The role of chloride, oxygen and aluminum on corrosion resistance of coiled-pipes in tubular furnaces of oil refinery

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Abstract. In this article has studied the negative roles of chlorides, dissolved oxygen and aluminum, which are existed directly in the oil or indirectly in the associated water on the corrosion resistance of the coiled-pipes of the tubular furnace inside KINEF refinery (Russia). In this paper, we studied the coiled-pipes of the ELOU-AVT-6 installation, which are subjected to severe destruction, and as a result, they are prematurely failed due to the negative effects of the studied impurities, which led to decrease their service life and the quality of oil products.

Introduction

In oil refineries, corrosion always occurs on different equipment, which is a serious problem and affects direct and indirect losses. [1-3].

The concentrations of these impurities are vary according to the source and nature of the crude oil itself. Regardless of their concentrations, they caused significant damage in the studied installation, which led to destroy the coiled-pipes, and as a result, the refinery stopped to work for up to six months.

In this paper, the process of destruction due to the corrosion in the ELOU unit (electrical desalting and dewatering) is described in detail. Tubular furnaces at ELOU-AVT-6 installations are used to heat oil, and they provide the main heat flux introduced into the distillation columns, and, accordingly, determine the energy potential of oil separation capacity [4-6]. The tubular furnace consists of two chambers (radiation and convection), in which coiled-pipes are sequentially placed [7–10]. Tubular furnaces are one of the most heat-stressed structures [11, 12].

It is known that corrosion in coiled-pipes occurs because of the interaction of oil impurities with the coiled-pipe material; in addition to a number of other factors also affect its development [4], like thermite reaction, due to the presence of aluminum in West Siberian oil (4-75 g/T) [13] as well as the contents of dissolved oxygen and moisture in crude oil which adversely affect the condition of surfaces and cavities, especially on the inlet parts of coiled-pipes [6], in addition to the pitting corrosion which occurs predominantly due to the presence of chlorides due to the presence of chlorides in West Siberian oil (32.5-1251 g/T) [13-16].

The purpose of this work is to study the side effects of the oil impurities on the corrosion resistance of the coiled-pipes. It is necessary to determine the causes of damage occurred in coiled-pipes under study. This makes it possible to know the optimal conditions to prepare the oil for refining to give higher protection against corrosion, which in turn lead to decrease the number of accidents in tubular furnaces and increase their service life.

Characteristics of West Siberian Crude oil

In our work, we analyzed the West Siberian crude oil to determine the metal content. The concentration of various metals in West Siberian crude oil is shown in Table 1, for a sample was taken at KINEF refinery before refining.

| Table 1. Metal content in West Siberian crude oil |
|-----------------|--------|--------|--------|--------|--------|--------|--------|--------|
| Metal | Fe    | V      | Al     | Ni     | As     | Zn     | Mn     | Co     |
| C_M ppm |       |        |        |        |        |        |        |        |
| Fe     | 24.9  |        |        |        |        |        |        |        |
| V      | 21.68 |        |        |        |        |        |        |        |
| Al     |      | 18.4   |        |        |        |        |        |        |
| Ni     |      |        | 12.75  |        |        |        |        |        |
| As     |      |        |        | 2.9    |        |        |        |        |
| Zn     |      |        |        |        | 2.88   |        |        |        |
| Mn     |      |        |        |        |        | 1.1    |        |        |
| Co     |      |        |        |        |        |        | 0.15   | 0.09   |

It is easily can be noted that the content of vanadium, aluminum and nickel are higher in West Siberian crude oil than in other standard similar types of Russian oil [17].
Methodology

To analyze the causes of the destruction of coiled-pipes of tubular furnaces at KINEF refinery, samples of destroyed coiled-pipes were taken from the refinery after the accident had happened and led to stop the production line.

Coiled-pipes brand 15X5M of a tubular furnace are used at KINEF refinery (martensitic grade steel—low-alloy and heat-resistant steel). The chemical composition of steel "15X5M" is shown in table 2.

| C, % | Si, % | Mn, % | Ni, % | S, % | P, % | Cr, % | Mo, % | W, % | V, % | Ti, % | Cu, % | Others |
|------|-------|-------|-------|------|------|-------|-------|------|------|-------|-------|--------|
| to 0.15 | 0.5 to 0.5 | to 0.6 | to 0.025 | to 0.03 | 4.5-6 | 0.45-6 | to 0.3 | to 0.05 | to 0.03 | 0.2 | Fe – Rest |

For the study, 8 samples of coiled-pipes were selected. All samples were subjected to preliminary machining: cutting, grinding, polishing and etching. To determine the causes of damage and destruction, fragments of the coiled-pipes were studied at various sites in the tubular furnace, to analyze them and, therefore, determine the composition of the coiled-pipes and the quantitative transition of the main elements due to the corrosion. When conducting the study, the following methods were consistently used:

- Chemical analysis and determination of metal content in West Siberian crude oil, performed by using atomic absorption spectroscopy VARIAN-SPECTRA AA 220 FS.
- Microstructural analysis with determination metals content and metal compounds in the coiled-pipes of tubular furnaces, performed by using scanning electron microscope TESCAN VEGA3.
- Microspectral X-ray analysis with determination the phases in coiled-pipes alloys together with (Oxford INCA Energy EDX - energy dispersive X-ray spectroscopy).
- Analysis of the corrosion ability of the coiled-pipes by method of weight loss (corrosion measurements).
- Analysis the electrochemical corrosion of the coiled-pipe by potentiodynamic polarisation method by using potentiostat /galvanostat CS350 (with SCE — Saturated calomel electrode).

Results and their discussion

The structure of the coiled-pipes samples was determined under a scanning electron microscope TESCAN VEGA3 and shown in various spectra. For non-affected areas, without any signs of corrosion (spectrum 8) and for affected areas exposed to corrosion (spectra 10, 17 and 9) are shown in table 3.

| № Spectrum | The content of elements in the scanned area, wt-% |
|------------|-----------------------------------------------|
| 8          | Fe,% 66.12, Cr,% 4.27, Si,% 19.64, O,% 9.98, Cl,% 1.69, S,% 8.5, Al,% 0.5, K,% 5.2, Cu,% 1.5, Zn,% 1.3, Ca,% 1.2 |
| 9          | Fe,% 56.41, Cr,% 5.5, Si,% 2.03, O,% 2.02, Cl,% 1.69, S,% 0.85, Al,% 1.57, K,% 0.48 |
| 10         | Fe,% 32.68, Cr,% 9.7, Si,% 6.21, O,% 19.64, Cl,% 5.02, S,% 1.57, Al,% 0.62, K,% 3.76 |
| 17         | Fe,% 34.88, Cr,% 3.69, Si,% 6.21, O,% 33.8, Cl,% 2.37, S,% 2.55, Al,% 1.68, K,% 8.33 |

Table 3. Comparison of affected (9, 10, 17) and non-affected areas (8) of the coiled-pipes of tubular furnace
Figure 1. SEM pictures to the transitional zone of the coiled-pipe (left side 1: 50) (right side 1: 100)

Figure 2. The location of the specter of the coiled-pipe in non-affected area (1: 200)

Scanning of the damaged corroded areas is shown by spectra 9 and 10 in Figure 3.

Figure 3. Spectrum 9 and 10 of the coiled-pipe in the damaged area (1: 100).
The right-hand side is the coiled-pipe material; the left-hand side is a scale, formed because of a long stay of the coiled-pipe under the burners of the tubular furnace, with transitional zone corrosion. Spectrum 8 is characterized by a relatively high content of oxygen (taking into account that it is a non-affected area) 10%, and spectrum 9 is characterized by a high content of aluminium 6.85% and oxygen 20% and spectrum 10 is characterized by a very high content of oxygen 40.18% and high content of chloride 5.52% and relatively high content of sulphur.

The different state of the surface according to the type of corrosion is due to the heterogeneity of the chemical composition. It is proved that the main type of local corrosion is pitting corrosion while the secondary is corrosion by electrochemical cells. Because of the high content of chloride, which is likely explains the low resistance of the alloy of the coiled-pipe to pitting corrosion. On the other hand, a low content of copper leads to the formation of electrochemical corrosion at a lower rate [18-20].

The role of aluminum

Due to the origin of West Siberian crude oil and its nature, this oil is a carrier of aluminum salts with a content 10-60 g/T, therefore, irreversible damage and destruction of the coiled-pipes happen not only because of corrosion, but also as a result of a thermite reaction, the thermite reaction is an extremely exothermic reaction, which significantly accelerates the corrosion process and caused an extreme burnout.

The next table 4 summarizes the thermite reactions that might happened with their enthalpies formation for metals and oxides and have been calculated Thermite Enthalpy and Heat of Thermite Reaction.

| Thermite | \( \Delta H^\text{r}_T \text{, kJ/mol} \) | \( \Delta H^\text{r}_x \text{, kJ/mol} \) | Q, kJ / T Oil |
|----------|--------------------------|-----------------|--------------|
| \( \text{Fe}_2\text{O}_3 (\text{hematite red color}) \to \text{Al} \) | \(-822.2\) | \(+847.6\) | 156.96 — 941.78 |
| \( \text{Fe}_3 (\text{magnette black color}) \to \text{Al} \) | \(-1120.9\) | \(+3316.5\) | 1535.42 — 9212.5 |
| \( \text{Cr}_2\text{O}_3 \to \text{Al} \) | \(-1128.4\) | \(+541.4\) | 100.26 — 601.55 |
| \( \text{SiO}_2 \to \text{Al} \) | \(-859.4\) | \(+761.4\) | 70.5 — 423 |
| \( \text{CuO} \to \text{Al} \) | \(-155.2\) | \(+1204.2\) | 223 — 1338 |

| Total heat released kJ for one ton of West Siberian crude oil | 2086.14 — 12516.83 |

Thermite reaction happens according to redox to mechanism, as described in the following general equation

\[
\text{Al} \to \text{Al}^{3+} + 3e^- \\
M^{n+} + ne^- \to M \\
n\text{Al} + 3M^{n+} \to n\text{Al}^{3+} + 3M
\]

By calculating the heat released because of thermite reactions (by taking into account the content of aluminum in West Siberian crude oil in the range of 10-60 g/T) we find that 2086.14 - 12516.83 KJ is released through the thermite reactions in every ton of West Siberian crude oil which lead to a sharp increase in temperature which accelerates corrosion and causes extreme burnout.

- The role of oxygen
Oxygen plays a double role; on the one hand it is an oxidizing agent and on the other hand, it is a depolarizing agent, which allows continually consume electrons from iron oxidation (corrosion) [21]. Because if there is no consumption for the electrons of corrosion, corrosion will stop, in addition to the depolarization of hydrogen adsorption on the cathodes as shown in table 5.

Table 5. Roles of oxygen in the corrosion process

| Oxidizing agent | Depolarizing agent |
|-----------------|--------------------|
| \(M + O_2 \rightarrow M^{II}O\) | Basic or neutralized electrolyte concentrated with oxygen |
| \(2M^{II}O + \frac{1}{2}O_2 \rightleftharpoons M^{III}O_3\) | Depolarization of hydrogen adsorption on the cathodes |
| \(2M + 3O_2 \rightleftharpoons 2M^{II}O_3\) | Acidic electrolyte concentrated with oxygen |

\[O_2 + 4H^+ + 4e^- = 2H_2O\]
\[2H^+ + 2e^- \rightarrow H_2\]

Corrosion of steel is strongly affected by the amount of oxygen dissolved in the oil or in the associated water as well as the temperature. The effects of oxygen dissolved in electrolyte with this special composition \((Na^+ = 115ppm, Ca^{2+} = 12ppm, Mg^{2+} = 0.972ppm, SO_4^{2-} = 3.8ppm, Cl^- = 198.8ppm)\) as well as the temperature on samples of coiled-pipes (10°C, 25°C, 50°C) are indicated in figure 4 and table 6.

Table 6. The concentration of dissolved oxygen in the electrolyte and the weight loss of the of the coiled-pipe

| T, °C | \(O_{2,\text{diss}}, \text{ppm}\) | \(\Delta m, \text{mg}\) |
|-------|-----------------|-------|
| 10    | 11.8            | 39.41 |
| 25    | 8.7             | 82.86 |
| 50    | 5.3             | 107.38|

Figure 4. Weight loss and dissolved oxygen VS. Temperature

From the figure 4 we can notice that by increasing the temperature, the concentration of dissolved oxygen decreases while the corrosion rate increases. The diagrams indicates clearly the importance of avoiding continuous exposure of crude oil supply or water-in-oil emulsions to the air in high temperature systems like the tubular furnaces [22-25].

- The role of chlorides and pitting corrosion

The chlorides in oil react with metal oxides to form completely soluble metals chlorides, as shown in the following reactions

\[M^{II}O + 2HCl \rightleftharpoons M^{II}Cl_2 + H_2O\]
\[M_2^{III}O_3 + 6HCl \rightleftharpoons 2M^{II}Cl_3 + 3H_2O\]

To study the electrochemical behavior of the coiled-pipe we used galvanostatic polarization method (potentiostat /galvanostat CS350 (with SCE — Saturated calomel electrode)) using electrolyte with
special composition \((Na^+ = 115\text{ppm}, Ca^{2+} = 12\text{ppm}, Mg^{2+} = 0.972\text{ppm}, SO_4^{2-} = 3.8\text{ppm}, Cl^- = 198.8\text{ppm})\) at 25°C. The potentiodynamic polarisation curve is shown in the figure 5; it is obvious that this type of corrosion is pitting corrosion. The electrochemical parameters of the corresponding pitting corrosion from the potentiodynamic polarisation curve are summarized in the table 7.

In figure 5, we can notice that there is a clear and wide passivation threshold (0.62 V width; passivation current density \(3.2 \times 10^{-5} \text{A/cm}^2\)), which is shown by the stability of the current densities within that range of anodic potentials. We can propose mechanism of anodic protection to protect coiled-pipes against pitting corrosion, by applying an anodic current and potential in the range of passivation threshold, which aims to accelerate the formation of the passivation layer when it is destroyed. Firstly, by applying an anodic current of a few amperes during parts of the second to form the insulating passivating layer and secondly, by applying a current of only \(3.2 \times 10^{-2} \text{mA/cm}^2\) (and potential -740 mV/SCE) for the continuation of protection. It is noticeable that the formation of such this passivation layer does not require a high amount of electricity.

Anodic protection could then be recommended to:
- Avoid the risk of pitting corrosion on coiled-pipes alloys in studied electrolyte.
- Limit the risk of general corrosion on coiled-pipes alloys in studied electrolyte.
- Limit fouling, loss of heat transfer and the drop in the flow rate inside the coiled-pipes.

### Conclusions

Pitting corrosion occurs due to high content of chlorides in West Siberian oil. Thermite reaction occurs due to the high content of aluminum in West Siberian oil.

The alloy of the studied coiled-pipe has good corrosion resistance because of the passivation threshold, which has obtained in a wide range of potentials -800 to -230 mV/SCE with current density over \(3.2 \times 10^{-5} \text{A/cm}^2\), which represents the reliable potentials to avoid pitting corrosion.

The difference between \(E_{RS}\) and \(E_{RP}\) is relatively small (where \(E_{RP}\) is more than \(E_{RS}\), two and a quarter times), so the metal has the ability to easily restore the passivating surface layer.

In conclusion, the susceptibility of the studied coiled-pipes alloy of tubular furnaces to pitting corrosion is very high and anodic protection is one among several possible solutions but this requires additional studies to prove the economic feasibility of this method in the protection of coiled-pipes.

It is necessary to set up a high-quality installation for deaeration in order to control the content of oxygen in the incoming crude oil.

It is necessary to create a technique to extract aluminum (and other metals) from the crude oil avoiding the thermite reaction, which accelerates corrosion as well as causes burnout of the walls of coiled-pipe.
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