the cooling and condensation process, the resulting interaction products react with each other and with the equipment metal [12, 13]:

$$HCl + NH_3 \Leftrightarrow NH_4Cl \quad (3)$$

$$H_2S + NH_3 \Leftrightarrow NH_4HS \quad (4)$$

$$NH_4HS + NH_3 \Leftrightarrow (NH_4)_2S \quad (5)$$

$$Fe + 2HCl \Leftrightarrow FeCl_2 + H_2 \quad (6)$$

$$FeCl_2 + \Leftrightarrow (NH_4)_2S \Leftrightarrow FeS + 2NH_4Cl \quad (7)$$

For hydrotreating (gidroochistka) units, the presence of polythionic acids is also characteristic; they are formed during the cooling of equipment, during shutdown periods, and after the completion of catalyst regeneration.

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The following factors significantly influence the occurrence of local corrosion types:

– Corrosive factors associated with the operation of the units in the working regime;

– The formation of corrosion-aggressive condensates as a result of steaming (proparivanie) apparatus and pipelines before carrying out repair work, as well as the interaction of corrosion-active deposits within them with atmospheric moisture and air oxygen during equipment downtime (during repair work or for other reasons).

Composition and aggressiveness of deposits and steaming condensates, and their influence on local corrosion types. During operation in the working regime, the gradual accumulation of deposits (precipitates formed on the metal surface), consisting of corrosion products, organic components of the technological medium, and various impurities, occurs within the equipment. Tables 1 and 2 present generalized data on the average composition of deposits and steaming condensates in the column equipment of primary oil refining units, obtained as a result of long-term analyses.

It is evident from the presented data that the pH indicator of the aqueous solution of deposits in the columns is characterized by acidity and a high metal content (up to 40–55%). Furthermore, sulfur compounds with various oxidation states are present in their composition in significant amounts, while chlorides (with rare exceptions) are almost absent.

Deposits in apparatus and pipelines can be divided into two groups:

– Deposits formed as a result of corrosion of the equipment metal;

– Deposits formed from technological medium components and impurities during the operation of the units in the working regime.

The first type of deposits includes corrosion products: iron hydroxides $Fe(OH)_2$, $Fe(OH)_3$, iron oxides Fe_3O_4, α-, γ-Fe_2O_3, oxyhydroxides (α-, γ-, Δ-, β-FeOOH), iron sulfides, and chlorides. The second type of deposits consists of organic components and compounds formed during the working regime of the unit: NH_4Cl, NH_4HS, $(NH_4)_2S$.

Table 1.

Average composition of deposits obtained from the upper section of primary oil refining units after steaming before repair.

Column	pHmedium	$Fe^{2+,3+}$	S_{total}	S^{2-}	SO_4^{2-}	Cl^-
Evaporation (Steaming)	3.3–4.9	1.2	13–28	4–24	9–20	up to 0.8
Atmospheric	4.5–6.5	1.0	5–17	2–17	2–15	0.7–7

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Secondary Rectification	3.65–4.5	50–55	1–3.5	0.2–0.8	1–3.5	traces
Stabilization	3.65–4.5	40–45	10–14	8–10.5	5–9	none
Vacuum	3.4–4.2	40–45	0.5–2.5	0.5–1.8	1.3–2.5	traces

Table 2.

Average composition of steaming condensates from the column equipment of primary oil refining units (based on long-term analysis results). Numerator - at the beginning of steaming, denominator - at the end of steaming.

Column	pH	$Fe^{2+,3+}$	Cl^-	S^{2-}	$S_2O_3^{2-}$	SO_3^{2-}	SO_4^{2-}
Evaporation	3.2–5 / 3.2–4	0.8–1.2 / 11–20	31.5–420 / 8–1200	2–3.2 / 3–4.9	none–2.9 / 2–5	2–3.4 / none–4	40–315 / 315–760
Atmospheric	4.6–5 / 5–5.4	15–21.6 / 40–168	49–370 / 390–2300	none–0.4 / 0.4–2.2	none–7.0 / 5–17	9–95 / 7–41	30–59 / 218–885
Atmospheric Steaming (strippings)	4.8–5.8 / 6–6.3	1.9–93.4 / 2.1–13.2	2.5–30 / 2–15	0.3–0.5 / none–1.5	7–1.8 / 1.2–6.3	6.5–11 / 3–5	8–173 / 21–75
Vacuum	4.8–6 / 6–9	70–90 / 100–120	30–155 / 2–20	0.2–1.6 / none–5	0.6–5 / none–2	5–10 / 3–5	60–135 / 115–270

* $[NH_4^+]$ — up to ~ 6 mg/dm³.

During the equipment downtime period (prostoy), the effect of oxygen and moisture on the metal can be evaluated based on the atmospheric corrosion rate values of carbon steel in an industrial atmosphere under a shed. This value for an oil refinery is approximately 0.004 mm/year (for clean metal) [14]. As air humidity increases, the corrosion rate of carbon steel rises sharply and reaches < 0.05–0.07 mm/year at 100% humidity [14].

According to [15], metal corrosion during equipment downtime is divided into three conditional groups depending on air humidity:

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–"Wet" corrosion — observed during the condensation of moisture in the form of droplets; such conditions occur when the relative humidity of the medium is around 100%;

–"Damp" corrosion — occurs under the thinnest layer of electrolyte formed as a result of adsorption or chemical condensation, when the medium humidity is above 40%;

–"Dry" corrosion — occurs when air humidity is less than 40%.

In practice, it is not always possible to clearly distinguish these three types of corrosion, as the presence of corrosion products and deposits on the metal surface significantly alters the corrosion rate and the character of its progression. Chloride deposits formed in the condensate increase the corrosion rate of steel in damp air from 0.05–0.07 to 0.3 mm/year, i.e., by 4–6 times [16]. They mainly consist of iron oxides, oxyhydroxides, and hardness salts. For these, the pH values of the aqueous solution are close to neutral.

CONCLUSION. The conducted analyses show that the corrosive state in primary oil refining units directly depends on the aggressiveness of technological streams and the composition of salt deposits formed during condensation processes. The iron content reaching up to 55% in samples taken from the upper part of the columns and the sharp shift of the pH indicator toward an acidic environment (3.2–4.5) testify to the intensive destruction of the metal.

Specifically, it was found that during equipment downtime, the combined effect of atmospheric moisture and chloride deposits increases the corrosion rate by 4–6 times. Therefore, in creating an effective anti-corrosion protection system, it is a vital necessity to consider not only the operating regime parameters but also the influence of aggressive condensates during shutdown and steaming periods.

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