The role of multi-phase metal content in corrosion and premature failure mitigation of steel equipment in oil refineries. Part 1

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The very complex nature of hydrocarbon raw materials, such as crude oil, and all kinds of reactions and mutual interactions of all its components and phases with each other and with steel equipment (base metals, alloying elements and inclusions), as well as the applied temperatures and pressures in refining processes, in addition to the technical conditions of the steel equipment and storage and transportation conditions of crude oil, all this makes it almost impossible to completely dehydrate and desalinate crude oil, which is the real cause of most of the inevitable problems. Taking into account high corrosion rates, premature failures and the growing number of accidents and emergency stops, researchers face a challenging task and a great responsibility to provide a more comprehensive understanding of corrosion, and proposing deeper corrosion mechanisms that take into account the role of multiphase metal components, which are not less important than the influence of other corrosive components.

Keywords: crude oil, corrosion, steel coils, premature failure, inclusions, trace metals, nickel, vanadium, oil refinery, tubular furnace

DOI: 10.17580/cisisr.2023.01.15

Introduction

The oil phase alone does not lead to corrosion according to its nature, but crude oil, which is a complex mixture of three phases, contains huge amounts of impurities. Sometimes corrosion rate can reach enough high levels that threaten not only the integrity (safety) of the oil refinery but the whole environment [1, 2].

The impurities according to corrosion can be divided into two main categories: corrosive and non-corrosive components [3]. Non-corrosive components in their turn can be divided into: corrosion-accelerating components, corrosion-slowing components and non-influencing «neutral» components. Thus, some impurities can stimulate other components to be more corrosive, i.e. more aggressively-involved in the corrosion process.

Corrosion is a very deep and complex concept because it is the intersection of several sciences and the overlapping of various factors, which present great challenges to control it and prevent its continuation or growth [4, 5].

Corrosion requires three main pillars together and at the same time to initiate and grow: corrosive components (CO₂, H₂S, Cl⁻, etc.), electron-consuming components (components for consuming corrosion electrons) (depolarizing components at the cathodic areas), electron-conducting components (components for electronic conduction from corroded (anodic) areas to cathodic areas that consume these electrons by depolarizers) [6, 7]. The absence of either of them leads directly to slowing down the corrosion process and even stopping it completely.

The use of corrosion inhibitors may represent a quick solution to reduce corrosion rates, but it is not an ideal solution, since it has its drawbacks [8]. Other conventional solutions are too expensive to be applied in oil refineries. It is better to seek for long-term unconventional solutions through a deeper strategy to reduce corrosion [8-10]. For this, it is necessary to provide a deeper conception of the corrosion mechanics that takes into account not only the role of the corrosive components, but also the components that increase the aggressiveness role of the corrosive components themselves.

The aim of this study is to investigate the effects of heterogeneous metals in the steel coils structures and understanding their negative role in the corrosion and premature failure of steel equipment with introducing the associated mechanisms. This makes it possible to propose chemical and / or thermal pretreatments that can achieve more corrosion-resistant steel structures with a certain content, distribution and size of electron-conducting components (electrically conductive components). This technological solution can significantly reduce the corrosion rate and improve industrial and environmental safety during oil refining processes.

Research methods

The experiments are included a study of the effect of the temperature of heat treatment and its duration on the
amount, distribution and size of intermetallic inclusions [11]. For electron-structural analysis of steel coils samples, an analytical scanning electron microscope «TESCAN VEGA 3 LMH» with a digital X-ray energy dispersive microanalyser «Oxford Instruments INCA Energy 250/X-max 20» was used. For morphological analysis of steel coils samples, an optical microscope «ZEISS Axio Lab.A1» (Germany), equipped with a digital camera «Axiocam ERc 5s» and specialized software for image processing was used.

Corrosion rates of steel coils used in tubular furnaces were determined through immersion testing by short-term laboratory simulation of real conditions: either using water-oil emulsion with different organic trace metals contents to investigate the role of organometallics in the corrosion process; or using samples of heat-treated and untreated steel coils to study the role of intermetallic inclusions in the corrosion process.

**Results and discussion**

In our previous work, we studied the low-carbon steel coils used in tubular furnaces (15Kh5M) and reported that the microstructure of the steel coils 15Kh5M - retained austenitic and martensitic phases [12].

**Premature failure analysis**

A premature failure analysis of the steel coils of tubular furnace in oil refinery was carried out after an oil leak occurred, which led to an explosion and therefore to an emergency stop for maintenance and replacement of the damaged coils [8]. The analysis showed that failure is mainly caused by corrosion [13].

Double corrosion occurs of low-carbon steel coils (15Kh5M) used in tubular furnaces in two different separated areas: on the inner surface of the steel coil in contact with the flowing medium, and on the outer surface of the steel coil under the protective thermal-insulation layer from exposure to flue gases [14]. In the corroded sites, corrosion of a dual nature was observed: localized and uniform/general. Localized corrosion is the most aggressive and dangerous type, which is likely to lead to premature failure (Fig. 1).

Electronic images (Fig. 1) show that corrosion occurs mainly in two separate areas: the first area - on the inner surface of the cross-section of the steel coil, and the second area - on the outer surface of the cross-section of the steel coil under the protective (thermal insulating) layer. In both places, the most aggressive corrosion was seen in the lower part of the cross section of the steel coil, where the greatest proportion of damage was observed. In terms of corrosion
on the outer surface of the steel coil under the insulation layer, this can be explained by the action of gravity, so trapped or penetrated moisture accumulates in the lower half of the cross section of the coil. Regarding to corrosion on the inner surface of the steel coil in contact with the fluid medium, this can be explained by the influence of the different densities of the involved phases in the fluid medium, in addition to the influence of the heating temperature, which allows continuous renewal (refreshing) of the micro-layer of the aqueous phase in contact with the lower inner cross-sectional surface of the steel coil.

Through SEM images and EDS analysis, the composition and relative quantities of the inclusions can be obtained in a non-destructive way. As shown in the Fig. 1, localized corrosion in both areas (on the lower inner surface of the steel coil or on the outer lower surface of the steel coil under the protective (thermal-insulating) layer) is initiated by the role of sulfide intermetallic inclusions: to a greater extent by electrochemically-active sulfide inclusions and to a lesser degree by electrochemically-inactive or less electrochemically-active sulfide inclusions compared to the steel coil [15].

The Fig.1 shows SEM image and EDS analysis for different inclusions (a, b and c) in the middle of the lower half of the cross-section of the steel coil: 1 - outer protective (thermal-insulating) layer, 2 - transitional corrosion zone (protective (thermal-insulating) layer / non-corroded areas), 3 - non-corroded areas, 4 - transitional corrosion zone (non-corroded areas / scale of different kinds (corrosion products layer, deposition of inverse solubility salts and coke)).

Analysis results showed an increase in the concentration of the inclusions of oxygen type either towards the deeper corroded areas or the hotter areas or both, while the role of the organic metals was clearly observed on the inner surface of the steel coil in contact with the flowing medium (c on the Fig. 1) (water-in-oil emulsion, including dissolved oxygen and mechanical impurities). This proves that organic metal components in the oil phase, even in very small amounts, can have a significant effect on the deterioration and premature failure of steel coils and equipment.

In addition, it can be seen that the role of sulfide-type inclusions is more significant in the corrosion of new sites (corrosion initiation stages) (b on the Fig. 1) compared to the oxide-type inclusions, which are more obvious in the cracks branching (a on the Fig. 1). By comparing these inclusions, it can be noticed that polymetallic inclusion (c on the Fig. 1) is much more complex in terms of composition and quantities [16].

The high concentration of copper and nickel (c on the Fig. 1) indicates that in spite of the large formation constants of chelates and complexes of copper, nickel, vanadyl, and others compared to iron cations Fe²⁺, a significant increase in the concentration of Fe²⁺ ion cations as a result of corrosion causes some iron cations to compete with cations of copper, nickel, vanadyl, and others for binding to organic ligands. According to the following relationship (proportion) \( (\text{Fe}^{2+})(\text{M}^{2+}) \propto (\text{PF-Fe})/(\text{PF-M}) \), where PF - porphyrin. An increase in one of these two ratios leads to an increase in the other. This causes some of the transition metal cations to be limitedly released. Even in trace amounts, these micro-cathodic impurities can participate in reduction reactions and thus increase the corrosion rate of steel. Metal cations trapped (retained) in the chelate shell (chelating cage) can be called «electrochemically inactive (or inert) trace (micro) impurities», while these impurities, when released from the chelate shell (chelating cage), are considered «electrochemically active trace (micro) impurities». Since they can play a role in corrosion process due to their ability to form galvanic pairs [17]. This could explain the reason behind the presence of traces of transitional heavy metals (vanadium, nickel, etc.) in petroleum coke deposited on the inner surfaces of steel coils and equipment as well as poisoning of the catalysts through their intermediate compounds [18].

The use of thermal insulating layer on the outer surface of steel coils began for reasons unrelated to corrosion protection, but rather for economic reasons related to energy conservation issues [12], and in addition to protect the outer surface of low-carbon steel coils from the negative effects of combustion products of fuel (flue gases), but this unfortunately led to high corrosion rates for the steel surface under the insulating protective layer [19].

It is worth noting that the corrosion rate of the steel surface under the protective layer of thermal insulation can be tens of times faster than the corrosion rate of the same steel surface in natural environmental conditions [9].

Russia is a cold-weather country most of the year with high humidity due to the large amounts of seas, rivers, and lakes, canals or artificial and natural waterways with a heavy rainfall and snowfall. Therefore, it is likely that insulation layer in principle retains some of the moisture between the protective (insulating) layer and the outer surface of the steel coil [20].

In addition to the fact that the protective (insulating) layer itself is defective and therefore not completely impermeable and therefore moisture and condensed water vapor can penetrate through the gaps in the protective (thermal-insulating) layer and reach the outer surface of the steel coil. The most likely defective points in the protective layer are the bends (elbow joints) of the steel coils, where it is impossible to get a completely flawless protective (insulating) layer.

Taking into account the fact that the protective layer consists of several protective parts along the steel coil, which are connected to each other by contact joints (contact connections). These contact joints are also potential areas through which moisture and condensed water vapor can penetrate and reach the outer surface of the steel coil.

Long-term exposure to flue gas temperatures inside the tubular furnace can have a negative effect by damaging the thermal insulation material through changes in its mechanical properties and thus its permeability. Especially in areas of mechanical weakness and poor insulation, which provides routes (paths) for water and condensed moisture to reach the outer surface of the steel coil to pass through a closed cycle of an endless sequence of evaporation and condensation, which is extremely aggressive to the integrity of the steel coils of the tubular furnace [21]. A significant amount of water vapor can condense on the colder edges of the protective thermal...
insulation layer and penetrate through it to the outer surface of the steel coil, either through contact joints (between parts of the protective layer) or through damaged areas (defective points).

On the other hand, the temperature of the tubular furnace can certainly lead to evaporation of moisture. However, when analyzing the causes of premature failure of steel coils (zone 2 on the Fig.1), we can observe a high rate of corrosion under the protective layer of thermal insulation. This can be explained by the retention of a significant percentage of moisture after the insulation process (before the operation of the furnace), as well as because of the damaged parts of the protective thermal insulation layer, which provides alternative routes (paths) for water penetration and condensation on the outer surface of the steel coil.

To simulate the heating process inside the steel coils and to measure the corrosion rate, we made the following labware setup (Fig. 2).

The Fig. 2 schematically shows an experimental installation for measuring the rate of corrosion, consisting of a three-necked heat-resistant round-bottomed flask, an electric stirrer and a heating plate, two condensers, an overhead mechanical stirrer, an oxygen cylinder, a pressure manometer (regulator with a pressure gauge), samples of steel coils, supporting stands, clamps, rubber tubing, a trap for oxygen exceeding the saturation threshold (water tank).

It is worth noting that the oxygen flow rate was very low and the oxygen trap was used to balance the pressure inside and outside the flask, as well as to ensure that the corrosion rate inside the flask was measured at saturation levels, since undissolved oxygen exceeding the saturation threshold is transferred to the trap.

We used two condensers to achieve two goals: the first to ensure that the oxygen saturation level was maintained throughout the heating period as mentioned before, and the second to ensure the hydrocarbons and water were vaporized and condensed back into the flask «refluxing cycle» rather than being lost.

Study of the effect of heterogeneous metal content of steel coil as a result of heat treatments on its corrosion rate. Samples of steel coil were prepared for corrosion tests by a standard method [22]. Heat treatment was carried out in a specially assembled laboratory installation from our previous studies [12,23].

The influence of heterogeneous metal content of steel coils (15Kh5M) was studied by using different samples of heat-treated steel coils, differing from each other in inclusions (quantity, distribution and size) without changing the composition of the corrosive medium (organic and aqueous phases). Samples of steel coils (15Kh5M) were immersed in a medium consisting of 50% : 50% (crude oil phase - aqueous phase). The aqueous phase was consisted of 50% sodium chloride solution (3.5% wt.), acidified with hydrochloric acid.
acid \((\text{pH} = 5)\) and 50 % all-season electrolyte in a heated flask with a mechanical stirrer [12]. The aqueous phase used in the corrosion tests was prepared from analytical grade materials and deionized water. Several organic phases with different content of trace metals were used [22, 24-26]. Corrosion test experiments were carried out under oxygen saturation and heating conditions for 5 days (Fig. 2).

The trapped inclusions by the steel cage, that cannot come into direct contact with the flowing medium can be described as «electrically-inert inclusions», i.e. do not transfer electrons. Taking into account that the corrosion cannot occur without contact with the flowing medium. However, when these same inclusions are able to come into direct contact with the flowing medium they become «electronically-active inclusions», i.e. are able to transfer electrons. According to their electrochemical behavior, they can participate in corrosion process. The most important role of the inclusions is to provide a connecting bridge (path) for the electrons from the anodic to the cathodic regions.

Heat treatment was carried out on the basis of relatively rapid heating of two sets of steel coils samples to 500 °C and 600 °C degrees, followed by holding for an hour, then cooling by air to room temperature [12]. Because of heat treatment, the retained austenite gradually transforms into its equilibrium phases (ferrite and cementite) [27, 28]. This is accompanied by diffusion of carbon from martensitic grains due to its excessive content, which leads to its deposition at grain boundaries, which leads to a decrease in the concentration of carbon inside the martensitic grain, which in turn undergoes a phase transformation, leading to the formation of ferrite. The same occurs for bainite grains, but more slowly and with periodic annular deposits [29]. This is reflected in an increase in the number of ferrite grains and their size relatively at 500 °C and significantly at 600 °C, as shown in Fig. 3, where sample - A without heat treatment, sample - B with heat treatment: +250 °C/h, 500 °C/30 min, -20 °C/s, sample - C with heat treatment: +250 °C/h, 500 °C/1h, -20 °C/s, and sample - D with heat treatment: +250 °C/h, 600 °C/1h, -20 °C/s.

By comparing the inclusions, we can observe that the inclusions before the heat treatment were smaller in number but, conversely, larger in size, making them ideal sites for the initiation and growth of corrosion of the surrounding steel areas with a corrosion rate of 1.654 mm/year (Fig. 4). As the temperature increases, two very important processes occur regarding inclusions: the first is slow diffusion due to their size, and the second is their decomposition, which leads over time to a relative increase in their smoothness and therefore faster diffusion that is accompanied by the formation of more homogeneous (better zone leveling) microstructures.

![Fig. 3. Schematic diagram of steel morphological microstructure before and after tempering](image-url)
This is observed by increasing the corrosion resistance by 17.53 % and 44.08 % during heating at 500 °C for half an hour and one hour, respectively comparing to the A-sample (without heat treatment) (Fig. 4).

On the other hand, excessive heating (to higher degrees or for longer periods) promotes the accumulation of inclusions of various types in smaller groups of larger size, which again increases their ability to initiate corrosion of the surrounding steel areas [30]. In addition to the strain caused by excessive grain growth, which leads to more distortions and dislocations, making the microstructure itself more susceptible to intergranular and around-inclusionary corrosion [17, 31]. This is can be easily noticed by increasing the corrosion rate by 17.6 % for D – sample (1 hour at 600 °C) comparing to C – sample (1 hour at 500 °C) (Fig. 4).

The increase in the corrosion rate in D – sample compared to the rate-limiting stage (C – sample) (Fig. 3 and 4) can be explained by increasing the number of released sulphide inclusions from the steel cage as a result of their electrochemical corrosion and/or chemical dissolution (due to low pH), which tend to move up and accumulate or be captured by the protective layer or scale, causing an increase in its ionic and electronic conductivity, accelerating the reduction reactions rates, thus corrosion rate in its turn is accelerated. While the complex oxide inclusions released from the steel cage and as a result of their resistance to electrochemical and/or chemical dissolution, tend under the influence of their density to move downward, occupying the edges and tips of the cracks, which stimulates crack branching [14, 29, 32, 33].

This study showed that intermetallic inclusions and microstructure significantly affect the corrosion rate of the steel coils. Thus, the best results can be achieved by a convenient heat treatment that aims to make a balance between grains growth and zone leveling of impurities, inclusions and secondary phases in order to obtain the most corrosion-resistant microstructures with the best zone-leveling and distribution of intermetallic inclusions [34]. All this requires more attention to the phase equilibria analysis of binary and ternary system [35, 36], in order to avoid premature failure, catastrophic disasters and emergency stops.

**Conclusions and recommendation**

A comparative experimental study has proven the role of heterogeneous metal content in amount, diversity, distribution, composition, size and density in the steel microstructure, in accelerating the corrosion processes and premature failure of steel coils and equipment.

The study confirmed that the cause of premature failure is mainly due to metallically-induced corrosion (corrosion caused by intermetallic inclusions), which is intensified (enhanced) constantly due to the appearance of more inclusions of different types during continuous corrosion processes and the gradual dissolution of impurities, associated with hydrolysis processes and low pH.

A more homogeneous microstructure (evenly distributed inclusions with better zone leveling) and low-stress grain boundaries provide better corrosion resistance.

Experimental studies have shown that the most favorable areas for initiation of localized corrosion (the most dangerous type of corrosion) are steel areas around intermetallic sulphide inclusions, while the most preferable areas for initiation of secondary branching of primary cracks are steel areas around intermetallic oxide inclusions.

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