Corrosion Problems and Solutions in Oil Refining and Petrochemical Industry

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Abstract. The aim of this work is to describe and analyze corrosion problems and their solutions at units of oil refining and petrochemical industry. Low- and high-temperature corrosion phenomena and factors influencing them are discussed. Typical and unique corrosion failure case studies and their prevention at refinery and petrochemical units are described and analyzed. Sulfidic corrosion, naphthenic acid corrosion, and corrosion at the overhead of aromatic column at the petrochemical plant are illustrated. Corrosion management plays vital role in the solving of corrosion problems. The results are summarized in new book "*Corrosion Problems and Solutions in Oil Refining and Petrochemical Industry*" published by Springer.

Keywords: oil refining, petrochemical industry, failures, management.

Introduction

Metallic equipment and constructions at oil refineries and petrochemical plants contact crude oils, petroleum products and fuels, solvents, water, atmosphere, and soil. All processes with participation of aggressive substances occur in metallic equipment at temperatures from $-196^{o}C$ to $+1,400^{o}C$ and pressures from vacuum to 1,000 bar. Oil refineries and petrochemical plants represent also a high hazard industry with media which are flammable, explosive, toxic to human health or harmful to the environment. The combination of numerous factors makes refinery equipment very vulnerable to a variety of corrosion phenomena that can lead to serious accidents.

On the one hand, oil refining and petrochemical industry has accumulated large experience. On the other hand, the introduction of new technologies, materials, strict requirements to the quality of fuels and to the reduction of environmental pollution state new problems to safe functioning of equipment and constructions.

In order to understand and to solve corrosion problems in refinery and petrochemical units, corrosion and materials specialist should learn diverse physicochemical processes which are the basis of production of fuels and other chemicals. During my long carrier in oil refining and petrochemical plants, above 3,000 corrosion events were analyzed and the reasons were defined. It was established that people are responsible in 65-85% of corrosion cases. Using proper corrosion management it is possible do diminish them.

In spite of many conferences, publications, researches, reports and achievements in refining and petrochemical corrosion control and monitoring, a number of corrosion problems is increasing in the last 20 years because of four factors. The first - the introduction of new processes. The second - some universities and colleges removed corrosion courses they had before in the engineering curricula. The third - corrosion engineers in most of oil refineries and petrochemical plants were replaced with consultants. The fourth - corrosion specialists retire and are not replaced.

There are many ways to avoid or control corrosion hazard: selection of corrosion resistant or suitable materials, correct design, use of anti-corrosive chemicals, control of technological parameters, use of coatings, cathodic protection, and what is very important, inspecting and control at all stages of application of these actions.

New generations of engineers come and face the problems which were solved and even documented. There are good books [1-8] and standards [9-12] but most new information is dispersed in literature or is present in the heads of specialists like tacit knowledge.

In this work, considering corrosion cases at different units, I tried to unify and allocate them according to appropriate systems and phenomena. You will find description of processing conditions, materials of constructions, history and service period, visual examination and findings, characterization of failure phenomenon, causes of failure and its explanation, solutions, and practical recommendations.

1 Process Units in Oil Refineries and Petrochemical Plants

Like evolution of our planet, life and technology, oil refining industry has been developing with increasing complexity since its foundation in 1859. Unit operations involve diverse physicochemical processes. The dream of the creator of the Periodic Table of elements, Dmitri Ivanovich Mendeleev is, that any chemical plant should be wasteless and is realized in the refinery: a product obtained in one unit is the raw material for the other unit. Nearly all wastes are utilized.

There are associated facilities, such as cooling water system, power station (with water treatment and steam providing), and units related to the protection of the environment and people (the utilization of hydrocarbon wastes, purification of wastewater and emitted gases, and deodorization). Any oil refinery is a very complicated alive "organism". Each oil refinery has its own unique processing scheme which is determined by the process equipment available, crude oil characteristics, operating costs, and product demand. There are no refineries absolutely identical in their operations but most corrosion problems and solutions may be similar. The following units are discussed in present work: distillation, visbreaker, and petrochemical plant (BTX unit - benzene, toluene, xylene).

2 Physicochemical Properties of Crude Oils

In order to understand corrosion problems and solutions in oil refining and petrochemical industry, we will describe physicochemical characteristics of crude oils and their corrosiveness. Other media, such as water (cooling water, boiler feed water, extinguishing water), steam, different gases and chemicals also can participate in corrosion of equipment at refining and petrochemical units.

2.1 Physicochemical Composition of Crude Oils

Crude oil is a mixture of numerous liquid hydrocarbons containing dissolved gases, water, and salts. Crude oils are, in fact, emulsions - drops of aqueous solution dispersed throughout the continuous hydrocarbon phase. Interstitial or connate water is always present in crudes. These water drops vary from almost fresh to saturated aqueous solutions of salts and are the main cause of crude corrosiveness. Crude oils in addition to hydrocarbons can include also compounds containing sulfur, nitrogen, oxygen, and metals. All these contaminants may be present in crude oils as dissolved gases, liquids and solids or distinctive phases.

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Microorganisms also can be present in crudes in active or dormant state. Every crude contains about the same kinds of compounds, but in different proportions. As a result, crude oil differ by their corrosiveness.

2.2 Corrosiveness of Crude Oils

Chemistry of crude oils is so complicated and there are so many factors influencing corrosiveness of crudes that it is difficult and even in most cases impossible to predict their corrosiveness according to physicochemical composition. Usually corrosiveness of crude oils is defined by total acid number (TAN), total sulfur content, water and salt content, and microorganisms. The combination of these parameters and components influences corrosion by different manner and differently at stages of preparation, transportation, storage, and processing crude oils at refineries. Both TAN value and total sulfur content do not always define corrosiveness of crudes. For instance, H_2S and alkanethiols are corrosive to carbon steel, while thiophenes are not corrosive. The problem is complicated by the fact that H_2S and alkanethiols reacting with iron form iron sulfide scale which under particular conditions can be protective. Sometimes crudes containing relatively high water content can inhibit corrosion and, vice versa, crudes may be corrosive at relatively low water concentrations. Only experiment can respond on the question about corrosiveness of crudes.

3 Physicochemical Basics of Corrosion at Refineries' Units

Corrosion of metallic equipment and structures at refineries' units occur in different media and phases under very wide conditions. It is possible to divide corrosion at refineries' and petrochemical units into five groups:
   a. Low temperature ($T<100^{o}C$) corrosion in the presence of electrolytes (usually water and aqueous solutions of electrolytes, such as dissolved corrosive gases (e.g., HCl, H_2S, and NH_3), or dissolved salts (e.g., NaCl and Na_2SO_4).
   b. High temperature ($T>200^{o}C$) corrosion by non-electrolytes (usually gaseous H_2S and H_2; naphthenic acid corrosion; hot ash corrosion; oxidation by oxygen in furnaces).
   c. Intermediate temperature ($100^{o}C<T<200^{o}C$) corrosion which can occur either in the presence of electrolytes (e.g., amines) or non-electrolytes (SO_2, SO_3) depending on substances and conditions.
   d. Corrosion in natural environments: in the atmosphere, soil, and natural waters.
   e. Specific corrosion phenomena: acid dew point corrosion, corrosion under thermal insulation, boiler feedwater corrosion, and steam condensate corrosion.

3.1   Low-Temperature Corrosion

Most low-temperature corrosion problems in oil refineries and petrochemical plants are not caused by hydrocarbons that are processed but by various inorganic compounds, such as H_2O, H_2S, HCl, NH_3, NaOH, H_2SO_4, Na_2CO_3, and dissolved oxygen. Organic acids that are contained or occasionally formed in hydrocarbons and amines using as neutralizers and corrosion inhibitors in the overhead of distillation systems may also promote low-temperature corrosion. There are two sources of compounds causing corrosion: contaminants contained in crude oil and process chemicals. Prolonged use of aqueous solutions of amines for the absorption of acid gases H_2S and CO_2 at amine treating units can result in formation of corrosive heat stable amine salts. Use of sulfolane for a long time also can cause formation of destructive corrosive products (acids) at petrochemical plant. Electrochemical mechanism is realized in low-temperature corrosion phenomena.

3.2   High-Temperature Corrosion

High-temperature ($T > 200^{\circ}C$) corrosion pertains to the second large group of corrosion phenomena which occurs when exposed to non-electrolytes: sulfidic corrosion (named also sulfidation - oxidation by H_2S, S_8, and some other sulfur compounds,), naphthenic acid corrosion (NAC), hydrogen attack, hot ash (fuel ash or salt deposit) corrosion, oxidation (by oxygen gas), carburization, and 'metal dusting'. Non-electrochemical mechanism is realized in these corrosion phenomena. Non-electrolytes are generally gases (e.g., H_2S, H_2, O_2, and hydrocarbons) or liquids (e.g., naphthenic acids or S_8) at high temperature. Sometimes these corrosive components are present together. In these cases, we should analyze sulfidic corrosion with the presence of H_2, and NAC in the presence of H_2S. Such situations complicate corrosion mechanism and under particular conditions can either induce or decrease corrosion. For example, sulfidic corrosion proceeds more intensively in the presence of H_2, and inhibition of NAC occurs by sulfide scale formed in the presence of H_2S. Sulfidation and hydrogen attack are most dangerous corrosion phenomena because can lead to catastrophic unexpected pipe rupture, releasing flammable media, fires, explosions, and injuries [13, 14].

4   Corrosion Problems and Solutions at Oil Refinery and Petrochemical Units

Analysis of oil refining industry shows that whilst the number of refineries declined in the period between 1993 and 2007 the average capacity per refinery increased by nearly 30% [15]. This tendency remains also in nowadays and brings corrosion problems related to "childhood diseases" of new refineries and "adult diseases" of existent plants.

Because of specific media and conditions in oil refining and petrochemical industries in addition to general corrosion phenomena (in water, atmosphere, soil, etc.) occurring in any industry there are particular corrosion problems intrinsic only to them. They are: corrosion in crude oils, petroleum products and fuels, sulfidic corrosion, hydrogen attack, naphthenic acid corrosion, sour water corrosion, corrosion in amine solutions, and polythionic acid corrosion. Specific corrosion problems of sulfur compounds, naphthenic acids, hydrogen gas, and amine solutions which we can face with at high temperature and their solutions are presented in this work.

4.1 Corrosion by Sulfur Compounds

Sulfur compounds play essential role in corrosion of the equipment at oil refining and petrochemical units. For our convenience, we will distinct low-temperature ($T < 100-200^{\circ}C$) and high-temperature ($T > 200^{\circ}C$) corrosion with the participation of sulfur compounds. Hydrogen sulfide can participate in low- and high-temperature corrosion. Low-temperature corrosion in the presence of dissolved H_2S in aqueous phase, corrosion by ammonium bisulfide, sulfuric acid and polythionic acids can occur at $T < 100^{\circ}C$. Corrosion by sulfur compounds at high temperatures is discussed below.

4.1.1   Sulfidic corrosion

Sulfidic corrosion is corrosion of metals and alloys by particular sulfur compounds at high temperatures, usually in the range $230-540^{\circ}C$ [16, 17]. Not all sulfur compounds oxidize metals and alloys. Even some of them, thiophenes and sulfones, can inhibit corrosion of metals [1]. Their corrosiveness is realized under appropriate concentrations and temperatures, and is differently manifested on various alloys, even steels. The mechanism of sulfidic corrosion is the direct chemical oxidation of metals by sulfur compounds. The sulfidation mechanism is closely akin to air oxidation and the same alloying elements provide resistance

to attack. Carbon steel, low-alloy Cr-Mo steels, nickel, copper, zinc and their alloys are attacked by sulfur compounds at elevated temperatures. High-nickel alloys are most susceptible to sulfidation. Increasing chromium in iron-, nickel-, and cobalt-base alloys improves sulfidation resistance. Chromium and aluminum alloys are resistant to sulfidic corrosion. Sometimes severe sulfidation even occurs when the total sulfur content in hydrocarbon feed (e.g., naphtha or LPG) is very low (10-20 ppm) [18]. Iron sulfide can promote the adhesion of coke to the surface. In addition, iron sulfide can act as dehydrogenation catalyst to promote the formation of coke by asphaltenes [19, 20].

Case Study 1.   Corrosion of Tubes in Heat Exchanger (Visbreaker)

Conditions. The heat exchanger is intended for cooling cracked gas oil. Cracked gas oil entered into the shell of the heat exchanger at $340^{o}C$ and 4 bar and exited at $100–120^{o}C$.
Material of construction. Tubes – carbon steel ASTM A179.
Service period before the failure: 6 years.
Visual examination and findings. Severe corrosion of outer surfaces of tubes with many holes was found in the area of the impingement plate (Fig. 1). This plate consisted of carbon steel ˈprotectiveˈ strips from impingement attack and not as one whole part. Black deposits and thick black scale were found on outer surface of tubes. Chemical analysis showed that deposits and scale consisted of iron sulfides.

a   b   c
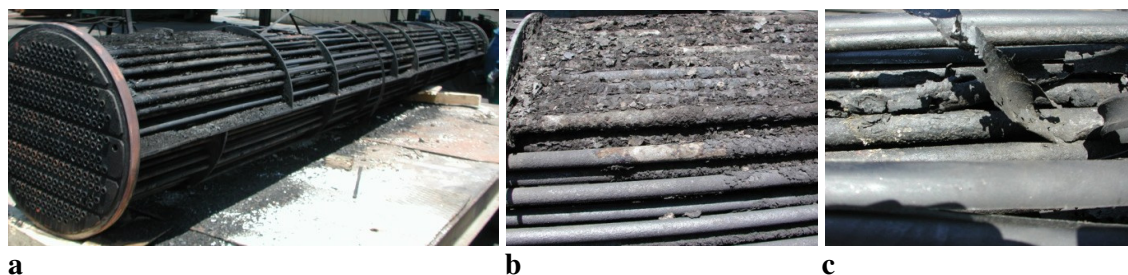
Fig. 1 a General view of failed heat exchanger. **b** The tubes with iron sulfide deposits at the top of the bundle in the area of ˈprotective stripsˈ from impingement attack. **c** The remains of corroded tubes in the area of ˈprotective stripsˈ.

Failure phenomenon: *High-temperature sulfidic corrosion-erosion.*
Cause of failure and its explanation. H_2S containing in cracked gas oil reacted with iron at high temperature ($\sim 340^{o}C$). H_2S is especially aggressive to carbon steel at $T>290^{o}C$. Cracked gas oil entered into the shell at $340^{o}C$ and 4 bar. Turbulent flow of hot ($\sim 340^{o}C$) gas oil in the area of carbon steel impingement strips (not plate!) caused erosion (impingement attack) in addition to sulfidic corrosion.
Solutions and recommendations.
(a) To install the impingement plate made from SS 304 (whole part and not in the form of strips). The area of the impingement plate should be 30% larger than the cross sectional area of the gas oil inlet pipe.
(b) To replace the material of tubes (carbon steel) with 5% Cr which recommended to use in contact with hydrocarbons containing >1 wt% S at $T>290^{o}C$.

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4.2   Naphthenic Acid Corrosion

The oil refining industry has seen a trend toward refining more highly acid crude oils since the early 1990s. This tendency also remains nowadays. The global supply of high acid crudes will increase four-fold since 2000 to 2020 [15, 21]. There are about 100 acidic crude oils (TAN>0.5 mg KOH/g oil), and their geography is very diverse [22-24]. Naphthenic acids (NA) are not corrosive at ambient temperatures and their aggressiveness is materialized at 190-400°C. NA containing in acid crudes can cause diverse problems in oil refining industry: formation of stable emulsions and fouling; appearance of nonextractable chlorides; environmental problems; diminishing inhibitor efficiency; and corrosion. Therefore, interest to NA is increasing significantly since 2000. There were a few (1-3) publications each year between 1920 and 1960. Then there was a small increase in the number of publications (7-10) per year in the late 1960s, which coincides with the beginning of the Athabasca acid oil sands refining in Canada [25]. The rapid increase in the number of publications (20-90) per year after 2000 accompanies improvements of analytical methods of detection of NA and use of opportunity acid crudes.

4.2.1 Combined Influence of NA and Sulfur Compounds on Corrosion of Carbon Steel

Most oil refineries run alternately different kinds of crudes and crude blends. Usually high sulfur (sour) crudes have low acidity and opposite, low sulfur (sweet) crudes have high acidity. Probably Piehl R. L. [26] was the first who noted that iron sulfide scale had a protective role against NAC, and competition between the sulfidic and NAC occurred.
Constant alternation of acid sweet crudes and low acid sour crudes in distillation units leads to complicated influence of corrosive components (sulfur compounds and organic acids, including naphthenic) in crudes on corrosion of carbon steel and low-alloy steels. NAC can be successfully inhibited on carbon steel and low-alloy steels by the moderate concentrations of H_2S in hydrocarbon media but can also be aggravated with higher H_2S concentrations. High concentrations of sulfur compounds increase high-temperature sulfur corrosion in hydrocarbon media. This situation is similar to passive region for dependence electric current - potential for some metals in definite electrolyte solution. Thus, the firmly established fact exists that H_2S can inhibit NAC at particular conditions depending on TAN, type of NA, temperature, flow rate, flow regime, and duration [27-30]. It is not simply to define this passive region (based on H_2S and NA concentrations) in real conditions at crude units because of many influenced factors. The case study no. 2 confirms such approach to the impact of the combined influence of sulfur content and acidity in crude oil and its fractions on their corrosiveness.

**Case Study 2.   Corrosion of Trays in Atmospheric Distillation Column**

Conditions. Various blends of crude oils have been used during 5 years and acid crude 'Azeri' has often been used during the last 2 years before the detection of severe corrosion of trays in the atmospheric crude distillation column (Fig. 2). Recirculation LAGO (Light Atmospheric Gas Oil) entered to the tray number 24 in the distillation column (the trays have downward numbering).
Materials of construction: Trays numbers 24 and 25 - carbon steel; the tray number 33 - SS 410 (12Cr).
Service period before the failure: 5 years.
Visual examination and findings. Severe general corrosion of trays (especially numbers 24, 25) and diminishing in 1 mm of the wall shell thickness of distillation column was found in the area of trays numbers 24-33. The thicknesses of the trays numbers 24, 25 diminished to

zero with the formation of the holes. Black (mostly), white and reddish (a little) deposits were found on these trays. Most deposits (62-90 wt%) consisted from corrosion products of iron and chromium sulfides. Severe corrosion of the tray number 35 and bubble caps made from SS 410 (12Cr) was also detected.

a   **b**   **c**   **d**
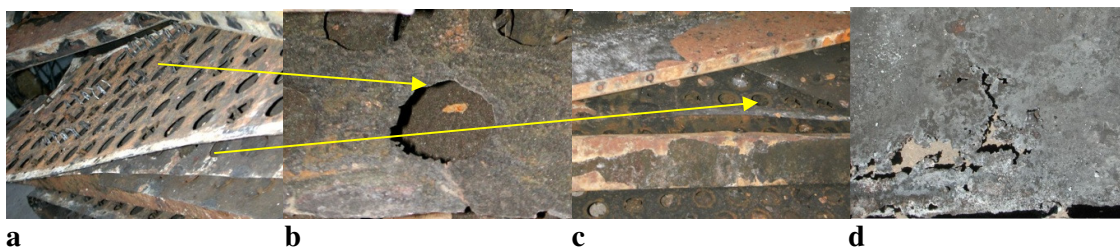
Fig. 2 Corroded carbon steel trays (original thickness - 3.5 mm; LAGO area) in crude distillation tower: **a-c** Tray number 24 (236-243°C). **d** Tray number 25(244-250°C).

Analyzing PI (Plant Information) data at the crude distillation unit, namely, by plotting on-line corroded thickness (yellow line) obtained by ER-probe (ER - Electrical Resistance) data against the sulfur concentrations in crudes, one can reveal periods of running low sulfur crude (high corrosion trends!), changing by the periods of running high sulfur crudes (low corrosion trends!) (Fig. 3).
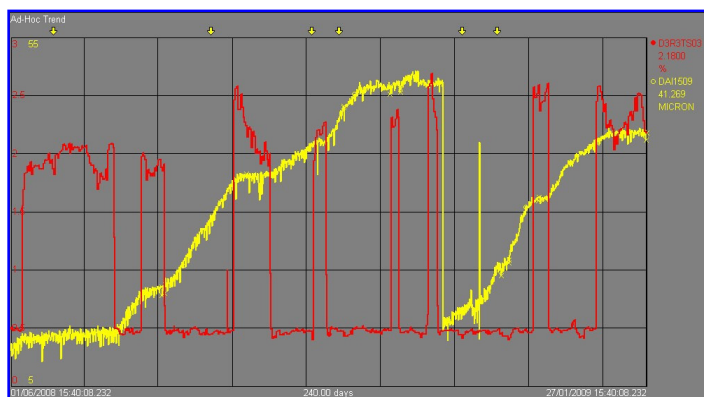
Fig. 3 Trend in atmospheric distillation column (PI data, 240 days): ER-probe readings (yellow) and sulfur content (red) in crudes. When corrosion rate (calculated as the differential of yellow line) is low there is no increase of yellow line with time (the corroded thickness of ER-sensor in microns is constant - no corrosion). When corrosion rate is high, the corroded thickness of ER-sensor increases with time and yellow line also increases (there is a constant slope of yellow line - corrosion rate is high).

<u>Cause of failure and its explanation</u>. Examination of corrosiveness of low sulfur relatively acid crude oil ʿAzeriʾ showed that corrosion rate of carbon steel varied from 0.02 to 0.1 mm/y at 300°C [31]. However, the most corrosive kerosene fraction boiled at 150-270°C with corrosion rate ~0.66 mm/year for carbon steel, and even could reach 1 mm/year for the fraction boiling at 230-260°C [31]. General corrosion rate of trays nos. 24 and 25 was 0.7 mm/year in the operating distillation column (during 5 years). This value (0.7 mm/year) coincides with corrosion rates (0.66-1 mm/year) obtained under laboratory conditions. Crude oil ʿAzeriʾ probably contains light naphthenic acids, cyclopentane and cyclohexane carboxylic acids, boiling at 216°C and 232°C respectively. Therefore, they appeared in the kerosene fraction boiling from 150 to 270°C and gave it a high acidity (~0.76 mg KOH/g) and consequently a high corrosiveness. This fact confirms high corrosiveness of kerosene fraction

distilled at 150 to 270°C [31]. Thus, the presence of light naphthenic acids accelerated significantly corrosion of carbon steel and SS 410 (martensitic stainless steel containing 12% Cr but does not contain Mo). SS 410 should be resistant to H_2S but does not resist to naphthenic (and other organic) acids.

Thus, the crude oil ˙Azeri' was pinpointed as being the most critical in creating increased corrosion risk during the processing at the crude distillation unit. Alteration of acid low sulfur crude oil ˙Azeri' and non-acid high sulfur crudes at the distillation unit during 5 years lead to rare situation. The presence of H_2S in distillate fractions in this case caused severe corrosion of carbon steel pure surface with formation of iron and chromium sulfides. Alteration of high sulfur non-acid crudes on acid low sulfur crude ˙Azeri' lead to dissolution and removing of iron and chromium sulfide layers and refreshing steel surface for further corrosive attack by hot organic acids (naphthenic acids among them) present in the crude ˙Azeri'. Further change on non-acid high sulfur crude caused severe corrosion of carbon steel by H_2S with formation new scale, etc., ... to the complete failure.

Solutions and recommendations.

(a) When acid low sulfur crude oils are interchanged with non-acid high sulfur crudes, alternate NAC and high sulfur corrosion occurs. In these cases, trays and bubble caps in distillation column in areas with T>200°C must be made from SS 316L or even better SS 317L.

(b) It is possible to inject corrosion inhibitor (Tannic Acid + IPA + Glycerine; 5-25 ppm) into LAGO circulated stream [32]. IPA - isopropanol.

4.3 Hydrogen Damages

Hydrogen damages can be divided into two groups based on two mechanisms: electrochemical processes (mainly at low temperature, up to ~100°C) arising from acid corrosion (including chemical cleaning and etching – "useful corrosion") and cathodic protection (when water molecules can be reduced to hydrogen atoms at certain negative electric potentials), and high temperature (between 200 and 900°C) arising from the presence of hydrogen gas at high pressures (4–30 MPa). It was suggested differentiating special case of appearing of hydrogen gas on carbon steel surface because of corrosion by organic acids (naphthenic acids among them) at 100–360°C [33, 34].

Low-temperature hydrogen attack can occur in the overhead of atmospheric and vacuum distillation columns, amine treating, isomerization, fluid catalytic cracking, and alkylation units. Corrosion by organic acids (naphthenic acids among them) can occur in distillation units: rectification columns, piping, and heat exchangers.

The following preventive actions of hydrogen failures at low temperature exist [11, 39, 40]:

(a) Metallurgical measures: selection of materials resistant to hydrogen damages; use of steels containing chromium and molybdenum; use of HIC (Hydrogen-Induced Cracking) resistant or killed steels; decrease of carbon content in steel. Steels are not subjected to cracking at hardness values ≤ 22 HRC.

(b) Correct fabrication technique: optimal heat treatment and proper welding; to use induction heating stress improvement, dehydrogenation heat treatment, and PWHT (Post-Weld Heat Treatment); to lessen cold working. Preheating steel sheets to 100-150°C and decreasing cooling rate after welding can diminish this susceptibility.

(c) Change of environmental conditions: removing sulfides, cyanides, and arsenic compounds; neutralization of acids; injection of inhibitors of acid corrosion and hydrogen penetration.

(d) Use of organic, inorganic, and metallic coatings.

High-temperature hydrogen attack (HTHA) takes place as a result of thermal dissociation of hydrogen molecules with the formation of hydrogen atoms, and their further penetration into metal or alloy. Hydrogen atoms can react with carbides (i.e. cementite Fe_3C) and carbon inside carbon steel forming methane gas (decarburization). As a result of this hydrogen damage, steel irreversibly loses mechanical properties, such as strength and toughness. HTHA can occur at hydrodesulfurizers, hydrocrackers, and catalytic reformer units.

Steels may be more resistant to hydrogen attack at high temperature by following actions:

(a) Proper and careful choice of alloy and correct design are the most reliable method to prevent HTHA [12]. Austenitic stainless steels (300 series), as well as 12Cr, 9Cr and 5Cr are resistant to HTHA at conditions normally seen at oil refinery units.

(b) Lowering the carbon content in the alloy and binding the remaining carbon into stable, dispersed carbides (addition of Cr, Mo, and V).

(c) Compliance with technological regime: strictly control designing processing parameters (temperature and pressure).

In spite of existing of different methods of hydrogen monitoring, there is no reliable method allowable predicting where and when hydrogen damage will happen.

4.4   Corrosion by Amine Solutions

Aqueous amine solutions have been used since 1930s to remove acid gas contaminants (H_2S or CO_2) by absorption from a process stream [37]. Following four amines are used: monoethanolamine (MEA), diethanolamine (DEA), methyldiethanolamine (MDEA), and diisopropanol amine (DIPA). Corrosion problems at amine treating units usually happen because of faulty plant design, poor operating practices, and amine solution contamination [1]. The four amines themselves are not corrosive to carbon steel, even can play the role of corrosion inhibitors under certain conditions. However, they can degrade during long circulation at high temperature (if steam temperature exceeds 150^oC), and destructed products of amines together with H_2S and other contaminants can cause corrosion problems.

Corrosion in amine treating units depends on amine type, acid gas removal service and molar ratio H_2S/amine (called also loading), and type and concentration of amine degradation products [38, 39]. Corrosion in amine units using MEA is more severe than in those using DEA, MDEA, and DIPA, because the former is more prone to degradation. MDEA is considered to cause the less corrosion problems compared to MEA, DEA and DIPA. In addition to H_2S, such contaminants as formic acid, acetic acid, glycolic acid, propionic acid, oxalic acid, chlorides, sulfates, thiosulfate, and thiocyanate can be present or produced by oxidation of hydrocarbons in the amine solution. These contaminants react with amine producing salts formate, acetate, glycolate, propionate, oxalate, and also chloride, sulfate, thiosulfate, and thiocyanate. They got the name *heat stable amine salts* (HSAS) or simply *heat stable salts* (HSS) because it is impossible to destroy them under normal regenerator conditions, namely, they cannot be recovered by heating. As a result, HSAS are accumulated in the amine solution which becomes more and more corrosive with time. The presence of HSAS also diminish the efficiency of the absorbing ability of amine solution by reducing the amount of pure amine. Therefore, maximum allowable concentration is 1 wt% HSAS in amine solution. When its quantity more than this value, unfavorable HSAS accumulating in amine solution give rise to severe corrosion, erosion, precipitation of solids, causing fouling and under deposit corrosion. Corrosion is most harsh at locations where H_2S is removed from rich (by H_2S) amine solution, namely, in reboilers. Really, temperatures, appearance of two-phase turbulence stream and flow velocity are the highest in these locations. Corrosion can be a problem on the rich-amine side of the heat exchangers, in reclaimers, and pumps. Hydrogen damages (blistering because of H_2S presence) can occur in the bottom of the absorber,

overhead condensers, and reflux drums. Aqueous amine solutions can cause SCC of carbon steel welds, therefore, PWHT at 620°C should be applied. The following solutions to lessen and prevent these detrimental corrosion-erosion and fouling problems exist:

(a) Correct molar ratio H$_2$S/amine. Operating practice requires to maintain the following parameters in amine treating units: MEA concentration should not exceed 20 wt%; acid-gas loading should be 0.35 mol H$_2$S/mol MEA and 0.05 mole H$_2$S/mole MDEA; and reboiler steam temperature less than 150°C.

(b) Neutralization with proprietary neutralizers.

(c) Clean-up the amine solution: change out, purge and make up fresh amine solution, vacuum thermal distillation, ion exchange, and electrodialysis [39-41].

(d) It is recommended to replace carbon steel with SS 304 if corrosion problems cannot be solved by improving operating conditions and purification of amine solution.

4.5 Petrochemical Plant

Petrochemical plant consists of units resembling those at oil refinery. And even many media and environment are similar. Raw original organic material comes from refinery. Reformate producing at the CCR (Continuous Catalytic Regeneration Reforming) and FCC (Fluid Catalytic Cracking) units is fed to petrochemical plant to produce aromatics. These specific organic solvents can dissolve water and oxygen [42-44]. For instance, the solubility of oxygen in benzene is 70 ppm and in water is 8.5 ppm at 25°C [8]. Moreover, if the solubility of oxygen in water is decreased with increasing temperature, that in benzene is increased. Chlorides also can be main corrosive contaminant in reformate coming from the oil refinery. Sulfolane widely used for extraction aromatics can degrade into acidic corrosive products. Specific corrosion case study is analyzed below.

Case Study 3. Corrosion of Fin-Fan Air Cooler Tubes at the Overhead of Aromatic Column

Conditions. An air cooler at the overhead of aromatic tower is intended for cooling the mixture of benzene, toluene, hexane, heptanes and pentane by air. The mixture of three last hydrocarbons (feedstock) flew from the CCR unit. The mixture of aromatic hydrocarbons exited from the aromatic tower and flowed inside the tubes at 60-80°C and vacuum 0.2-0.3 bar. A leak of hydrocarbons was identified from the air cooler.

Material of construction. Tubes - carbon steel ASTM A179. The wall thickness of tubes – 2.336 mm. Aluminum fins were installed on carbon steel tubes.

Service period before the failure: 11 years.

Visual examination and findings. Severe corrosion was found inside the tubes and aluminum fins (Fig. 4). Rust was formed inside the tubes. The wall thickness of carbon steel tubes decreased from original 2.336 mm to zero and tubes were ruptured.

a   b   c
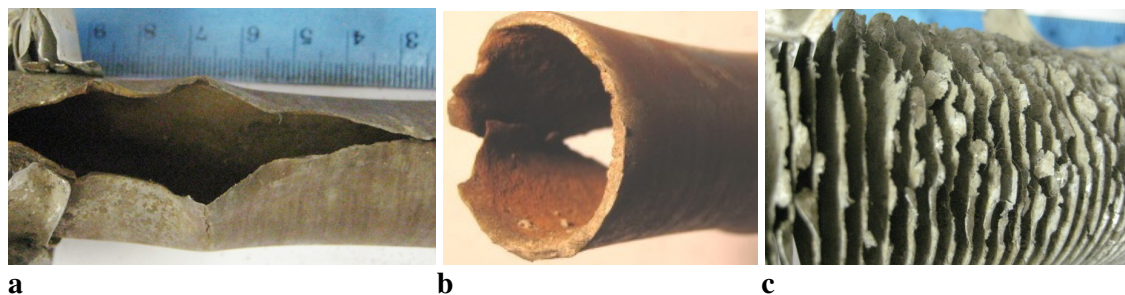
Fig. 4 a, **b** Ruptured carbon steel tube in the fin-fan air cooler at the overhead of aromatic tower. **c** Corroded aluminum fins

ED-XRF examination. Rust formed inside tubes contained (wt%) Fe (57.5), Cl (21.1), Al (9.9), Si (7.8), and S (2.7).
Failure phenomenon: *General corrosion.*
Cause of failure and its explanation. The presence of chlorides and water in the mixture of hydrocarbons caused severe corrosion of inner surface of carbon steel tubes in the air cooler. Chlorides when hydrolyzing gave rise to formation of hydrochloric acid which attacked inner surface of carbon steel tubes. Then, when holes were formed in tubes, corrosive acid solution escaped and corroded aluminum fins.
Solutions and recommendations.
(a) To install chloride absorber in the CCR unit.
(b) To replace carbon steel tubes with Ti Gr.2 which is resistant to chlorides and sulfur compounds.

5   Corrosion Management

Corrosion (if not managed, namely, controlled or prevented) can result in catastrophes. Therefore, oil refineries and petrochemical plants should manage their units safely. For this, they have to make efforts to control technological processes and organize corrosion management strategies in order to diminish corrosion accident risks to a minimum.
Corrosion management includes planning actions for determination of corrosion risk, performance requirements of standards, recommended practices and specifications for correct selection of materials, corrosion protection and monitoring methods. This should be carried out at the stage of design and then their realization in practice under inspection, control, and monitoring. Study of each accident with failure analysis, coordination, education, and knowledge transfer are also necessary components of *corrosion management methodology.*
Thus, corrosion management is a wide spectrum of measures and procedures of interaction between different services and specialties, from a worker to a head, from a chemical engineer to a purchaser and a lawyer.
Corrosion management program does not necessarily require establishing a "zero corrosion rate" system, but rather establishing operating limits, monitoring and inspection plans to assure acceptable corrosion rates which allow the system to function reliably and safely.
It was established that humans were responsible in 65-85% of corrosion cases in oil refining industry [45-48].
The human factor is a key issue in corrosion management and diminishing corrosion accidents. The causes of humans' mistakes are the lack of awareness, education, knowledge and training, incorrect design, insufficient control and supervision, lack of motivation and incentives to decrease the corrosion risk, wrong operation, and element of change.
Improving corrosion management we reduce the corrosion risk in oil refining and petrochemical industry and its negative influence on the environment and society. It is suggested to establish legislation about corrosion management on the state and federal levels (like legislation about pollutions and environmental protection), to improve education and knowledge transfer [49]. Penalties of management can force them to put more attention on corrosion problems and make it priority issue at oil refineries and petrochemical plants.
It is needed to work out corrosion management programs with planned investments at each stage of design, fabrication, implementation of anti-corrosion measures, operation, monitoring, inspection, maintenance, education, knowledge transfer, training, and research.

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