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Corrosion mechanisms in columns for atmospheric distillation of crude oil

Mechanizmy korozji kolumn destylacji atmosferycznej ropy naftowej

The paper presents the most common corrosion processes occurring in the columns for atmospheric distillation of crude oil. It describes the mechanisms leading to formation of the chemical compounds, which contribute to corrosion phenomena. The main technological factors influencing corrosion processes have been indicated. The paper also presents the interactions between particular corrosion mechanisms resulting in acceleration or inhibition of corrosion rate.

Keywords: atmospheric distillation of crude oil, overhead distillation column corrosion, hydrolysis of chloride salts and organic chlorides

W pracy przedstawiono najczęściej występujące procesy korozyjne w kolumnach destylacji atmosferycznej ropy naftowej. Opisano mechanizmy powstawania związków chemicznych, które przyczyniają się wtórnie do występowania korozji. Przedstawiono szczegółowe dane literaturowe związane z oceną zagrożeń korozyjnych. Wskazano główne czynniki technologiczne, które mają wpływ na rozwój procesów korozyjnych. Przedstawiono interakcje poszczególnych mechanizmów korozyjnych, zwiększające lub obniżające szybkość korozji.

Słowa kluczowe: kolumna destylacji atmosferycznej ropy naftowej, korozja górnej części kolumny atmosferycznej, hydroliza chlorków organicznych i nieorganicznych

1. Introduction

The corrosion processes occurring in the columns for atmospheric distillation of crude oil are of key importance regarding reliability of the entire system of crude oil processing.

Corrosivity of crude oil results mainly from a content of different corrosive components. The most important ones include: inorganic salts, organic chlorides, sulphur-, oxygen- and nitrogen-containing hydrocarbons, organic acids, hydrogen sulphide and carbon dioxide. Particular types of crude oil differ significantly in proper-

ties, in majority of cases processed crude oil is characterized by the density between 800 and 900 kg/m³ at 15°C, water content at the level of ca. 0.05% m/m, inorganic chloride salts content at 15–35 mg/kg level, organic chlorides at 0.02–0.06 mg/kg level, nitrogen 200–1500 mg/kg, asphaltenes from 0.03 to 2.3% m/m, sulphur content 0.3–1.8%, hydrogen sulphide 0.01–1.0 mg/kg and acid value at the level of ca. 0.05–0.5 mg KOH/g. The content of particular components varies depending on a type of processed crude oil, which translates into corrosivity of the technological streams during processing.

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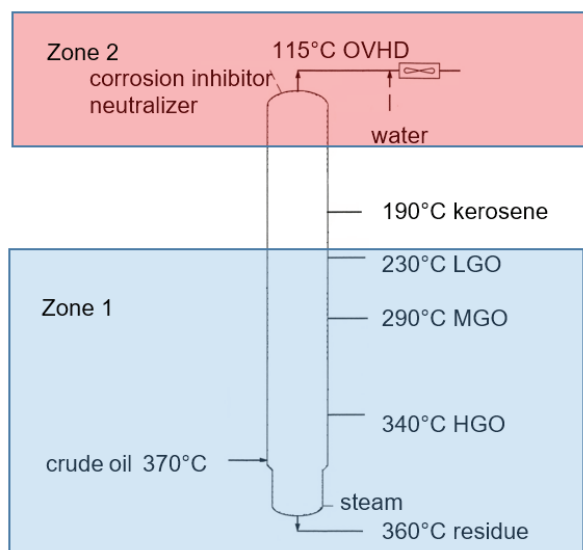


Fig. 1. Scheme of atmospheric distillation column with indicated corrosion risk zones

Rys. 1. Schemat kolumny destylacji atmosferycznej z zaznaczonymi strefami zagrożenia korozją

Prior to feeding into an furnace and further into an atmospheric column, the crude oil is subjected the preparation processes aimed at decreasing of its corrosivity. These processes include: decantation from above water phase in the storage tanks, precipitation of emulsion molecules of electrolyte in crude oil by an addition of demulsifiers, extraction of salts from crude oil using water. The above steps allow significant decrease in content of chlorides in the crude oil directed to processing. Small addition of soda lye solution is also applied in order to bind hydrogen chloride produced during hydrolysis of chlorides in the furnace and the column.

Corrosivity of crude oil during storage and at low temperatures is usually low because this property strongly depends on temperature. Temperature induces different types of chemical reactions, which produce secondary chemical compounds of high corrosion aggressiveness.

Crude oil of ca. 350–370°C is introduced to an evaporation chamber of the atmospheric column where it is subjected to rapid evaporation and separation into particular fractions differing in the boiling point. Addition of steam to a stripping section, which is located below the evaporation chamber, reduces partial pressure of particular components of crude oil and contributes to their better distillation. The atmospheric column is the place where a rectification process takes place, which consists in multistage distillation in which the compounds with lower boiling point lift to higher and cooler sections of the atmospheric column, while the compounds of higher boiling point undergo condensation and are collected in lower sections of the column. Gas components and light naphtha, which is directed to a naphtha stabilization section, are collected from the top of the column where the lowest temperature occurs. At the bottom of the column, the heaviest fraction is collected. It has not been distilled in the atmospheric column and is usually transferred to a vacuum column as an atmospheric residue (mazout).

During distillation chemical and electrochemical reactions between crude oil components take place due to high tem-

perature impact and addition of stripping steam to the column [1, 2]. The addition of steam influences on hydrolysis of organic and inorganic components of crude oil. Fig. 1 shows a scheme of the atmospheric distillation column with indicated corrosion risk zones.

2. Formation of the chemical compounds influencing on corrosion processes

Due to high temperature, there are a few processes, which influence on corrosion phenomena. First of all, there is thermal degradation of the hydrocarbons with such heteroatoms as sulphur, chlorine, nitrogen and oxygen [3]. In the case of organo-sulphur compounds, the degradation products include hydrocarbons and hydrogen sulphide [3, 4]. Degradation of organo-chlorine compounds produces hydrocarbons, hydrogen chloride and organic chlorides, often of different molecular mass than initially [5, 6]. Organo-nitrogen compounds undergo degradation forming hydrocarbons and ammonia, whereas in the case of oxygen-containing hydrocarbons the degradation products engulf hydrocarbons, carbon dioxide, oxides of hydrocarbons and oxygen [7, 8].

Discussed corrosion processes take place in lower part of the distillation column (zone 1), in the zone of >260°C fraction collection, which is the atmospheric residue and all diesel fractions.

3. Methods and Results

3.1. Types of corrosion processes occurring in upper parts of atmospheric distillation column – zone 2

3.1.1. Hydrolysis of inorganic salts

In the low temperature range (zone 2), close to the dew point temperature, in the upper part of the distillation column, there are the corrosion processes related to the degradation products formed in zone 1, namely hydrogen chloride, ammonia chloride and steam. Braden et al. and Duggan with co-workers show that hydrogen chloride present in this section is produced via thermal degradation of inorganic salts contained in crude oil [9, 10].

The most frequent salt present in crude oil directed to the column is NaCl, then MgCl₂ and CaCl₂, which occur at lower concentrations. Hydrogen chloride is formed as a result of contact between inorganic salts and steam (present in the atmospheric distillation column).

The process of hydrolysis of inorganic salts differs depending on the type of salt. Table 1 gathers the conditions for hydrolysis of inorganic salts. Following Table 1, it is evident that practically the hydrolysis of NaCl does not take place.

3.1.2. Corrosion in hydrochloric acid

The presence of hydrogen chloride in aqueous environment leads to formation of hydrochloric acid. This phenomenon occurs in water condensation zone, most frequently inside a vapour pipe of the distillation column or in an air condenser after the column [11]. Most construction materials exhibit relatively low resistance to hydrochloric acid. The attack usually takes the form of local corrosion in a relatively narrow zone of water condensation. Corrosion rate

Table 1. Hydrolysis reactions for inorganic salts

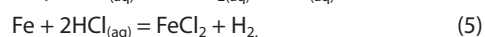
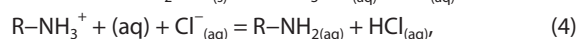
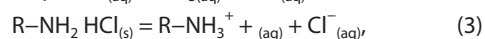
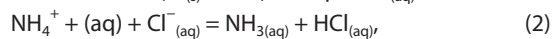
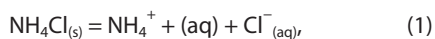
Tabela 1. Reakcje hydrolizy soli nieorganicznych

Reaction	Temperature of hydrolysis initiation [°C]	Degree of hydrolysis at 340°C [%]
$MgCl_2 + 2H_2O = Mg(OH)_2 + 2HCl$	120	90
$CaCl_2 + 2H_2O = Ca(OH)_2 + 2HCl$	210	10
$NaCl + H_2O = NaOH + HCl$	>500	2

primarily depends on concentration of hydrochloric acid, temperature of a medium and construction material of exposed installation.

3.1.3. Under deposit corrosion in ammonia chloride environment

Lordo identified NH_4Cl , connected with the presence of ammonia or amines and hydrogen chloride, as an important factor influencing on local corrosion in the atmospheric distillation columns [12]. It is formed in the reaction between NH_3 or amines and HCl vapour at the temperature of salt formation:



Ammonia could be inside the column because of many reasons, for instance due to presence of NH_3 during desalting or due to its application as a neutralizer (neutralization of acids). The process parameters should be adjusted in the way, which avoids the temperature of ammonia chloride formation for assumed quantities of substrates in the column. Formation of ammonia chloride is connected with partial pressures of ammonia and hydrogen chloride as well as with temperature following the relation:

$$K_d = [\text{NH}_3] [\text{HCl}], \quad (6)$$

where:

K_d – equilibrium constant,

$[\text{NH}_3]$ – vapour pressure of ammonia,

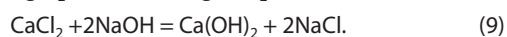
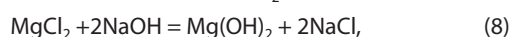
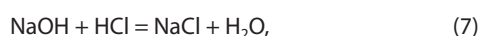
$[\text{HCl}]$ – vapour pressure of hydrogen chloride.

Ammonia chloride salts are strongly hygroscopic and they undergo hydrolysis upon reaching the dew point temperature. Under salt deposits, pH of the environment is very low leading to active local under deposit corrosion. Presence of oxygen in a vapour stream of the distillation column increases the corrosion risk. Corrosion attacks take place in the upper parts of the distillation columns, vapour pipes and air condensers.

3.1.4. Corrosion prevention methods in zone 2

The formation of hydrogen chloride due to inorganic salt hydrolysis could be limited via salt removal (desalting). Desalting prior to atmospheric distillation is the main tool limiting the quantity of inorganic chloride salts. The aim is to remove many impurities, mainly inorganic chloride salts, from crude oil. Typically, the concentration of chlorides is decreased to 4 ppm. This level of salt concentration in crude oil directed to distillation significantly limits the possibility of HCl formation in the distillation column. The analysis of Clarida et al. indicates that desalting system should reduce chloride ions content in crude oil to the level below 20 ppm in order to limit the corrosion rate [14].

To achieve that, a neutralization of crude oil is carried out using lye dosed after desalting process and before entrance to the column. The purpose of this operation is limitation of HCl formation due to hydrolysis. The following chemical reactions take place:



The main product is NaCl, which practically does not undergo hydrolysis to hydrochloric acid. Properly conducted process of crude oil desalting and neutralization substantially reduces the risk of hydrochloric acid formation from inorganic salt. Produced NaCl is

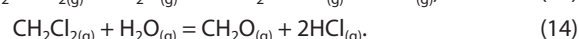
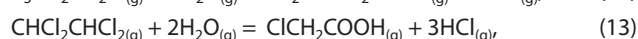
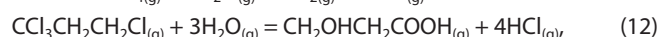
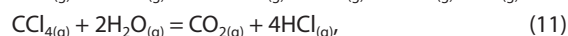
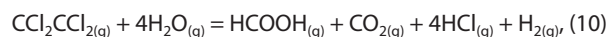
non-volatile and it does not distillate in the atmospheric column. Significant quantities of this compound are present in the atmospheric residue (even at the level exceeding 100 ppm) [15]. High salt (chlorides) content in the other installation processing the atmospheric residue could lead to chloride cracking of austenitic stainless steels. In order to further reduce the risk of corrosion in hydrochloric acid, a corrosion inhibitor, in the form of solution in naphtha, is dosed in the overhead and upper pumparound of the distillation column. The inhibitor forms a film on the wall of installation, which protects the surface from corrosion [16–18]. Additionally, to adjust pH of the stream, the amines (methoxypropylamine, ethanolamine) exhibiting passivating, neutralizing and oxygen scavenging properties are dosed into the overhead of the column. They effectively neutralize hydrochloric acid.

Unfortunately, all discussed actions do not provide complete protection against formation of hydrochloric acid contributing to local corrosion.

The main method of limiting corrosion in ammonium chloride environment is addition of washing water to the vapour pipes aimed at dissolution of formed salts. However, it is not feasible in the upper part of the column. That is why additional inhibitor protection is employed.

3.1.5. Hydrochloric acid corrosion in zone 2

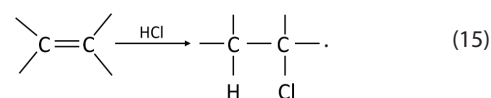
The research of Gutzeit reveals that hydrogen chloride can also originate from organic chlorides present in crude oil [13]. The investigations of Ma et al. concerning heavy crude oil types show that the content of organic chlorides is the highest in paraffin and light diesel fractions, while it is negligible in the atmospheric residue fraction [15]. There is significant content of nitrogen compounds, such as 5-chloro-2-methylaniline. The results obtained by Wu and co-workers for lighter crude oil types revealed presence of organic chlorides in the light fractions [20]. It should be emphasized that organic chlorides are not removed during desalting of crude oil. They undergo hydrolysis upon high temperature and steam impact, for example according to the following chemical reactions [20]:



The effect of hydrolysis is formation of hydrogen chloride and oxygen-containing organic compounds, such as carboxylic acids, oxides, aldehydes and ketones.

Elevated temperature and steam are indispensable for generation of hydrogen chloride from inorganic and organic chlorides. Hence, intensive corrosion in hydrochloric acid is not observed in the primary distillation columns where low water content occurs.

The chemical mechanisms related to presence of organic chlorides are more complex. Pagliano and others illustrated that the addition reaction of hydrogen chloride to olefins could take place inside the distillation columns, following the equation [21]:

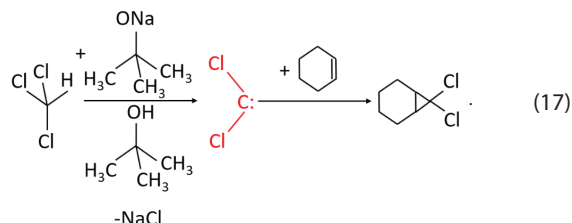


These processes yield secondary organic chlorides, which are characterized by higher boiling point. It results from the fact that crude oil is rich in olefins. Measured content of organic chlorides was higher after distillation than in raw crude oil, which could support the aforementioned mechanism. Organic chlorides are also subjected to thermal degradation, however, this process proceeds with low efficiency in the temperature range present inside the dis-

tillation column [22]. Chloroform, being the main component of organic chlorides in light crude oil, reacts with soda lye (a neutralizer), which could lead to formation of other organic chlorides [23]:



A product of this reaction is dichlorocarbene, which is very reactive and reacts with alkenes present in crude oil:

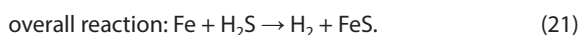
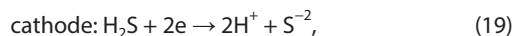
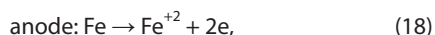


This process generates heavier chlorinated derivatives. Presented examples indicate high reactivity of organic chlorides that could result in significant corrosion risk [24].

Processing of the crude oil with high naphthenic acids content could increase inorganic salts concentration in desalted crude oil. Eaton et al. show that naphthenic acids contribute to the formation of an emulsion in the upper section of the distillation columns, which translates into an increase in corrosion rate [25]. High content of acids during crude oil desalting results in an increase in conductivity and emulsion formation, which reduce efficiency of this operation. Moreover, naphthenic acids catalyse hydrolysis of calcium and chlorine salts. Both factors significantly contribute to elevation of HCl concentration in the column.

3.1.6. H_2S corrosion in zone 2

High temperature (up to about 350°C) in the atmospheric column results in thermal cracking of the organic sulphur compounds in crude oil (thiols, sulphides, mercaptans). The effect of this process is the formation of hydrogen sulphide and hydrocarbons with a lower number of carbon atoms. Considerable corrosion risk usually appears when water condensation occurs. Due to the higher solubility and degree of dissociation of HCl as compared to H_2S , corrosion processes start when significant water condensation takes place, which is when a vapour stream leaves the air and water condenser. The mechanism of corrosion is generally described as acidic sour water corrosion [26]. The following corrosion reactions occur in hydrogen sulphide-containing aqueous environments [27, 28]:



A very detailed description of the corrosion mechanisms in hydrogen sulphide-containing aqueous media has been provided by Szyprowski [27]. The corrosion rate is mainly connected with the pH of an aqueous environment. Here, a decisive factor is an ionic form present in the environment. Depending on the pH of the aqueous environment, hydrogen sulphide can exist in the following forms: H_2S – undissociated, HS^- , S^{-2} [27, 29]. Corrosion rate increases with a decrease in pH, which is usually associated with an increase in hydrogen sulphide content in water (assuming no impact from other chemical components). The second factor is temperature [26]. Generally, the corrosion rate increases with an increase in temperature due to higher kinetics of proceeding electrochemical reactions (however, the solubility of hydrogen sulphide in water drops to a certain degree). Other factors are the flow rate of the stream and oxygen content [30]. It is considered that the corrosion rate increases rapidly after exceeding 50 ppb of oxygen

in water [26]. It must be emphasized that electrochemical corrosion in a hydrogen sulphide environment leads to a liberation of hydrogen, initially in the atomic form and finally in the molecular form in the steel structure. This phenomenon causes hydrogen embrittlement, also called wet H_2S degradation [26, 30].

Generally, hydrogen penetration is characterized by the following mechanism:

1. Corrosion of steel in hydrogen sulphide-containing aqueous environment, which causes general corrosion.
2. Corrosion produces atomic hydrogen, which penetrates metal structure.
3. As opposed to the typical hydrogen embrittlement, structural degradation of steel occurs when recombining hydrogen leads to the formation of blisters, cracks, and stress-induced cracks.

Typically, the higher the corrosion rate according to the corrosion mechanism in sour water, the higher volume of hydrogen penetrating steel. However, the level of hydrogen content results from the structural and mechanical properties of a construction (defects, magnitude of stress).

Corrosion attack takes the following forms of degradation [26, 31, 32]:

- Blistering – hydrogen blisters can form in both: the subsurface zone and the bulk of steel structure. The blisters appear due to the penetration of hydrogen generated by sulphide-induced corrosion on a steel surface. Hydrogen diffuses into steel and accumulates in the microstructural discontinuities.
- Hydrogen-induced cracking (HIC) – this process is more advanced than blistering. Formed hydrogen blisters cause an increase in stress. Additionally, they frequently occur at different depths within the material, which leads to the cracking of steel. Individual cracks between the blisters may link up, which often takes the form of a step. Thus, HIC is sometimes termed ‘step-wise cracking’. The HIC process occurs as a result of the synergistic impact of three factors: atomic hydrogen source, mechanical stress, and microstructural defects in steel. Post-weld heat treatment (PWHT) does not prevent this mechanism of corrosion.
- Stress-oriented hydrogen-induced cracking (SOHIC) – the SOHIC process is a more advanced form of HIC. Formed cracks are more spatially organized, they occur in layers. The main crack is perpendicular to the surface and is usually associated with the presence of residual stress. The cracks typically form in the vicinity of a weld, in the heat-affected zone.
- Sulphide stress cracking (SSC) – this is a typical cracking phenomenon connected with sulphide-induced corrosion and tensile stress. SSC can be initiated on steel surface in highly-localized spots, characterized by significant hardness, in the weld material and the heat-affected zone.

The factors influencing on degradation processes (apart from the factors causing corrosion in sour water) are sulphur content in steel and the hardness of steel. In the case of the stress corrosion cracking (SCC) mechanism, it is important to apply the PWHT procedure.

3.2. Types of corrosion processes occurring in bottom parts of atmospheric distillation column – zone 1

3.2.1. High-temperature sulphide corrosion

In the temperature range above 260°C (zone 1), which is in the bottom part of the atmospheric distillation column, hydrogen sulphide and naphthenic acids present in crude oil exhibit corrosion aggressiveness, usually contributing to general corrosion (at low content of naphthenic acids) of carbon steels [8].

The corrosion caused by sulphur compounds in the temperature range $230\text{--}540^\circ\text{C}$ is termed high-temperature sulphide corrosion. Hydrogen sulphide could react with steel structures of a petroleum

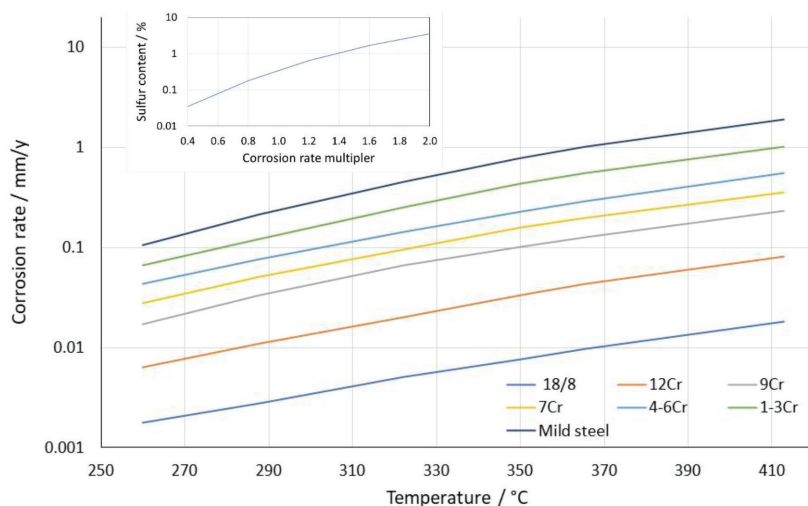


Fig. 2. The modified McConomy curves illustrating influence of the temperature on sulphide corrosion of metals and effect of percentage sulphur content on corrosion rate at 260–410°C

Source: [33, p. 162].

Rys. 2. Zmodyfikowane krzywe McConomy'ego ilustrujące wpływ temperatury na korozję siarczkową metali oraz wpływ procentowej zawartości siarki na szybkość korozji w temperaturach 260–410°C

Źródło: [33, s. 162].

installation, forming scale in the form of iron sulphide on a metal surface. The reaction between hydrogen sulphide and steel could be presented as follows:



This process leads to dissolution of a certain amount of the construction material, but to some extent it could also protect the metal surface against further corrosion induced by naphthenic acids via limitation of corrosive agents transport towards steel surface.

According to Gutzeit's theory, the rate of sulphide corrosion is described by the relationship [13] presented in Fig. 2.

Corrosion rate is the highest for carbon steels and increases with elevation of temperature. According to the API571 standard, the minimum threshold temperature is 204°C [33]. That is why the middle parts of the atmospheric distillation columns are usually made of carbon steel as they are exposed to the temperatures, at which no low- and high-temperature corrosion processes occur. However, this conclusion is not entirely correct because thermal degradation of organo-sulphur compounds could take place at lower temperatures. The investigations of Yang and co-workers show that efficient degradation of light thiols could occur already after reaching 100°C [34]. In the case of steels with higher chromium content, corrosion rate is limited [33]. For 5Cr steel, the threshold temperature for corrosion processes is 329°C. High chromium low alloy steel (9Cr) could be employed up to 400°C. Generally, for all materials corrosion rate increases with the increase in temperature and sulphur compounds content. However, the relationship between corrosion rate and temperature could be different in the entire temperature range. Ferritic (12% Cr) and austenitic steels possess superior resistance to high-temperature sulphide corrosion. The mechanism of their resistance consists in presence of a passive layer on the surface, which, however, can be destroyed in reducing conditions inside the column. In this case, application of the claddings made of these steels does not increase durability of the internal walls of the column.

High-temperature sulphide corrosion is usually described as a general mass loss or degradation of exposed metal surface accompanied by a formation of sulphide scale, as opposed to the cor-

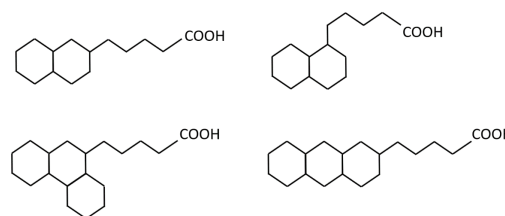


Fig. 3. Exemplary structures of naphthenic acids, which could occur in crude oil accumulations

Source: [37, p. 2].

Rys. 3. Przykładowe struktury kwasów naftenowych, które mogą występować w ropie naftowej

Źródło: [37, s. 2].

rosion caused by naphthenic acids, which has more local character. The mechanism of high-temperature sulphide corrosion is relatively frequent in petroleum installations, especially in furnaces, heat exchangers, columns and pipelines.

3.2.2. Naphthenic acid corrosion

Naphthenic acids are present in majority of raw crude oil and they are typical impurities causing corrosion of construction materials. Naphthenic acid corrosion (NAC) is a serious problem for the petroleum industry. It was identified for the first time in the 20s of the twentieth century and every year an increasing number of petroleum plants face that type of attack. Although naphthenic acid corrosion is a commonly known phenomenon, it is not fully understood due to complex impact of many factors on the corrosion mechanism.

The investigations on correlation between corrosivity of naphthenic acids and their molecular structure revealed two different fractions of naphthenic acids [35]. It was found that the group of naphthenic acids engulfing low molecular mass compounds, in the range 125–425 g/mol, exhibits significant corrosivity. On the other hand, the group of acids including the compounds of 325–900 g/mol molecular mass turned out to be non-corrosive. However, it was soon discovered that corrosion aggressiveness of naphthenic acids should not be related to their molecular mass. It was identified that an increase in the number of aromatic rings in a molecule decreases NAC [36].

Fig. 3 presents exemplary structures of naphthenic acids, which could occur in crude oil accumulations.

Wide variety of structures of naphthenic acids is the reason why crude oil contains many types of acids with unknown molecular structure.

The lower molecular mass of a chemical compound, the lower its decomposition temperature. This rule could support the statement that higher corrosivity of acids should not be correlated with their low molecular mass. The temperature 350–400°C corresponds to the maximum range for decarboxylation, which is mainly responsible for a decrease in acid value in liquid products of crude oil processing, thus for a decrease in corrosivity.

Many sources indicate that this type of corrosion attack could usually be encountered in distillation columns, pipelines, heat exchangers and other pieces of equipment contacting with the fractions of light and heavy diesel after atmospheric distillation and the fractions obtained after vacuum distillation, operating at the temperatures above 200°C. It was shown that the biggest quantity of naphthenic acids occurs in diesel and light lubricating oils. That is many petroleum plants conducted the investigations on crude oil corrosivity in the temperature range 200–400°C (at the temperature above 400°C no naphthenic acids are observed due to decarboxylation phenomenon).

However, more and more frequently the investigations are focused on the paraffin fractions from processing of strongly acidic crude oil accumulations because it was found that the fractions boiling at 190–210°C possess strong corrosive properties. This form of corrosion is termed low-temperature naphthenic acid corrosion [38].

Corrosion of carbon steel in naphthenic acids is a complicated process due to complexity of the naphthenic acid itself. Nevertheless, this type of corrosion could be generally presented using the following equation, where iron is the material undergoing corrosion:



Dissolution of iron in naphthenic acid produces hydrogen and salt of naphthenic acid – iron (II) naphthenate. The NAC process could be divided into four stages:

1. transport of naphthenic acid molecule from crude oil stream towards metal surface,
2. surface adsorption of naphthenic acid molecules,
3. chemical reaction between naphthenic acid and metal in the active sites of a construction material,
4. desorption of oil phase soluble corrosion product from the metal surface.

The investigations on corrosion aggressiveness of naphthenic acids reveal that they are the most corrosive at the temperature close to the boiling point in liquid phase. High corrosion rates could be attributed to the condensate layers formed on steel surface of the industrial structures, not to the vapours [13]. Significant corrosion potential of naphthenic acids at their boiling points explains why no particular temperature within the range 190–400°C is responsible for the peak rate of NAC and only allows correlation between corrosivity and presence of given types of naphthenic acids in crude oil.

Naphthenic acid corrosion is characterized as a local attack, especially in the regions of high flow rate of a medium or where high condensation of concentrated acid occurs, namely in the distillation columns and transmission lines. Corrosion products are not observed on the construction metal's surface as they are soluble in crude oil, which results in exposure of a bare metal. Thus, NAC could achieve high rates and cause local attack on the alloys, which in typical conditions are regarded as corrosion resistant ones.

NAC did not constitute significant corrosion risk due to processing of the Rebco type crude oil in Poland, which is characterized by low value of total acid number (TAN < 0.1). Significant excess of sulphur compounds in the Rebco oil (1.5% S) with respect to naphthenic acids content caused that NAC mechanism was not observed.

3.2.3. Influence of particular corrosion types in zone 1

Simultaneous occurrence of naphthenic acid corrosion and high-temperature sulphide corrosion is a complicated phenomenon due to numerous interactions between these processes. It was agreed that natural presence of sulphur compounds in crude oil could limit NAC of steel structure surface up to certain extent

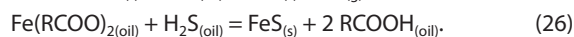
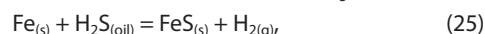
due to formation of a scale layer the metal surface. Nevertheless, presence of the protective layer does not impede NAC in 100%. It was proven that naphthenic acids could destabilize and modify the protective layers, such as oxides and sulphides, on metal surface allowing access of corrosive agents and resulting in an increase in NAC and sulphidation rate. The research of Kane and Cayard [39] on corrosion coupons provided an evidence that the scale layer underwent substantial dissolution upon presence of naphthenic acids. Analysis of mass loss and visual inspection confirmed the results of experiment. Pits and perforations were observed in the vicinity of the edges of sulphide-covered steel coupon. Local depletion of sulphide layer exposed bare metal substrate to naphthenic acids impact.

The interaction between naphthenic acid corrosion and high-temperature sulphide corrosion could be classified into three types, which could, but do not have to, occur in every petroleum plant:

- type I – corrosion caused by pure naphthenic acid,
- type II – high-temperature sulphide corrosion in case of lower concentration of naphthenic acids,
- type III – naphthenic acid corrosion inhibited by hydrogen sulphide.

The first type is characterized by corrosion in pure naphthenic acid. It corresponds to the situation when no protective film (in the form of iron sulphides) is observed on the surface or when very thin film is present due to low quantities or lack of sulphur compounds in crude oil. The second type is associated with high-temperature sulphide corrosion at low concentration of naphthenic acids and it is characterised by an increase in sulphidation upon low quantities of naphthenic acids. The third type occurs when naphthenic acid corrosion is inhibited by presence of sulphur compounds in crude oil and corresponds to the situation when stable layer of iron sulphide is present on metal surface. NAC is slowed down due to action of stronger acid, namely hydrogen sulphide. The second and third types could be perceived as dominant corrosion types in a particular environment.

Both these mechanisms can occur simultaneously in a petroleum plant, hence they could be regarded as competitive. Despite the fact that the mechanisms of these phenomena are not sufficiently recognized, there is no doubt regarding the chemical reactions that take place. Naphthenic acids RCOOH react with iron, being the construction material of petroleum equipment, and give iron naphthenates $\text{Fe}(\text{RCOO})_2$, which are soluble in oil phase (equation 24). Hydrogen sulphide dissolved in crude oil, as a very reactive compound, could react with iron forming iron (II) sulphide FeS (equation 25), which is insoluble in oil phase. Moreover, hydrogen sulphide (if present in larger amount) could also react with formed iron naphthenates and recover naphthenic acids (equation 26), which would react with steel once again. In this way, the entire cycle repeats and degradation of construction material escalates:



In order to facilitate determination which of the corrosion processes is dominant, Craig elaborated naphthenic acid corrosion index (NACI) [40]. It is defined as the ratio of corrosion rate to mass of corrosion products formed on metal surface due to corrosion [mg/cm^2]. The value of NACI lower than 10 means that high-temperature sulphide corrosion is a dominant process. In the case of pure NAC, this index takes the value higher than 100. Between these two critical values, there is naphthenic acid corrosion partially inhibited by hydrogen sulphide.

3.2.4. Corrosion prevention in zone 1

Application of corrosion resistant construction materials is the main method of protection against naphthenic acid corrosion and high-temperature sulphide corrosion. Cladding with ferritic stainless steel is employed in case of the atmospheric distillation columns. Low-alloyed Cr-Mo steels with the maximum content of chromium up to 9% are used for the transmission pipelines.

4. Summary

For many years, corrosion of the atmospheric distillation columns has been a typical problem in petroleum plants. Despite application of numerous anticorrosion protection methods, the problems with degradation of construction materials have not been fully solved. It results from a variety of chemical reactions involving hydrocarbons with different heteroatoms, which occur at high temperature and upon steam presence. Rational production process requires utilization of various feedstock substantially differing in chemical composition, which has a significant impact on corrosion risk. Explanation of corrosion risk calls for precise evaluation of different secondary chemical compounds formed upon steam and temperature presence, which exhibit corrosion aggressiveness. A combination of technological and corrosion knowledge could definitely increase the potential for limitation of corrosion processes.

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