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Corrosion Control Mechanisms and the Effect of pH on Corrosion in the Crude Oil Refining Process

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Abstract

The consequences of corrosion in the crude oil refining process cannot be ignored due to the damage caused by the corrosion of oil equipment, and the serious losses that result from that. Therefore, in this research, methods of controlling the occurrence of corrosion in the crude oil refining unit in the Najaf refinery for four types of crude oil - API (28, 28.2, 29.2, and 30.2) were studied. Chemicals were added in different quantities and types before and during the crude oil refining process to the atmospheric distillation unit, where it was found that these chemicals have the ability to make a media within the limits of pH from 5.5 to 6.5, where the corrosion became little or no. Also, an anti-corrosion chemical was added, which reduced the incidence of corrosion in the overhead systems of crude oil refining equipment. In addition to treating the crude oil using desalter before refining it, where the mud and dirt and a large proportion of the salts in the emulsified water were removed from crude oil. The best results obtained were pH (6, 6, 5.7, and 5.5) and the percentage of iron ions Fe^{+2} (0.8, 1, 1.5, and 2.1) for four types of refined crude oil at using pump dosages for inhibitor (2.5, 2, 3.5 and 3.5), caustic soda (4, 6, 8, and 8) and neutralizer (2, 2.5, 3, and 3). This practical study showed the importance of adding chemicals in different quantities, as well as electrical and thermal treatment in controlling and preventing corrosion of oil equipment in the crude oil refining unit.

Keywords: Corrosion, refining unit, pH, overhead system, desalter

1. Introduction

Crude oil is a complex mixture, and all crude oils contain varying degrees of impurities. These impurities consist of water, salts, solids and various metals, and the harmful effects of these impurities are severe corrosion and refining unit disturbances. These effects can shorten unit operating life and reduce equipment performance [1, 2]. Corrosion is a major problem in crude oil refining processes due to complex operating conditions such as high temperature, high pressure, pH value and metals ions concentration. Because of this, decommissioning of operational units is carried out to maintenance the resulting corrosion damage which is often costly, it seems necessary to conduct a program of observations on all operational units, especially those with highly corrosive [3-7]. Carbon steel is mainly used in the majority of components of crude oil refineries, and by almost (80%), because it is resistant to most types of corrosion specially from hydrocarbon impurities at temperatures below 205°C is available [8,9]. Corrosion in the overhead system of the crude oil distillation unit arises from the presence of hydrogen chloride. The source of hydrogen chloride is the decomposition of magnesium chloride ($MgCl_2$) and calcium chloride ($CaCl_2$) present in the crude oil content at temperatures exceeding 120 °C, as well as from the decomposition of any organic chloride [8,10,11].

Hydrochloric acid corrosion is caused by dilution of hydrochloric acid vapor in liquid water. In particular, the first water droplets that form during condensation can be very acidic and can cause localized but severe corrosion at very low pH. Hydrochloric acid is mainly formed by hydrolysis occurring inorganic chloride salts of ($MgCl_2$ and $CaCl_2$) when crude oil is preheated by heat exchangers and in a crude distillation unit (CDU) furnace [12]. Sodium chloride does not decompose to a large extent under crude oil refinery unit furnace temperature conditions. Therefore, sodium chloride is not considered a contributor to the corrosion of the CDU upper distillation tower system. Table (1), shows the hydrolysis reactions involved in this context [13, 14].

Table (1) Hydrolysis reactions of salts of chlorides at different temperatures [13].

Reaction	Approximate starting temperatures
$MgCl_2+2H_2O \longrightarrow Mg(OH)_2+ 2HCl$	120 °C
$CaCl_2+2H_2O \longrightarrow Ca(OH)_2+ 2HCl$	210 °C
$NaCl+H_2O \longrightarrow NaOH+ HCl$	> 500 °C

In the absence of water, hydrogen chloride does not corrode carbon steel significantly. The crude oil distillation tower top system condenses the water that absorbs hydrogen chloride to form hydrochloric acid. Also, condensed water absorbs ammonia (NH_3), which combines with hydrogen chloride to form ammonium chloride (NH_4Cl). In cases where the water returns to the vapor state, solid precipitates of ammonium chloride are formed [8, 10, 13]. The studies that have been done confirm that hydrochloric acid is not corrosive at temperatures above aqueous dew point but at temperatures equal to or below aqueous dew point hydrochloric acid readily dissolves in water to form corrosive hydrochloric acid. At temperatures above aqueous dew point, hydrochloric acid may react with some alkaline species to form corrosive salts [13, 15, 16]. The corrosion also occurs due to the presence of hydrogen sulfide, naphthenic acids (organic), and other pollutants in the crude oil. Neutralized salts (ammonium chloride and sulfides) with condensed water can also cause corrosion [8]. In addition when temperatures exceed 230°C, high temperature sulfur attack problems and corrosion of naphthenic acid may begin. In the upper system of the crude oil refinery unit, acidic deposits of condensate forms at less than 120°C, and therefore often require the use of one or more highly alloyed materials in their composition [8, 17]. Previous studies showed that it is easy to predict the corrosive compounds in the crude oil refining process, mainly HCl, H_2S, organic and inorganic chlorine, and sulfur. Due to the diversity of corrosive compounds, different types of corrosion have occurred in different parts of the crude oil refinery as shown in Table (2), [18-20].

Table (2) Corrosive compounds by location of equipment in a crude oil refining unit [18].

Location /equipment	Corrosive compounds
Tank	HCl, H_2S ,dissolve O_2 and water
Preheat exchanger	HCl, H_2S
Furnace	H_2S and S-compounds
Flash zone	H_2S, S-compounds and organic acids
Middle zone	H_2S
Top zone	HCl and water
Tower overhead system	HCl, H_2S and water
Bottom exchanger	H_2S and S-compounds

Corrosion prevention and control in crude oil distillation units have been greatly encouraged to reduce maintenance and overhead costs. Corrosion problems are solved by basic application (treatments) of physical and chemical processes [21, 22]. The mechanisms used to control the occurrence of corrosion in refineries are: blending, de-watering, caustic injection, desalting, injection of chemical agents, water washing, and materials selection [1, 12]. One of the most important methods to control the occurrence of corrosion is to use the relevant chemical doses in the appropriate location to protect the parts of the refinery from corrosion [18]. To reduce the hydrolysis and thus hydrochloric acid in the crude oil distillation unit. Dilute sodium hydroxide (NaOH) is usually dosed injected into the crude oil upstream of the desalter. The caustic soda will then convert most of the unstable chloride salts such as ($MgCl_2$, $CaCl_2$) and/or the already formed hydrochloric acid (HCl) into NaCl which leaves the distillation column through the bottom [12, 14].

As a first step in the refining process, to reduce corrosion, plugging, and fouling of equipment and to prevent poisoning the catalysts in production units, pollutants must be removed by desalting. Desalting is the means by which inorganic salts that cause fouling or that hydrolyze and form corrosive acids are largely removed. As well, chemicals are added in the form of demulsifiers to break the oil/water emulsion [3, 8, 23, 24].

The role that the addition of chemicals plays to break emulsions of crude oil is very impressive. These chemicals act as demulsifiers, once absorbed on the water-oil interface, they will rupture the stabilizing film surrounding the oil drops, hence the emulsions are broken [25]. The efficiency of the desalting operation is often directly related to the occurrence of corrosion in the crude oil distillation units as well as in other parts of the refinery [8, 21]. Various treatments are used to lessen acid attack from condensed water containing hydrochloric acid, including neutralizing compounds such as ammonia, organic amines, film-forming inhibitors, water washing systems, and precise overhead temperature control. Care must be taken to implement one or more of these treatments because not introduction of the treatments may lead to contamination, corrosion under the sediment, and other problems [14].

The desired result of the upper pH control program is to produce a non-corrosive environment primarily by neutralizing the acidic components in the upper liquid. This is done by injecting ammonia, an organic neutralizing amine, or a blend of the two. The required pH control range depends on the concentrations of different components of the corrosive environment [26, 27]. Typically, the pH range is (5.5 to 6.5) required for overhead systems. It is important to realize that the materials of the neutralizers may only have a different effect on the pH at the point of initial condensation. At this point, the pH can be higher or lower, depending on the specific product [1, 28]. Current laboratory studies highlight the control of corrosion in atmospheric distillation unit overhead systems by chemical treatment utilizing different corrosion inhibitors having various functional groups [10]. Most overhead corrosion control programs comprise injections of proprietary film-forming organic inhibitors, which are ordinarily referred to as "films". These inhibitors establish a thin, constantly replenished film that forms a protective barrier between the acids in the system and the metal surface beneath the film. For best results by proper pH control is fundamental [29, 30]. Filming inhibitor injection rates will vary with time and between oil refineries. There is a surface adsorption/desorption steady state established which varies based on the severity of corrosion in the system, and the inhibitor concentration. Factors that affect the solubility of an inhibitor in liquids, like pH, and affect the ability of an inhibitor to adsorb on the surface, like temperature. Inhibitors can also have a cleaning effect and may even remove some iron sulfide deposits, especially at high injection rates [1, 31]. This study aims to control and prevent the occurrence of corrosion in the crude oil refining unit by using desalination and adding different chemicals and studying their effect in terms of the occurrence or non-occurrence of corrosion.

2. Experimental Work

2.1 Feed

Crude oil is provided by Oil Pipeline Company as feed for crude oil refining unit. Crude oil properties are list in Table (3).

Table (3) Properties of crude oil.

Properties	Crude oil- (1)	Crude oil- (2)	Crude oil-(3)	Crude oil-(4)
API gravity @ 60 °F	30.2	29.2	28.2	28
Specific gravity @ 60 °F	0.8750	0.8805	0.8860	0.8871
Salt content mg/L	52.4	101	153	201

2.2 Materials

2.2.1 Demulsifier

Demulsifier type (chemic 2439) was used to separate water and salts from crude oil, the properties of demulsifier are list in Table (4).

Table (4) Properties of demulsifier type (chemic 2439).

Properties	Values
Density @ 20 °C	0.94 ± 0.02 g/cm^3
Viscosity @ 20 °C	< 50 cps
Flash point °C	> 62
Pour point °C	< -30
Solubility	Soluble in hydrocarbons

2.2.2 Caustic Soda (NaOH)

Caustic soda (NaOH) was used to convert unstable salts into thermally stable salts, the properties of caustic soda (NaOH) are list in Table (5).

Table (5) Properties of Caustic soda (NaOH).

Properties	Values
Molecular weight g/g mol	39.998
Specific gravity@ 20 °C (sold)	2.13
Melting point °C	318
Boiling point °C	1390
Solubility @ 20 °C	Soluble in water

2.2.3 Neutralizer (Amine)

Amine was used as neutralization for pH of crude oil refining unit, the properties of amine are list in Table (6).

Table (6) Properties of neutralizer (amine).

Properties	Values
Density @ 20 °C	0.98± 0.02 g/cm^3
Viscosity @ 20 °C	<10
Flash point °C	<61
Boiling point °C	105
Odor	Slightly ammonia
pH (1% solution)	11.2
Solubility	Soluble in water

2.2.4 Inhibitor (Anti-Corrosion)

Inhibitor (anti-corrosion) was used as filmier for the overhead distillation tower; the properties of inhibitor are list in Table (7).

Table (7) Properties of inhibitor (anti-corrosion).

Properties	Values
Density @ 20 °C	0.93± 0.02 g/cm^3
Viscosity @ 20 °C	< 100
Flash point °C	> 61
Solubility	Soluble in hydrocarbons and organic solvents

2.3 Process Description

2.3.1 Crude Oil Refining in Unit under Study

Four types of crude oil were refined in the atmospheric distillation unit which has a standard configuration with facilities for desalinating crude oil at the Midland Refineries Company/ Najaf Refinery. The unit consists of an atmospheric distillation tower containing 29 trays, furnace, exchangers, vessels, and pumps, it is equipped with a control system in addition to desalter as displayed in Figures (1) & (2).

The crude oil feed - API (28 or 28.2 or 29.2 or 30.2) is received from the P-311A/B main feed pump and sent through a series of heat exchangers to a temperature of about 155 °C. The oil leaving the heat exchangers is also heated to 310 °C in a crude oil heater H-241 and enters the atmospheric distillation tower where it is fractionated into the following products:

1. off gas.
2. Light naphtha (L.N).
3. Heavy naphtha (H.N).
4. Kerosene (KER).
5. Gas oil (G.O).
6. Residue crude oil refining (RCR).

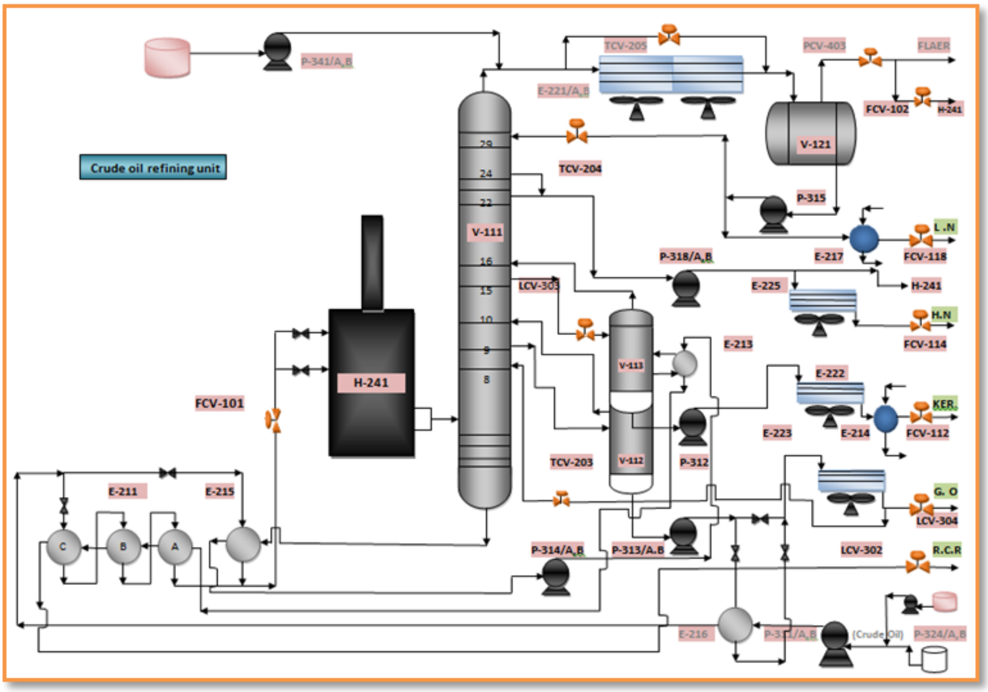

Fig. (1): Scheme of the crude oil refining unit for Najaf refinery.

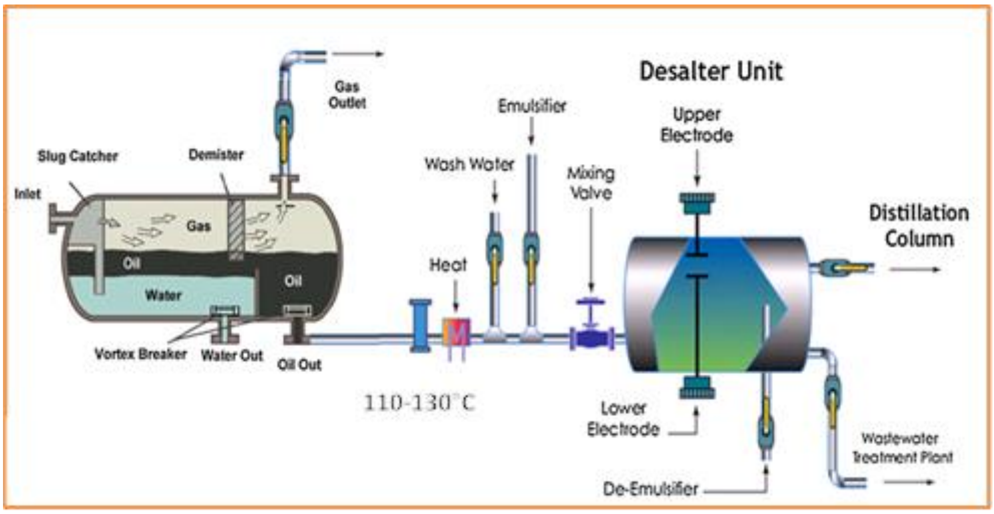

Fig. (2): Desalter system.

2.3.2 Corrosion Control Mechanisms

2.3.2.1 Caustic soda Injection

Before entering the crude oil into the refining unit, four different doses of caustic soda were injected into crude oil downstream of the desalter and controlled by a reciprocate pump P-324A/B stroke with four values (2, 4, 6, 8) at a concentration (5%) after dissolving it in water for the purpose of converting unstable salts ($MgCl_2$, $CaCl_2$) present in the crude oil into thermally stable salts (NaCl) at a temperature 120°C as shown in equations (1 and 2) [13,14]. Also, at the same time, the pH between the ranges (5.5-6.5) of the crude oil refinery unit was controlled by injecting four different amounts of caustic soda in addition to injecting four different amounts of amine into the overhead line entering the refinery tower.

$MgCl_2 + 2\,NaOH \longrightarrow Mg(OH)_2 + 2NaCl$………(1)

$CaCl_2 + 2\,NaOH \longrightarrow Ca(OH)_2 + 2NaCl$………(2)

2.3.2.2 Desalting

There are salts in the water accompanying the crude oil during its extraction from oil wells in varying proportions (depending on the source of the crude oil), and also some of it is mixed with the crude oil itself in the form of granules. The most dangerous salts are magnesium chloride and calcium chloride because they decompose at a temperature of 120, during crude oil refining processes, causing corrosion of the crude oil distillation unit equipment [13, 14].

Therefore, before the process of refining the crude oil, the water and salts are removed or separated from the crude oil by applying a high voltage to a special vessel called a desalter, heating, and adding a demulsifier to the crude oil.

Where crude oil is pumped at a temperature of (110-130) °C to a desalter as shown in Figure (2). Four different doses of demulsifier are injected onto the crude oil line and controlled with a reciprocate pump stroke of four values (1, 2, 3, 4). Then purified water is injected into this mixture at a temperature of 60 °C. The heat factor increases the movement and collision of water droplets with each other, which leads to their gathering in larger volumes and thus setting them at the bottom of the vessel.

Before entering the mixture of crude oil, demulsifier and pure water into the separation vessel, the whole mixture is mixed by the mixing valve at four pressure difference values ΔP = (0.2, 0.3, 0.4, 0.5 bar). Then it is sent to the separation vessel to remain for four different periods which are (35, 40, 45 min) and the time of the crude oil stay in the separation vessel is controlled by controlling the unit capacity, and a high voltage is applied to the mixture inside the separation vessel where the induction polarization causes the drop distortion by rupturing the interlayer of the emulsified drops to result in the separation of the water droplets from the crude oil. The separated and pure water droplets injected on the crude oil line merge and settle at the bottom of the separation vessel, thus increasing the speed of separation of the crude oil from the water containing salts.

Also desalter that worked to eliminate the crude oil of suspended impurities and solid granules such as sand, corrosion products (rust), paraffin wax crystals and insoluble salts, and reduce the amount of ash in the crude oil.

Crude oil comes out with a small percentage of salts from the top of the separation vessel as shown in Figure (2), after spending a period of time ranging from (35-45 min) which is proportional to the unit capacity and the size of the separation vessel, after which the crude oil completes its path to the rest of the heat exchangers and other equipment in the crude oil refining unit.

2.3.2.3 Neutralizer (Amine) Injection

Neutralizer was injected in different doses on the line entering the top of the V-111 distillation tower as shown in Figure (3), by reciprocating pump P-341A/B after being mixed and dissolved in water at a ratio of 85 % water to 15% of neutralizer.

Four different doses of neutralizer were injected and controlled by stroke for a reciprocatig pump P-341A/B with four values (1.5, 2, 2.5, 3). The injection quantity was determined by trial and error method to obtain the specific specifications of the condensate water in the upper system of the refinery tower that exits from the bottom of the separation vessel V-121 as shown Figure (3), which should be within the following ranges (pH = 5.5-6.5 and Cl^- = 1-4). Usually, the injection amount is regulated depending on value of pH of the water and the concentration of chloride ion Cl^- in it, in conjunction with the regulation of the amount of caustic soda (NaOH) injection to its effect on the value of pH and the chloride ion Cl^-.

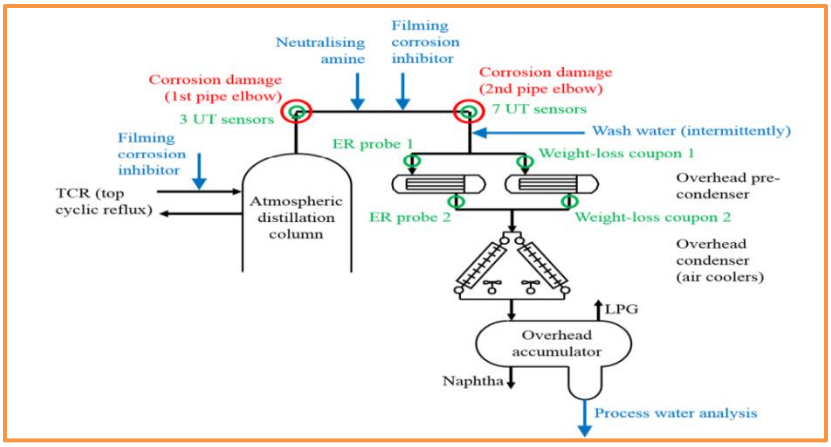

Fig. (3): Overhead system of the distillation tower.

2.3.2.4 Inhibitor (Anti-Corrosion) Injection

Inhibitor was injected in different doses on the line entering the top of the V-111 refinery tower as shown in Figure (3) by reciprocating pump P-341A/B after mixing it with heavy naphtha at a ratio of 92 % of heavy naphtha to 8% of inhibitor. Four different amounts of inhibitor were injected and controlled by stroke for reciprocating pump P-341A/B with four values (2, 2.5, 3, and 3.5).

The amount of injection of the inhibitor depends on the result of examining the iron ions Fe^{+2} in the water leaving from the bottom of the separation vessel V-111, which should be a maximum of 1ppm in order to reduce the further occurrence of corrosion in the crude oil refinery equipment.

Where the inhibitor material worked to form a film on the surface of the metal for the top of the V-111 refinery tower by cutting the electrical circuit and preventing the transmission of electrons from the metal and this leads to reducing the rate of occurrence of the corrosion process, and the inhibitor material is very sensitive to acidic changes in the media and is best effective at pH = 5.5 - 6.5. In general, it is also an excellent remover of metal surfaces from corrosion products and other contaminants sticking with them.

3. Results and Discussion

Several laboratory tests were performed to determine the salt content of the crude oil entering and leaving the desalter, checking the pH values and chlorine ions Cl^- of the crude oil with and without desalter, as well as checking the iron ions Fe^{+2} of the condensed water leaving the V-111 vessel.

In the case of injecting doses of caustic soda into the crude oil line by the reciprocating pump when the stroke is 2 and the crude oil fed to the unit has a low salt content (52.4 mg/l). At the same time, doses of the neutralizer amine are injected by the reciprocating pump at 1.5 stroke on the inner line above the crude oil distillation tower. Where the results of pH = 5.5 and chlorine ion equal to 3 were obtained, and these results were acceptable compared to the previous results of Al-dura refinery, where the corrosion rate was low.

Either in the case of the type of crude oil fed to the unit with a salt content of medium (101 mg/l), high (153 mg / l), or very high (201 mg / l) and at the same chemical injection doses (caustic soda and neutralizer amine) as shown in Table (8), which shows that the pH value began to gradually decrease due to the increase in the percentage of salt in the crude oil, and this is confirmed by the increase in the value of chlorine ion as a result of the increase in the rate of decomposition of calcium and magnesium salts as shown in equations (1,2), and thus led to an increase in the rate of corrosion occurrence, where the value of iron ions Fe^{+2} was 1 and increased to 5, then 20, then increased to >30 as a result of an increase in the percentage of hydrochloric acid is corrosive to metal.

As the hydrochloric acid (HCl) reacts with iron, the main component of the equipment metal in the refinery, to produce ferrous chloride (FeCL), which in turn reacts with the hydrogen sulfide(H_2S) originally present in the crude oil content, producing ferrous sulfide (FeS) and more hydrochloric acid (HCl) as shown in equations (3,4,5 and 6). Thus, the additional hydrochloric acid continues to form periodically, causing corrosion to the metal of the refinery equipment.

$MgCL + 2H_2O \longrightarrow Mg(OH)_2 + 2HCL$……..….(3)
$CaCl_2 + 2H_2O \longrightarrow Ca(OH)_2 + 2HCl$…..……….(4)
$Fe + 2HCL \longrightarrow FeCL_2 + H_2$……………..(5)
$FeCL_2 + H_2S \longrightarrow FeS + 2HCL$…………....(6)

When increasing the doses of caustic soda injection in the crude oil line to stroke (4-6) and the neutralizer amine to stroke (2-2.5) in the event that the crude oil feeding the unit is low in salt content (52.4 mg/l). This resulted in a rise in the pH value to become more acceptable, in addition, the chlorine ion values were within the acceptable limit as shown in the Table (8). But when the doses of caustic is increased by a greater percentage to the stroke of 8, as well as the increase of the neutralizer amine to the stroke 3, the pH rises to 6.8 more than the permissible limit (5.5-6.5) and the chlorine ion disappears (Nil), which indicates an excessive increase in the injection of caustic soda, which may precipitate in furnace tubes (H-241) cause stress corrosion over time, as well as deposits in heat exchangers, causing clogging and corrosion, and consequently their efficiency decreases.

The results appear in Table (8) when the crude oil contains medium salt content (101 mg/l) that is fed to the refining unit as well as when the doses of caustic soda and neutralizer amine are increased on the crude oil line, a significant improvement in the pH and chlorine ion values and away from the acidic media. But in the case of crude oil with high salt content (153 mg/l) and very high (201 mg/l) the increase in caustic soda injection doses and neutralizer amine did not affect the pH and chlorine ion values significantly, as the pH remained low and chlorine ion very high due to the ratio of magnesium and calcium salts present in the crude oil have decomposed and thus caused various types of corrosion to the metal of the equipment. In order to reduce and control the percentage of salts present in the crude oil content, the crude oil must be entered into the desalter before entering the crude oil refining unit.

Table (8) pH and chlorine ion (Cl^-) values for condensed water coming out of a vessel (V-111) without using a desalter.

Stroke pump for caustic soda	Stroke pump for neutralizer	Crude oil-(1)		Crude oil-(2)		Crude oil-(3)		Crude oil-(4)	
		pH	Cl^-	pH	Cl^-	pH	Cl^-	pH	Cl^-
2	1.5	5.5	3	5.2	10	4.5	100	4	160
4	2	5.8	2	5.5	8	4.8	80	4.5	100
6	2.5	6	1.5	5.7	6	5	50	4.9	70
8	3	6.8	Nil	6	4	5.2	23	5	30

There are four important factors in the success of the work of the desalter, which are the temperature of the crude oil, the demulsifier, the pressure difference at both ends of the mixing valve, and the time the crude oil remains inside the desalting vessel [3, 8].

The crude oil was heated before entering the desalter because the increase in temperature led to increase in the difference between the density of the crude oil and the water containing salts, and thus the speed of separation between them increased. The increase in temperature also led to increase in the kinetic and latent energy of the foaming solution, which helped it to weaken the protective membrane as a result of the expansion of water droplets, and it facilitated their union, and the increase in temperature reduced the viscosity of the crude oil, which made it easier for the demulsifier to separate the water from the crude oil. An experiment was made to raise the temperature of the crude oil entering the desalter to 150 °C, and this is more than what is allowed, as it led to the evaporation of water and oil extracts, and thus reached the electrodes, and then the desalter system stopped working. According to practical experiments, it was found that the best temperature for the crude oil entering the desalter is (110-130)°C.

The effect of other factors applied in the desalter system was very clear by reducing the percentage of salts in the crude oil entering the refining unit as shown by the values in Tables (9, 11). Where four different doses of the demulsifier were injected by a pump stroke (10, 12, 13 and 14) on the crude oil line with four types of it at different times and then mixed with a fixed proportion of fresh water, then each time the mixture was mixed by the mixing valve with a pressure difference of four different values (0.2, 0.3, 0.4 and 0.5 bar).

The best result was obtained by decreasing the quantity of salts in the crude oil coming out of the desalter in the case of the first and second types of crude oil that are fed to the desalter, which are from (52.4 to 37.0 mg/l and 101 to 53 mg/l) at a pressure difference (0.3, 0.4 bar), the amount of demulsifier injection by strock (12 ,14) and the residence time inside desalter (40, 45 min) respectively. But when the pressure difference on both ends of the mixing valve for the two types of crude oil, the first and the second, was increased as shown in Table (9), the amount of salts removed from the crude oil decreased, as it became 40.7 mg/l instead of 37.0 mg/l, 58.6 mg/l instead of 53.0 mg/l, because the increase in the large pressure difference led to the formation of small drops of water in which the salts were dissolved. The smaller these droplets are, the more difficult they are to separate, and they can cross with the crude oil outside the desalter, reducing their efficiency [1, 3].

In the case of the third and fourth types of crude oil, the best results were obtained by decreasing the amount of salts from (153 mg/l to 76.2 mg/l and 201 mg/l to 85.8 mg/l) respectively at a high pressure difference on the mixing valve ends and the amount of injection of the demulsifier more, as well as a longer stay period for the crude oil inside the desalter vessel and this is because they contain a high amount of salts as it is the values are shown in Table (9).

Table (9) The operating conditions of the desalter and the amount of salts in the crude oil coming out of the desalter.

Stroke pump for demulsifier	Mixing valve pressure drop (ΔP) bar	Period stay of crude oil in desalting (min)	The salt content mg/l in crude oil-(1) out of desalting	The salt content mg/l in crude oil-(2) out of desalting	The salt content mg/l in crude oil-(3) out of desalting	The salt content mg/l in crude oil-(4) out of desalting
10	0.2	35	40.0	68.0	102	120
12	0.3	40	37.0	57.3	85.3	98.4
13	0.4	45	38.8	53.0	78.0	88.6
14	0.5	45	40.7	58.6	76.2	85.8

A significant improvement appeared in the tests of the values of pH and chlorine ion after the introduction of the four types of crude oil into the salt remover because the salt remover had an effect in reducing the amount of salts in the crude oil content. Table 10, shows that in the case of the first and second types of crude oil, it no longer requires the injection of large quantities of the neutralizer amine substance and caustic soda, because the result of the pH value became very high and the value of the chlorine ion became (Nil) ie it disappeared due to the injection of large quantities of caustic soda compared to the amount of salts present in the crude oil content after introducing the crude oil to the desalter.

In the case of the third and fourth types of crude oil, the results of the pH values were acceptable and the chlorine ion Cl^- values to some extent required an increase in the injection of an additional amount of caustic soda as shown in Table (10), for the purpose of reducing the chlorine ion values and controlling the large salts of magnesium and calcium that have decomposed and it caused an increase in the value of the chlorine ion Cl^- and the latter, which increased the occurrence of corrosion in the parts of the refining equipment.

Table (10) pH and chlorine ion (Cl^-) values for condensed water coming out of a vessel (V-111) with using a desalter.

Stroke pump for demulsifier	Mixing valve pressure drop (ΔP) bar	Period stay of crude oil in desalting (min)	Crude oil-(1)		Crude oil-(2)		Crude oil-(3)		Crude oil-(4)	
			pH	Cl^-	pH	Cl^-	pH	Cl^-	pH	Cl^-
10	0.2	35	5.7	2	5.4	8	4.8	40	4.4	70
12	0.3	40	6	1	5.7	6	5.2	20	4.9	30
13	0.4	45	6.7	Nil	6	2	5.5	8	5.3	10
14	0.5	45	7.1	Nil	6.5	Nil	5.7	5.7	5.5	7

Table (11) The best operating conditions for the desalter and the percentage of salts in the crude oil before and after the desalter.

Type of crude oil	The best value of salt content mg/l desalter		Stroke pump for demulsifier	Period stay of crude oil in desalting (min)	Mixing valve pressure drop (ΔP) bar	The best value of pH for crude oil out from the desalter
	in	out				
Crude oil-(1)	52.4	37.0	12	40	0.3	6
Crude oil-(2)	101	53.0	13	45	0.4	6
Crude oil-(3)	153	76.2	14	45	0.5	5.7
Crude oil-(4)	201	85.8	14	45	0.5	5.5

Table (12), shows how occurrence of corrosion process was prevented in the upper parts of the crude oil refining unit. Four different doses of anti-corrosion substance (inhibitor) were injected by the reciprocating pump on the upper line entering the crude oil distillation tower and in the case of using the first type of crude oil as a material unit feed. The results of the tests for the condensed water coming out from the bottom of the pot (V-121) showed that the percentage of iron ions Fe^{+2} ranged between (1-0.55) and it was good in terms of controlling and preventing corrosion.

In the case of the second type of crude oil, there was a need to increase the dose of the inhibitor injector because the result of the corrosion rate was high, represented by the percentage of iron ions, which was 5 ppm, and then began to decrease to (2, 1 and 0.8 ppm) after increasing Injection doses of the inhibitor. At the same time, it must be maintaining the media provided that it is not acidic, and the pH values range between (5.5-6.5) and at this pH range, the inhibitor material is more effective in forming an insulating layer that adheres to the metal wall to prevent corrosion.

In the case of the third and fourth types of crude oil, the increase in the injection of inhibitor doses had a role in decreasing the incidence of corrosion, as the percentage of iron ions decreased from (20 to 1.5 ppm), (>30 to 2.1 ppm), but not completely because the media remained almost acidic with pH limits (4.8-5.7), (4.4-5.5) respectively. This is due to the high percentage of salts present with the crude oil, so the crude oil must be further processed before it enters the crude oil refining unit by increasing the amount of caustic soda injection and introducing the crude oil to the desalter to of reduce the proportion of salts.

Table (12) The percentage of iron ions (Fe^{+2}) in the condensed water coming out of a vessel (V-121) for four types of crude oil.

Stroke pump for inhibitor	Crude oil-(1)	Crude oil-(2)	Crude oil-(3)	Crude oil-(4)
	Fe^{+2} (ppm)	Fe^{+2} (ppm)	Fe^{+2} (ppm)	Fe^{+2} (ppm)
2	1	5	20	>30
2.5	0.8	2	5	20
3	0.6	1	2	5
3.5	0.55	0.8	1.5	2.1

4. Conclusion:

The use of desalting to remove salts and water mixed with crude oil has achieved great success, as four different types of crude oil were treated by desalting, which reduced the percentage of salts to a minimum (37.0, 53.0, 76.2 and 85.8 mg/L). The process of injecting caustic soda into the crude oil resulted in the conversion of a large proportion of unstable salts ($MgCl_2$, $CaCl_2$) into thermally stable salts (NaCl) at a temperature of 120°C, and at the same time it had an effect in improving the pH value. The corrosion rate in the crude oil refining unit equipment was controlled by making the media with a pH value between (5.5-6.5) by injecting an amine neutralizer with an anti-corrosion (inhibitor) into the upper system of the refinery tower, and this led to reducing the occurrence of corrosion in the upper and other parts of the refining unit were reduced to a minimum, where the best and lowest results for iron ions Fe^{+2} values were (0.8, 1, 1.5, and 2.1). The inhibitor was very sensitive to changes in acid function and was best effective at pH = (5.5 - 6.5).

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