Increasing the corrosion resistance of tubular furnace elements at temperature range 400-700°C in accelerated testing for real operational conditions

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ABSTRACT: The presence of impurities in the crude oil especially trace metals and chlorides are the primary responsible for the deterioration of the coiled-pipes of the tubular furnaces, and therefore for their premature failure. Mainly as a result of the acceleration of different types of corrosion processes in addition to the catalyst poisoning reaction. The small quantities of such these impurities which are existed in the heavy crude oils are large enough to cause significant industrial problems annually, environmental hazards and economic losses. Coiled-pipes of tubular furnaces are subject to extreme operating conditions from the prolonged exposure to the high temperatures and the aggressive environments on their alloys, because of these types of furnaces are constantly working (24 hours a day — 7 days a week). The inevitable consequences for the coiled-pipes utilization (or other elements) of the tubular furnaces can be summarized as; the reducing of the corrosion resistance of the coiled-pipes alloys, the increasing of the tendency to unexpected coiled-pipes ruptures, releasing flammable materials, fires, explosions, injuries and unfortunately deaths. As long as corrosion is the most dangerous process, which can negatively affect the elements of the tubular furnaces and especially on the coiled-pipes, this research is devoted to find a solution for very important industrial problem of the premature failure of the coiled-pipes of the tubular furnaces of the dewatering and desalting installation at oil refinery «ELOY» which is located in Syria by using two furnaces to make a closed small-scale heating cycle with temperature range 400 - 700°C. Role of different kinds of chlorides which are existed in the Syrian heavy crude oil is carefully studied due to their high concentrations; accordingly, a whole mechanism for chloride corrosion cycle inside the coiled-pipes of tubular furnaces is suggested. Roles of trace metals which are existed in the Syrian heavy crude oil are also studied in deep in addition to their possible roles in the resulting corrosion types. The responsible mechanisms for each type of corrosion are proposed too.

1 GENERAL INSTRUCTIONS

1.1 Introduction

After an accident occurred at the studied oil refinery in Syria because of the corrosion of the coiled-pipes of the tubular furnace, this led to cease the production for few months, which led to import of oil-products from abroad, which in turn exacerbated the economic burden. Scientific research about corrosion and corrosion resistance at temperature range 400 - 700°C and

about the role of trace metals which are existed in both phases of crude oil on scales and deposits forming (corrosion products) in the inner surface of the coiled-pipes of the tubular furnace are almost rare in the literatures, which reflects the importance of this research.

Spontaneous physicochemical destruction and premature failure of the coiled-pipes of the tubular furnaces at oil refineries, leading to irretrievable loss of their alloys, due to their chemical or electrochemical interaction with the flowing crude oil can be defined as corrosion. As a result of the corrosion processes, the inner surface of the coiled-pipes is visibly destroyed (Saakyan et al. 1982, Isaev 1997 & Goldobina et al. 2019, Ivanik et al. 2017). A large amount of crude oil as well as natural gas is lost annually from through defects and the premature failures in oil- and/or gas-pipelines and coiled-pipes of tubular furnaces, which leads to environmental pollution, emergency situations, oil and/or gas shortages to consumers, and penalties (Bakesheva et al. 2019). For the purpose of coiled-pipes, trunks and oil and/or gas pipelines safe operation, two types of wall metal anticorrosion protection can be generally used - the passive (insulation coating) protection and the active (electrochemical) protection (Tsenev et al. 2017). Corrosion processes require annually huge repair and maintenance expenses to the oil, gas and petrochemical industry (Bobritsky & Yufin 1988, Kondrasheva et al. 2014 & Volovikov 2010), which can cause serious injuries and unfortunately deaths, explosions, fires, catastrophic disasters, environmental pollution and economical losses every year; due to the mutual effect of both crude oil impurities and the temperature on the coiled-pipes of the tubular furnaces (Alekseev & Smirnov 1955, Alekseev 1972 & Baratov et al. 1990).

Syria is a relatively small oil producer, according to global or even regional standards, that accounted for just 0.5% of the global production in 2010, falling to less than 0.05% by 2016 according to the International Monetary Fund, i.e. the Syrian oil production has fallen by ten times in six years due to the consequences of the devastating war, the accompanying international sanctions and the deterioration of installations and equipments.

1.2 *Aims of study*

The aims of this research are: to determine the possible roles of metals and/or metallic components in the crude oil on the severe corrosion at the studied temperature range; to determine the most possible corrosion types; and to determine the effectiveness of a specific inhibitor in reducing the corrosion rate of the coiled-pipe of tubular furnaces.

1.3 *Used methods*

Chemical analysis for determination the metals content in Syrian heavy crude oils is done by burning the Syrian heavy crude oil sample and then by analyzing the obtained carbon residual by using sequential X-ray fluorescence spectrometer XRF-1800; Chemical and microstructural analysis for determination the metals content in coiled-pipes is done by using an analytical scanning electron microscope — VEGA3 TESCAN; X-ray microanalysis for the determination of phase's composition in coiled-pipe is done by using oxford INCA energy EDS; Determination of corrosion ability of the coiled-pipe and the effectiveness of studied inhibitor in reducing the corrosion rate of the coiled-pipes at the studied temperature range is done by using weight loss method.

2 RESULTS

2.1 *Closed small-scale heating cycle*

The closed small-scale heating cycle consists of four basic elements, as shown in Figure 1: horizontal tube furnace, pump (air-cooled thermic fluid pump - AT. DIN24256), silit (silicon carbide) furnace and system filling valve (VF06 Sealed System Filling Valve). Inside the horizontal (ceramic) tube furnace (with the dimensions 30cm (length)* 3.3cm (diameter)), we put

Figure 1. Closed small-scale heating cycle.

a stainless steel tube (AISI 321 grade) (with the dimensions 30cm length * 2.8cm diameter * 0.5cm thickness) and inside this stainless tube we fixed a coupon (with the dimensions 3cm length * 1cm width * 0.5cm thickness) from the same alloy of the coiled-pipe of the tubular furnace between two obstacles (barriers/pieces) of the same alloy of the stainless steel alloy in order to stay in the horizontal (ceramic) tube and not to move with circulating (flowing) emulsion. Inside the silit furnace (heating camera with the dimensions 250mm height * 160mm length * 160mm width), we put tank (with the dimensions 23cm height * 14cm length * 14cm width) and we put inside the tank 4L of the flowing emulsion. The flowing emulsion consists of a mixture of laboratory prepared salt electrolyte (90% = 3.6L) (with the composition shown in the Table 5) and Syrian heavy crude oil (10% = 400mL)) (with metal composition shown in the Table 4). The two furnaces were set at the same studied temperature. Tests were performed with and without the studied inhibitor by applying weight loss method.

The surface of each coupon was abraded mechanically with (320, 400 and 600) grades of SiC (silicon carbide) abrasive paper, washed with distilled water, dried with clean tissue paper, immersed in ethanol, dried with clean tissues paper and weighted before and after the experiment, then the weight loss was determined. The corrosion rate and the effectiveness of the inhibitor in reducing the corrosion rate were calculated by using the following equation:

$$CR_{i, mdd} = \frac{\Delta m, g}{A, Cm^2.t, sec} (10^5)(86400)$$

$$\%_i = \frac{CR_0 - CR_i}{CR_0} (100)$$

Where: CR_i — Corrosion rate with the studied inhibitor; CR_0 — Corrosion rate without inhibitor; mdd = mg/dm²/day; Δm — Weight loss of the coupon of the coiled-pipe; A — Surface area of the coupon; $\%_i$ — Inhibitor effectiveness in reducing the corrosion rate.

The studied emulsion enters the stainless-steel tube at point 1, which is placed inside the horizontal tube furnace, where the coupon of the coiled-pipe is fixed between two obstacles of the same alloy of the stainless steel. The emulsion exits from the stainless-steel tube at point 2 to enter the thermic fluid pump at point 3 in order to continue to reach the silit furnace to enter the tank at point 4 and to exit at point 5 to continue to enter the filling valve at point 6. All the connecting lines were made of thick wall copper tubing.

The two furnaces ensure that the temperature of the flowing emulsion will be constant inside the stainless-steel tube, where the coupon is placed in. The filling valve (VF06 Sealed System Filling Valve) and the thermic fluid pump (AT. DIN24256) control the flow through the stainless-steel tube (flow rate 1L/min) and to assure proper performance of the closed small-scale heating cycle. The filling valve for closed heating systems (VF06) is a combination-filling valve for sealed heating systems, incorporating a pressure-reducing valve, stop valve, a non-return valve and hose connections. The thermic fluid pump –(AT. DIN 24256) with no additional cooling required (air-cooled).

It should be noted that the composition of the flowing emulsion under the experimental condition is 90% laboratory prepared salt electrolyte: 10% heavy Syrian crude oil, while the percentage of the formation water (salt electrolyte) of the flowing emulsion under the real operative condition inside the coiled-pipes of the tubular furnace is only 0.5% formation water according to the Syrian standards (and according to the Russian requirements 0.2% formation water), because of that; the real corrosion rates can be calculated by multiplying the accelerated corrosion rates by 0.5/90 for the Syrian requirements (and by 0.2/90 for the Russian requirements).

The cause of use laboratory prepared salt electrolyte instead of the formation water and the cause of use the ratio (90% laboratory prepared salt electrolyte: 10% heavy Syrian crude oil) instead of the ratio (99.5% heavy Syrian crude oil: 0.5% formation water (salt electrolyte)) are due to two reasons: Firstly, to accelerate the process of corrosion, since the effectiveness of the studied inhibitor in reducing the corrosion rate will not change. Secondly, to follow the safety procedures because the crude oil is a flammable liquid and the experiments required high temperatures.

2.2 Microstructure and elemental composition of coiled-pipe

The alloy grade of coiled-pipes of tubular furnaces which is used in the studied oil refinery is «10X17H13M2T» — austenitic steel, its chemical composition is shown in Table 1.

The structure of the coiled-pipe is shown under the scanning electron microscope in spectra, as shown in figures (2 - For non-affected (clean) areas (sites), without any signs of corrosion and 3 - For affected (corroded) (transitional) areas (sites)) and their composition are shown in tables (2 and 3).

Table 1. Chemical composition of steel «10X17H13M2T».

C, %	Si, %	Mn, %	Ni, %	S, %	P, %	Cr, %	Mo, %	Cu, %	Fe, %
≤0.1	≤0.8	≤2	12-14	≤0.02	≤0.035	16-18	2-3	≤0.3	Balance

Table 2. Analytical composition of eight spectra of coiled-pipe in non-affected (clean) areas (sites).

№ Spectrum	O, %	Si, %	Ni, %	Mn, %	Mo, %	Cr, %	Fe, %	Total
Spectrum 1	1.01	0.2	9.18	0.1	0.61	8.54	80.36	100
Spectrum 2	0.25	0.44	6.41	0.54	1.25	11.39	79.72	100
Spectrum 3	0.36	0.59	10.25	1.05	0.96	14.11	72.68	100
Spectrum 4	1.95	0.32	12.15	0.35	2.01	13.56	69.66	100
Spectrum 5	—	0.41	9.73	0.12	1.85	11.03	76.86	100
Spectrum 6	2.47	0.26	4.26	1.36	1.31	14.73	75.61	100
Spectrum 7	—	0.11	7.12	0.34	0.31	12.67	79.45	100
Spectrum 8	1.65	0.61	11.54	0.21	0.97	11.93	73.09	100
Min.	—	0.11	4.26	0.1	0.31	8.54	69.66	
Max.	2.47	0.61	12.15	0.54	2.01	14.73	80.36	

Table 3. Analytical composition of three spectra of coiled-pipe in affected (corroded) (transitional) areas.

№ Spec.	Fe %	V %	Cl %	O %	Mn %	Cr %	Co %	Ni %	Cu %	Zn %	Sn %	Si %	S %
Spec.11	7.85	11.24	4.13	4.58	—	0.73	—	22.96	41.37	2.14	4.39	0.61	—
Spec.12	3.98	—	—	—	—	—	0.82	37.64	50.21	5.5	1.86	—	—
Spec.15	7.84	13.43	9.71	5.01	1.36	2.61	17.03	20.05	21.76	1.25	11.39	0.57	0.63
Min.	3.98	—	—	—	—	—	—	20.05	21.76	1.25	1.86	—	—
Max.	7.85	13.43	9.71	5.01	1.36	2.61	17.03	37.64	50.21	5.5	11.39	0.61	0.63

Figure 2. Electronic image-position of eight spectra of coiled-pipe in non-affected area — scale 1: 100.

In Figure 3 the left side is the material of the coiled-pipe, and the right side is the scale, formed as a result of the long stay of the coiled-pipes under the influence of the burners of the tubular furnace in addition to the effects of different types of corrosion processes. Between the material of the coiled-pipe and the resulting scale there is the transitional zone of corrosion.

Figure 3. Electronic image-position of three spectra of coiled-pipe in affected (transitional) zone — scale 1: 100.

2.3 Trace metals in Syrian heavy crude oil

6.0259g of Syrian heavy crude oil was placed in a crucible, the crucible was placed inside the heating chamber of the silit furnace, where the Syrian heavy crude oil was burned at 350°C and the furnace was turned-off immediately after the self-ignition is stopped, the crucible was kept inside the turned-off furnace to cool down to room temperature, after that it weighted again and the weight of the carbon residual was 1.1451g, the weight percentages of the elements inside the carbon residual was analyzed by XRF as shown in Table 4.

Where: %M_C — Weight percentage of element in the carbon residual; %M₀ —Weight percentage of element in crude oil.

2.4 Corrosion experiments

Inorganic salt precipitation is one of the main problems in oilfield operations and many factors can affect scale and fouling formation and their inhibition (Khormali et al. 2018). The availability of abrasive sand particles in the flowing crude oil inside the coiled pipes of the tubular furnaces is considered to be a factor that contribute to the emergence of grooving corrosion (Popov et al. 2019). To prevent the destruction processes and premature failures for reliable operation of oil and coiled-pipes, tanks and oil and/gas pipelines caused by metal corrosion some solutions are needed (Sultanbekov et al. 2019). Using of coiled-pipes made of high-strength composite corrosion resistant materials it must be an intuitive solution (Nikolaev et al. 2017). For an example, using of Ni-resist cast-iron alloys for critical elements of tubular furnaces operating in oil refineries (Bevza et al. 2018) should be a wise decision. Despite the development of corrosion-resistant alloys over the past few decades, cheap and non-resistant alloys are still used in oil, gas and petrochemical industries (Alec 2010 & Nesic 2005) especially in Syria - taking into account the bad economic circumstances as a result of the war consequences – then the only possible way to protect the coiled-pipes of tubular furnace is by adding a corrosion inhibitor, (Achour et al. 2010 & Jevremović et al. 2013).

Corrosion experiments on coiled-pipes coupons were made by using an emulsion (90% laboratory prepared salt electrolyte: 10% Syrian heavy crude oil). The laboratory prepared salt electrolyte (pH = 5.5) having the composition which is shown in Table 5 is used; firstly, without inhibitor, and secondly, with the studied inhibitor (SNPCH-6030 «b») in three

Table 4. Metal content in Syrian heavy crude oil.

Element	%M _C *10 ⁴	%M ₀ *10 ⁴
S	5.42	1.03
V	94.19	17.90
Ni	41.99	7.98
Fe	30.89	5.87
Zn	19.84	3.77
Mn	14.05	2.67
Cu	4.79	0.91
Pb	3.68	0.70
Co	3.31	0.63
Cr	2.74	0.52
C	balance	balance

Table 5. The composition of the laboratory prepared salt electrolyte.

Chem. compounds	NaCl	MgCO ₃	CaCl ₂	MgSO ₄	HCl
C, M	8.5(10 ⁻³)	1.6(10 ⁻⁶)	5.5(10 ⁻⁴)	5.7(10 ⁻⁴)	3.2(10 ⁻⁶)

different concentrations 100ppm, 150ppm and 200ppm. The main characteristics of this inhibitor are shown in Table 6.

- Influence of the temperatures on the accelerated corrosion rates (table 7):

From Figure 4, we can notice that at the lowest studied temperature 400°C, the curves are so close to each other because of the relatively close accelerated corrosion rates. By increasing the temperature, the curves move away from each other because of the diverging accelerated corrosion rates. The highest differential corrosion rates are recorded at the highest temperature 700°C.

- Influence of the inhibitor concentrations on the accelerated corrosion rates (Table 8):

Table 6. The main characteristics of the used inhibitor (SNPCH-6030 «b»).

Parameter	Parameter value
Mass fraction of active substance, %	33-37
Mass fraction of phosphorus, %	0.15-0.32
Mass fraction of nitrogen, % not less than	0.13
Pour point, °C not higher than	-50

Table 7. The relationship between the temperatures and the accelerated corrosion rates.

T, °C	CR _{i,mdd} (10 ⁵)-100ppm	CR _{i,mdd} (10 ⁵)-150ppm	CR _{i,mdd} (10 ⁵)-200ppm
400	43128,75	32053,02	12985,3
500	89582,74	43073,15	18884,4
600	115533,14	59817,07	16176,03
700	151752,20	103168,4	19373,14

Figure 4. The relationship between the temperatures and the accelerated corrosion rates.

Table 8. The relationship between the inhibitor concentrations and the accelerated corrosion rates.

(i), ppm	CR _{i,mdd} (10 ⁵)-400°C	CR _{i,mdd} (10 ⁵)-500°C	CR _{i,mdd} (10 ⁵)-600°C	CR _{i,mdd} (10 ⁵)-700°C
0	71623,31	153158,02	207651,24	301293,01
100	43128,75	89582,74	115533,14	151752,20
150	32053,02	43073,15	59817,07	103168,4
200	12985,3	18884,4	16176,03	19373,14

From the Figure 5, it can be seen that the accelerated corrosion rate decreases with the increasing of the inhibitor concentration. In general, as the temperature increases, the corrosion rate (with/without inhibitor) increases; these increases of the corrosion rates are increased by decreasing inhibitor concentration to reach the maximum corrosion rates without the inhibitor at all studied temperatures, comparing with the accelerated corrosion rates with inhibitor, which indicates that the studied inhibitor (SNPCH-6030 «b»)) has an effective role in slowing down the corrosion of the coiled-pipes.

In the range of inhibitor concentration (0 - 100ppm), the accelerated corrosion rate is reduced linearly for the four studied temperatures (400°C, 500°C, 600°C and 700°C) with their slopes ($-28494.56 (10^{-5})$, $-63575.28 (10^{-5})$, $-92118.1 (10^{-5})$ and $-149540.81 (10^{-5})$) respectively. The 700°C-line inside the linear range (0 - 100ppm inhibitor concentration) decreases more rapidly by $[-149540.81 (10^{-5})/-28494.56 (10^{-5}) =] 5.2$ times, and 600°C-line by $[-92118.1 (10^{-5})/-28494.56 (10^{-5}) =] 3.2$ times, and 500°C-line by $[-63575.28 (10^{-5})/-28494.56 (10^{-5}) =] 2.2$ times by comparison with 400°C-line.

- Influences of inhibitor concentrations on the inhibitor effectiveness in reducing the accelerated corrosion rates (Table 9):

As shown from Table 9, the highest inhibitor effectiveness in reducing the accelerated corrosion rate was recorded for 200ppm inhibitor concentration, at 400°C was 81.87%, while was 87.67% at 500°C, and was 92.21% at 600°C, and was 93.57% at 700°C (which is the highest inhibitor effectiveness ever recorded while the lowest inhibitor effectiveness ever recorded is 39.8% for 100ppm inhibitor at 400°C).

Figure 5. The relationship between the inhibitor concentrations and the accelerated corrosion rates.

Table 9. Impact of temperature on the relationship between inhibitor concentrations and inhibitor effectiveness.

T, °C	%100ppm	%150ppm	%200ppm
400	39.8	55.2	81.87
500	41.5	71.9	87.67
600	44.4	71.2	92.21
700	49.6	65.7	93.57

3 RESULTS INTERPRETATION

Taking into consideration that «ELOU» installation — electrical desalting and dewatering installation, NaOH and NH_3 are added in «ELOU» installation before heat exchangers by (2 - 4%) of the amount of crude oil to be refined individually and separately. $\text{NaOH}_{(l)}$ is added to the «ELOU» installation (as anti-hydrolysis agent) to control $\text{HCl}_{(l)}$ (hydrochloric acid) by converting acidic metal chlorides salts (especially CaCl_2 and MgCl_2) to NaCl and by converting $\text{HCl}_{(l)}$ (hydrochloric acid) - which is generated from the hydrolysis process of the acidic chlorides salts - to NaCl. $\text{NH}_{3(g)}$ is added to the «ELOU» installation (as a neutralizer) to control $\text{HCl}_{(g)}$ (hydrogen chloride) by converting $\text{HCl}_{(g)}$ into $\text{NH}_4\text{Cl}_{(s)}$. It should be noted that the amount of ammonia should be controlled carefully because: the under-dosing of $\text{NH}_{3(g)}$ amount can lead to acid corrosion, while over-dosing of $\text{NH}_{3(g)}$ can cause localized underdeposit corrosion, because the excessive formation of $\text{NH}_4\text{Cl}_{(s)}$ salt, which can cause fouling and later sublimation, and the cycle goes on.

3.1 Role of chlorides

The chlorides are always existed in the crude oil (water-in-oil type emulsion), which are considered one of the most dangerous and aggressive components at the studied temperature range, because of the high conductivity of chlorides and therefore of their high tendency to form more stable emulsion, which can lead to presence higher concentrations of chlorides in the dewatered and desalted crude oil after the «ELOU» installation, this possible functional failure or at least low efficiency of the «ELOU» installation definitely can accelerate the corrosion rate of the coiled-pipe leading to the premature failure. Because of that, the corrosion control in the tubular furnaces of «ELOU» installation is very difficult to achieve. The following points can explain the possible roles of chlorides:

- Role of inverse solubility salts

It is a well-known fact that by increasing the temperature, the dissolution of all salts, which are existed in the flowing emulsion inside the coiled-pipes, can be increased but their solubility at the studied temperature range is determined only by Le Chatelier's principle. Calcium and magnesium salts can play a role in the deterioration of the coiled-pipe because of their inverse solubility, which can lead to their sedimentation, which in turn can lead to form hard impermeable scale that eventually can lead to overheating and burning-out (thermal failure) of the coiled-pipes of the tubular furnace.

- Role of acidic salts

Acidic salts like chlorides (in the first place) and sulfates (in the second place) are harmful due to their hydrolysis processes at the studied temperature range to their derivatives acids, which can lead to increase the local acidity of the medium, which in turn can lead to severe local corrosion in the forms of deep pits, crevices and cracks (Rogachëv & Mukhametshin 2018).

- Role of volatile metallic chlorides

The $\text{HCl}_{(g)}$ (hydrogen chloride) in the coiled-pipes at the studied temperature range can cause localized corrosion as a result of the formation and sublimation of volatile metallic chlorides, especially iron chloride and copper chloride $\text{FeCl}_3 = 318.4^\circ\text{C}$, $\text{CuCl}_2 = 523.6^\circ\text{C}$ (Maier 1925).

- Role of molten metallic chlorides

In spite of molten metallic chlorides are corroding salts and strong ionic electrolytes, which can play an effective role in the electrochemical corrosion but this role is secondary at the studied temperature range (400 - 700°C) due to their higher melting temperatures (melting point of metallic chlorides $\text{MgCl}_2 = 714^\circ\text{C}$, $\text{KCl} = 772^\circ\text{C}$, CaCl_2 , $\text{NaCl} = 808^\circ\text{C}$) (Maier 1925).

- Possible mechanism of the chloride corrosion cycle

The most common source of $\text{HCl}_{(g)}$ vapor/condensate inside the coiled-pipes of tubular furnace comes from hydrolysis process of acidic chloride salts. Eventually all chloride salts in

crude oil will be converted to hydrogen chloride $\text{HCl}_{(g)}$ as a result of the high temperature and hydrolysis processes inside the coiled-pipes of the tubular furnace. NaCl is more common in desalted crude oil feeds than MgCl_2 and CaCl_2 but it is more resistant to hydrolysis. MgCl_2 and CaCl_2 start to hydrolyze above (121°C) and (204°C) respectively while NaCl is more stable and will not hydrolyze under (232°C) (Bagdasarian et al. 1996, Valenzuela & Dewan 1999 & Kapusta et al. 2001).

Hydrogen chloride $\text{HCl}_{(g)}$ can move quickly inside the coiled-pipes, and one part of hydrogen chloride can easily dissolve in water vapor (water condensate), resulting in local mediums with very low pH values it can reach to 1 - 1.5pH (Rogachëv & Mukhametshin 2018), which can lead to dissolve the protecting films/scales or corrosion products to reach the bare metal surface and make deep pits, crevices and even cracks. The second part of hydrogen chloride can react with ammonia vapor $\text{NH}_{3(g)}$ to form $\text{NH}_4\text{Cl}_{(s)}$ ammonium hydrochloride salt (exothermic reaction). If $\text{NH}_4\text{Cl}_{(s)}$ salt deposits become wet, they can be very corrosive to the alloy of the coiled-pipe and cause localized under-deposit corrosion because of the hydrolysis of NH_4Cl . If NH_4Cl salt deposits do not become wet, under the influence of the high temperatures they can be sublimated to form $\text{NH}_{3(g)}$ and $\text{HCl}_{(g)}$, which lead to under-deposit corrosion (endothermic reaction). The third part of hydrogen chloride can react easily with active metals and their oxides, hydroxides, and carbonates to produce chlorides with the presence of moisture in the transitional zones or in the scales or corrosion products.

Thus, as a result, the cycle of chloride corrosion will continue endlessly and will lead eventually to total premature failure of the coiled-pipes. Since the concentrations of chlorides in the emulsion will considerably affect the corrosion rate, thus developing the suitable technology to reduce the concentration of chlorides in pre-treatment of the oil before entering the furnace will have great effect on reducing the corrosion rate.

3.2 Role of metals

Metals can accelerate corrosion and can also cause catalyst poisoning, fouling and catalyzing undesired side reactions. Impurities like nickel, copper and cobalt in the transitional zones are nobler metals than iron. They can play a negative role through electrochemical corrosion, especially according to their relatively high concentrations in the transitional zones (which needs further research). Vanadium compounds can form vanadium pentoxide V_2O_5 , which is conditioned by oxygen availability (most of the spectra of the affected zones proved the oxygen availability of about 5%). Vanadium pentoxide V_2O_5 has relatively low melting point 690°C ; this liquid (melted) vanadium pentoxide is strongly corrosive for the coiled-pipes alloy (Bakirova et al. 1984 & Qasim 2017). As shown in the following reaction, where hydrochloric acid $\text{HCl}_{(l)}$ is oxidized to the corresponding halogen by V_2O_5 , which in turn, is reduced to ionic form of vanadium compound, thus vanadium is also responsible for the deterioration of the coiled-pipe alloy as a result of V_2O_5 forming.

Since manganese is existed in the Syrian heavy crude oil up to more than 2.5g/t and in the coiled-pipe alloy up to 2%, maybe it has a possible role in promoting the formation of Cr_2O_3 scale (Sudhangshu 2018) (which needs a further research). Cr_2O_3 scale which has good resistant to hot, acidic and electrochemical corrosion, but its low amount makes its role in corrosion resistance limited. Chrome (which is a corrosive-resistant metal) has high resistant for hot, acidic and electrochemical corrosion. Since coiled-pipe alloy of grade «10X17H13M2T» contains 16 – 18 %Cr and 2 – 3 %Mo as corrosion-resistant alloying elements, this alloy shows better corrosion resistance comparing with other alloys containing low content of chrome, because of the formation and accumulation of thin, chemical stable and passive oxide film of Cr_2O_3 . Without chrome as an alloying element, the corrosion rates of the coiled-pipes alloy it would be much worse. However, further corrosion protection is needed for coiled-pipe alloy in the «ELOY» installation against hot, acidic and electrochemical corrosion, due to the high

temperatures and the aggressive medium by applying inhibitor as was suggested in our research (SNPCH-6030 «b») for its considered role in slowing the corrosion rate of the coiled-pipes.

4 CONCLUSIONS

The highest inhibitor effectiveness (SNPCH-6030 «b») in reducing the accelerated corrosion rate was recorded for 200ppm inhibitor concentration, at 400°C was 81.87%, while was 87.67% at 500°C, and was 92.21% at 600°C, and was 93.57% at 700°C (which is the highest inhibitor effectiveness ever recorded while the lowest inhibitor effectiveness ever recorded is 39.8% for 100ppm inhibitor at 400°C). Despite the positive role of chrome as an alloying element in coiled-pipe alloy to protect from corrosion but it is still not enough according to the high temperatures and the aggressiveness of the medium, because of that further corrosion protection (additional protection) is needed for coiled-pipe alloy in the «ELOY» installation against hot, acidic and electrochemical corrosion by applying the studied inhibitor (SNPCH-6030 «b») as we suggested in our research for its significant role in slowing the corrosion rate of the coiled-pipes. The high contents of vanadium and chloride in Syrian heavy crude oil, in addition to the high content of nickel, copper and cobalt in the transitional zones and of course the high temperature inside the coiled-pipe of the tubular furnaces are the main reasons for the severe corrosion of the coiled-pipe which led to the premature failure. Mixed mechanism between sedimentation — sublimation and redox reactions was proposed to interpret the hot corrosion of the coiled-pipe. Mixed mechanism between dissolution — sedimentation reactions and hydrolysis reactions was proposed to interpret the acid corrosion of the coiled-pipe. Mechanism of electrochemical reactions (galvanic effect) was proposed to interpret the electrochemical corrosion of the coiled-pipe in the transitional zone with the presence of nobler metals than iron, mainly in the water vapor/condensate inside the coiled-pipe and less possibly in molten salts (due to their higher melting points than the studied temperature range).

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